

UNIVERSIDADE DE LISBOA
FACULDADE DE CIÊNCIAS



**Ciências
ULisboa**

**Assessment and optimisation of uncertainty in identifying the origin of oil spills in
the marine environment**

“Documento Definitivo”

Doutoramento em Química
Especialidade de Química Analítica

Ana Catarina Carvalho da Rocha

Tese orientada por:
Doutor Ricardo Jorge Neves Bettencourt da Silva
Doutora Carla Maria Ferreira Mesquita Palma

Documento especialmente elaborado para a obtenção do grau de doutor



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“If I have seen further it is by standing on the shoulders of Giants”
“Se eu vi mais longe foi por estar de pé sobre ombros de gigantes”

Isaac Newton

To my parents and sister
Aos meus pais e irmã

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Abstract

The identification of an oil spill source involves the analysis by gas chromatography-mass spectrometry of spill samples (Sp) and suspected source samples (SS), followed by data processing to determine and correlate oils' fingerprints, which are composed by a set of abundance ratios of oil-discriminating compounds, *i.e.*, diagnostic ratios (*DR*). Due to their simplicity, conventional approaches for *DR* comparison, such as Student's *t* statistics (S-t) and a maximum relative difference (single criterion, SC), have been used, but they rely on frequently invalid assumptions, compromising the reliability of the identifications. This fact was proven by an alternative and innovative approach based on Monte Carlo Method (MCM) simulations of correlated *DR*, implemented in a user-friendly Microsoft Excel spreadsheet that accurately describes the probability distributions of *DR* or differences between *DR* means and defines statistically sound criteria for the *DR* comparison. Analytical data from samples of spill scenarios reproduced in intercomparison tests were applied to the developed tool, which provided MCM, S-t, and SC confidence intervals for *DR* comparison in several comparison conditions, enabling the reliable performance assessment of each approach in claiming compositional equivalence. The probabilities of true and false compositional equivalence claims were estimated, considering one or more *DR* comparison trials, revealing that the quality of the identifications improves if up to three trials are contemplated. The findings enable to propose an uncertainty-based strategy ruled by solid and objective criteria that control not only the probabilities of compositional equivalence claims of different Sp and SS pairs but also their ratios, *i.e.*, likelihood ratios, allowing us to distinguish competing sources and identify the most likely spill source with high reliability. This research proves that MCM outperforms traditional approaches by also exposing their vulnerabilities and represents an important advance in spill source identification methods, as well as its evidence presentation and interpretation.

Keywords: Evidence interpretation; Monte Carlo Method; Oil fingerprinting; Oil spill; True and false results rate

Resumo

A atual dependência da sociedade face aos combustíveis fósseis emerge numa intensa exploração do petróleo e elevado tráfego marítimo. Esta conjuntura desperta uma crescente preocupação relativamente à ocorrência de derrames de óleos¹ no meio marinho devido aos seus graves impactos ambientais, socioeconómicos e para a saúde pública. Estes derrames são resultado de acidentes ou descargas deliberadas e a sua magnitude depende da quantidade e do tipo de óleo derramado, da localização do derrame, das condições ambientais do local, assim como das medidas e tempo de resposta ao seu combate. Várias políticas, regulamentos, legislações, acordos e convenções têm vindo a ser implementados visando prevenir, mitigar e combater estes atos de poluição, penalizar responsáveis e compensar partes lesadas. Contudo, identificar os responsáveis de tais incidentes pode-se tornar desafiante, pois exige provas concretas e credíveis para evitar que inocentes sejam incriminados com penas severas. Neste sentido, a ciência e a lei atuam em consonância com análises forenses a servirem como evidência de peso para o processo judicial. Estas análises são realizadas em amostras do derrame (Sp) e em amostras recolhidas nos locais considerados suspeitos da sua origem (SS) visando avaliar equivalência/diferença das composições químicas dos óleos, vulgo impressões digitais. A impressão digital de um óleo é, assim, definida por um conjunto de razões entre abundâncias de compostos discriminadores de ramos petrolíferas, comumente designadas de razões de diagnóstico (DR). Duas metodologias de referência que podem ser utilizadas para realizar estas análises são o método Nordtest e o referencial normativo EN 15522-2. Ambas recorrem à análise por cromatografia em fase gasosa acoplada a detetor de espectrometria de massa (GC-MS) pois esta possibilita a quantificação de uma ampla gama de hidrocarbonetos de diferentes classes. Estas metodologias não só avaliam conjuntos de DR distintas, como também envolvem condições e métodos de comparação de DR diferentes. Enquanto o método Nordtest aplica a estatística *t-Student* (S-t) para comparar valores médios de triplicados de DR, determinadas sob o formato $A/(A + B)$, a norma EN 15522-2 recorre a uma diferença máxima relativa (critério único, SC) para comparar valores médios de duplicados de DR, calculadas no formato A/B . Porém, ambos os métodos assumem pressupostos ou aproximações que afetam a veracidade das comparações de DR e, consequentemente, da declaração de equivalência composicional entre amostras comparadas, como a normalidade das distribuições de probabilidade das DR, no caso da S-t, e uma dispersão máxima empírica de 5%, no caso de SC.

¹ Termo usado neste trabalho para referir qualquer crude, derivado refinado, ou misturas entre estes e com *biodiesel* visto que qualquer um destes é passível de ser derramado no meio marinho.

Ademais, para que detenha validade em contexto jurídico e auxilie a tomada de decisão sobre a culpabilidade ou absolvição, a evidência apresentada, *i.e.*, a declaração de equivalência composicional entre Sp e SS, exige ser robusta, objetiva e fidedigna. Nesse sentido, é importante que a evidência seja acompanhada da razão de verossimilhança (*LR*), uma ferramenta essencial no âmbito judicial que possibilita avaliar a sua força probatória no apoio à hipótese do promotor de justiça comparativamente com a hipótese da defesa. A determinação da *LR* no âmbito de ilícitos de poluição por óleos não tem sido tão veemente estudada comparativamente às outras áreas da ciência forense. Ainda assim, em alternativa às declarações qualitativas baseadas unicamente nas avaliações dos dados das análises (*i.e.*, correspondência positiva/provável/negativa entre amostras ou processo inconclusivo), a metodologia EN 15522-2 recomenda que a evidência seja apresentada recorrendo a uma escala de conclusões alicerçada no valor da *LR*. Portanto, para garantir identificações sólidas, claras, credíveis e defensáveis é crucial a aplicação de modelos estatísticos adequados, sejam eles métodos de interpretação de resultados que permitam a descrição realista das variáveis em estudo, como de estimativa de probabilidades de declaração de equivalência composicional de diferentes pares de amostras para o cálculo da *LR*.

Diante das limitações e lacunas expostas, a investigação apresentada objetivou desenvolver métodos e ferramentas que aperfeiçoassem procedimentos bem como avaliassem e reduzissem a incerteza das identificações, com particular ênfase na abordagem usada na comparação de impressões digitais de óleos e na quantificação e avaliação do valor probatório da evidência. Neste sentido, foi criada uma abordagem nova e inovadora para comparar composições de óleos que é baseada em simulação de *DR* pelo Método de Monte Carlo (MCM). A simulação de *DR* é sustentada em dados de dispersão e de correlação de sinais cromatográficos dos compostos diferenciadores de ramas petrolíferas, obtidos pela análise por GC-MS, e que conferem as características das amostras em estudo aos valores aleatórios simulados. Esta abordagem foi produzida em folha de cálculo do Microsoft Excel, transformando-se numa ferramenta computacional *user-friendly*. Inicialmente, a ferramenta foi concebida para comparar valores médios de *DR* observados numa amostra com o valor único de *DR* observado noutra amostra pelas abordagens MCM e S-t (*Single&Multi_DR_Modelling*). Posteriormente, foi otimizada para comparar também valores médios de *DR* observados em duas amostras pelas abordagens MCM, S-t e SC (*Single&Multi_DR_Flex_Modelling_EN15522*). Desta forma, obtém-se as distribuições de probabilidade não só de *DR* observadas numa amostra, como também de diferenças de valores médios de *DR* observadas em duas amostras, cujos percentis definem os

critérios de comparação das razões para níveis de confiança estipulados. As abordagens S-t e SC, também implementadas na ferramenta computacional, proporcionam a avaliação do desempenho de cada abordagem na declaração da equivalência composicional entre amostras e a validação do modelo MCM. A ferramenta computacional é flexível quanto às condições de comparação de *DR*, designadamente a seleção das razões que caracterizará cada óleo, o número de análises replicadas, o formato de cálculo das razões e o nível de confiança da comparação. Os dados simulados são também empregues na estimativa das probabilidades de equivalência composicional entre amostras.

Uma mistura de crudes e amostras de vários *Round Robin Tests* representativas de diferentes óleos e, assim, caracterizadas por diferentes conjuntos de *DR*, foram analisadas por GC-MS. À ferramenta computacional de simulação foram aplicados os dados analíticos permitindo validar o modelo de simulação, verificar os desvios à normalidade das distribuições de probabilidade das *DR* e das diferenças de valores médios de *DR* e avaliar o desempenho das abordagens MCM, S-t e SC segundo diferentes condições de comparação, com foco especial nas condições sugeridas pelas metodologias Nordtest e EN 15522-2. Os resultados obtidos expuseram desvios à normalidade das distribuições de probabilidade das *DR* e das diferenças de valores médios de *DR*, com impactos na amplitude dos limites de confiança e consequências na avaliação da equivalência/diferença das *DR* comparadas. Os ensaios realizados segundo diferentes condições de comparação de *DR* revelaram que, apesar das abordagens convencionais serem eficazes, a abordagem MCM supera as limitações destas, pois é mais ponderada e se adapta melhor às características probabilísticas das *DR*, conduzindo a declarações de equivalência composicional de duas amostras mais credíveis. A relação entre as probabilidades da verdadeira e da falsa declaração de equivalência composicional de amostras, assim como o recurso a mais do que um ensaio de comparação de *DR* para estimá-las foram também investigados. Mais três ferramentas computacionais foram desenvolvidas com a finalidade de estimar as probabilidades de falsas declarações de equivalência composicional, designadamente *MCM_False_Compositional_Equiv_Claim*, *S-t_False_Compositional_Equiv_Claim*, e *SC_False_Compositional_Equiv_Claim*. Os estudos evidenciam que quando considerados diferentes ensaios de comparação de *DR* as probabilidades da verdadeira e da falsa declaração de equivalência composicional de duas amostras são afetadas e naturalmente o valor da *LR*. A *LR* mostra ser consideravelmente maior quando usados resultados obtidos de três ensaios de comparação de *DR* pela abordagem MCM aplicada às condições das duas metodologias. Nas abordagens S-t e SC, esse aumento ocorre sobretudo quando são aplicadas as condições de

comparação de *DR* específicas definidas para cada uma das abordagens. Também neste aspeto, a abordagem MCM ostentou um melhor desempenho ao produzir evidências de peso acrescido face às abordagens convencionais, em especial com estimativa de probabilidades de verdadeira declaração de equivalência composicional superiores. As avaliações dos resultados obtidos proporcionaram definir uma estratégia de identificação de potencial fonte poluidora que permite reduzir a sua incerteza e melhorar a discriminação entre fontes suspeitas concorrentes. Esta é apresentada segundo uma árvore de decisão onde critérios específicos para *LR* e para as probabilidades da declaração de equivalência composicional entre *Sp* e as duas *SS* mais prováveis de serem a origem do derrame são considerados, a fim de se obter uma evidência com qualidade adequada.

O trabalho realizado, ao recorrer a métodos estatísticos apropriados, resultou na conceção de uma nova abordagem para a comparação de impressões digitais de óleos, que oferece uma base mais sólida e confiável comparativamente com as abordagens tradicionais. É um estudo pioneiro na avaliação objetiva e estatisticamente robusta do desempenho de métodos de comparação de *DR*, que demonstra as limitações dos métodos convencionais e expõe os benefícios da utilização do método desenvolvido. A nova abordagem viabiliza a estimativa de probabilidades de declaração de equivalência composicional para a determinação de *LR*, sendo também um estudo que se destaca por oferecer ferramentas computacionais para esse fim. Os progressos relevantes acima mencionados, aliados à estratégia estabelecida de melhoria da qualidade das identificações, demarcam, assim, um avanço importante na análise forense de derrames de óleos.

Palavras-chave: Derrame de óleo; Impressão digital de óleo; Interpretação da evidência; Método de Monte Carlo; Taxa de resultados verdadeiros e falsos

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Annex C

Figure C.1. Combined SIM chromatograms of the spill (Sp) and suspected source samples, known to be and not to be the origin of the spills (SS1 and SS2, respectively), of the Round Robin Tests (RR) (a) 2018, (b) 2019 and (c) 2020. **321**

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Annex D

Figure D.1. Combined SIM chromatograms of the spill samples 1 and 2 (Sp1 and Sp2) and suspected source samples known to be the source of the spill (SS1) and not to be the origin of the spill (SS2 and SS3). 348

Figure D.2. Assessment of weathering and compositional equivalence of the spill samples 1 and 2 (Sp1 and Sp2, respectively) and the suspected source sample 1 (SS1), using PW-plots with data from the first *DR* comparison trial: (a) Sp1 vs. SS1 and (b) Sp2 vs. SS1. ● *n*-Alkanes; ● Isoprenoids; ● Branched alkanes; ● *n*-Alkylcyclohexanes; ● Decalins; ● Tetralins; ● Adamantanes; ● Diamantanes; ● Sesquiterpanes; ● Alkylbenzenes; ● Alkyltoluenes; ● PAH; ● Tricyclic terpanes; ● Hopanes; ● Steranes; ● Triaromatic steranes; ● FAME; --- evaporation curve, according to EN 15522-2; acceptable range for equivalence of compounds' contents in the spill and suspected source samples compared (85% to 118%). (1) Acenaphthylene, ANY, is often found at concentrations below the detection limit, yet abundant in burning residues. The EN 15522-2 standard defines it as a marker of the incidence of burning. 352

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- Table D.19.** First trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P_{2.5}$ and $P_{97.5}$) and 98% (P_1 and P_{99}), for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 3 (SS3, known not to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios. 378

- Table D.20.** Second trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P_{2.5}$ and $P_{97.5}$) and 98% (P_1 and P_{99}), for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 3 (SS3, known not to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios. 378
- Table D.21.** Third trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P_{2.5}$ and $P_{97.5}$) and 98% (P_1 and P_{99}), for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 3 (SS3, known not to be the origin of the spill), applying DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios. 379
- Table D.22.** Mean value (δ) and relative standard deviation (RSD), based on simulations of three DR comparison trials (1stT, 2ndT and 3rdT), of the probability of true compositional equivalence claim estimated for the comparison between the spill samples 1 and 2 (Sp1 and Sp2) and the suspected source sample known to be the origin of the spill (SS1), applying the DR comparison conditions represented by the Nordtest and EN15522-2 scenarios and by the SC, MCM and S-t approaches, both considering 95% and 98% confidence levels. 381
- Table D.23.** Mean value (ϵ) and relative standard deviation (RSD), based on simulations of three DR comparison trials (1stT, 2ndT and 3rdT), of the probability of false compositional equivalence claim estimated for the comparison between the spill samples 1 and 2 (Sp1 and Sp2) and the suspected source samples known not to be the origin of the spill (SS2 and SS3), applying the DR comparison conditions represented by the Nordtest and EN15522-2 scenarios and by the SC, MCM and S-t approaches, both considering 95% and 98% confidence levels. 382

List of Abbreviations, Symbols and Units

Abbreviations

1 st T	First comparison trial of diagnostic ratios determined in a spill sample and in a suspected source sample
2 nd T	Second comparison trial of diagnostic ratios determined in a spill sample and in a suspected source sample
3 rd T	Third comparison trial of diagnostic ratios determined in a spill sample and in a suspected source sample
AIS	Automatic Identification System
alkyl-PAH	Alkylated polycyclic aromatic hydrocarbons
AMN	<i>Autoridade Marítima Nacional</i> (National Maritime Authority)
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
Bonn-OSINet	Oil Spill Identification Network of Experts within Bonn Agreement
BUNKER	International Convention on Civil Liability for Bunker Oil Pollution Damage
BTEX	Set of the monoaromatic hydrocarbons Benzene, Toluene, Ethylbenzene, and the isomers <i>o</i> -, <i>m</i> - and <i>p</i> -Xylenes
C0-	Parent polycyclic aromatic hydrocarbon
C1-	Monoalkyl-substituted
C10	Decane
C12	Dodecane
C15	Pentadecane
C2-	Dialkyl-substituted
C3-	Trialkyl-substituted
C4-	Tetraalkyl-substituted
C30	triacontane
C40	tetracontane
C8	Octane
CEN	European Committee for Standardization
Cion	Confirmation fragment
CLC	International Convention on Civil Liability for Oil Pollution Damage

CLPM	<i>Comando Local da Polícia Marítima</i> (Local Command of Maritime Police)
COSIWeb	Computerised Oil Spill Identification database
CSN	CleanSeaNet Service
C _x	<i>n</i> -Alkane with <i>x</i> carbon number
DCPM	<i>Direção de Combate à Poluição do Mar</i> (Marine Pollution Response Directorate)
ECA	Emission Control Areas
EEZ	Economic Exclusive Zone
EMSA	European Maritime Safety Agency
ETFE	Ethylene tetrafluoroethylene
EU	European Union
FAME	Fatty acid methyl esters
FAME C _x : _y	Fatty acid methyl ester containing <i>x</i> carbons and <i>y</i> double bonds
FCUL	<i>Faculdade de Ciências da Universidade de Lisboa</i> (Faculty of Sciences of University of Lisbon)
FID	Flame ionization detection
FUND	International Convention on the Establishment of an International Fund for Compensation for Oil Pollution Damage
GC	Gas chromatography
GC-FID	Gas chromatography with flame ionization detection; also used to refer the equipment gas chromatograph coupled to a flame ionization detector
GC-MS	Gas chromatography with mass spectrometry detection; also used to refer the equipment gas chromatograph coupled to a mass spectrometer detector
GESAMP	Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection
HELCOM	Helsinki Commission, also known as Baltic Marine Environment Protection Commission
HNS	Hazardous and noxious substances
IH	<i>Instituto Hidrográfico</i> (Hydrographic Institute)
IMO	International Maritime Organization
INTERVENTION	International Convention Relating to Intervention in the High Seas in Cases of Petroleum Pollution Casualties
IOPC	International Oil Pollution Compensation Fund

IR	Informative ratio
ITOPF	International Tanker Owners Pollution Federation Limited
LPG	Liquefied petroleum gas
MARPOL 73/78	International Convention for the Prevention of Pollution from Ships
MCM	Monte Carlo Method
MS	Mass spectrometry
NOAA	National Oceanic and Atmospheric Administration
NR	Normative ratio
NRC	National Research Council of United States National Academy of Sciences
OPCR	International Convention on Oil Pollution Preparedness, Response and Co-operation
pPAH	Parental polycyclic aromatic hydrocarbons
PAH	Polycyclic aromatic hydrocarbons, also known as polyaromatic hydrocarbons
PARAFAC	Parallel factor analysis
PCA	Principal component analysis
Phy	Phytane
PM	<i>Polícia Marítima</i> (Maritime Police)
PML	<i>Plano Mar Limpo</i> (Clean Sea Plan)
PSC	Port State Control
PTFE	Polytetrafluoroethylene
PW-plots	Percentage of weathering plots
Qion	Quantitation fragment
RR	Round Robin Test
RSD	Relative standard deviation
SafeSeaNet	European Maritime Surveillance System
SAR	Synthetic aperture radar
SC	Single criterion
SIM	Selected ion monitoring mode for spectra recording
Sp	Spill sample
SS	Suspected source sample
SS _α	Suspected source sample most likely to be the spill source

SS_{β}	Suspected source sample that is the second most likely to be the source of the spill
SS_{γ}	Alternative suspected source sample of the spill
S-t	Student's t statistics
UCM	Unresolved complex mixture
USA	United States of America
US EPA	United States Environmental Protection Agency
VTS	Vessel Traffic Service

Symbols

$(1 - P)$	Complementary probability of the confidence level
$1T$	Single diagnostic ratio comparison trial
$2T$	Combined effect of two diagnostic ratio comparison trials
$3T$	Combined effect of three diagnostic ratio comparison trials
A	Chromatographic signal of compound A
$\bar{A}$	Mean value of chromatographic signal of compound A
$A/(A + B)$	Diagnostic ratio format; ratio between the chromatographic signal of compound A and the sum of the chromatographic signals of compounds A and B
A/B	Diagnostic ratio format; ratio between the chromatographic signal of compound A and the chromatographic signal of compound B
A/H	Ratio between the chromatographic signal of compound A and the chromatographic signal of an unweathered compound present in the same injection of compound A (normaliser compound, H)
$(A/H)_{\text{Min}}/(A/H)_{\text{Max}}$	Ratio between the lowest chromatographic signal of compound A from the set of triplicate injections and the highest chromatographic signal of compound A from the same set, both normalised to the chromatographic signal of an unweathered compound present in both injections (normaliser compound, H ; used in Chapter 3)
$(A/H)_{\text{OS}}$	Ratio between the chromatographic signal of compound A and the chromatographic signal of an unweathered compound (normaliser compound, H), both present in the injection of the oil spill sample (used in Chapter 3)

$(A/H)_{OS}/(A/H)_{SS}$	Ratio between the chromatographic signal of compound A in the oil spill sample and the chromatographic signal of compound A in the suspected source sample, both normalised to the chromatographic signal of an unweathered compound present in both injections (normaliser compound, H ; used in Chapter 3)
$(A/H)_{Sp}$	Ratio between the chromatographic signal of compound A and the chromatographic signal of an unweathered compound (normaliser compound, H), both present in the injection of the oil spill sample (used in Chapter 4 and 5)
$(A/H)_{Sp}/(A/H)_{SS}$	Ratio between the chromatographic signal of compound A in the spill sample and the chromatographic signal of compound A in the suspected source sample, both normalised to the chromatographic signal of an unweathered compound present in both injections (normaliser compound, H ; used in Chapter 4)
$\overline{(A/H)}_{Sp}/\overline{(A/H)}_{SS}$	Mean value of the ratio between the chromatographic signal of compound A in the spill sample and the chromatographic signal of compound A in the suspected source sample, both normalised to the chromatographic signal of an unweathered compound present in both injections (normaliser compound, H ; used in Chapters 4 and 5)
$(A/H)_{Sp MIN}/(A/H)_{Sp MAX}$	Ratio between the lowest chromatographic signal of compound A from the set of triplicate injections of the spill sample and the highest chromatographic signal of compound A from the same set, both normalised to the chromatographic signal of an unweathered compound present in both injections (normaliser compound, H ; used in Chapter 4)
$(A/H)_{SS}$	Ratio between the chromatographic signal of compound A and the chromatographic signal of an unweathered compound (normaliser compound), both present in the injection of the suspected source sample
$(A/H)_{SS MIN}/(A/H)_{SS MAX}$	Ratio between the lowest chromatographic signal of compound A from the set of triplicate injections of the suspected source sample and the highest chromatographic signal of compound A from the same set, both normalised to the chromatographic signal of an unweathered compound present in both injections (normaliser compound, H ; used in Chapter 4)
A_P	Pearson's second coefficient of skewness of the probability distribution of a diagnostic ratio
$ A_P $	Absolute value of the Pearson's second coefficient of skewness of the probability distribution of a diagnostic ratio

A_{pi}	Pearson's second coefficient of skewness of the probability distribution of the diagnostic ratio i
B	Chromatographic signal of compound B
$\bar{B}$	Mean value of chromatographic signal of compound B
B/H	Ratio between the chromatographic signal of compound B and the chromatographic signal of an unweathered compound present in the same injection of compound B (normaliser compound, H)
$(B/H)_{OS}/(B/H)_{SS}$	Ratio between the chromatographic signal of compound B in the oil spill sample and the chromatographic signal of compound B in the suspected source sample, both normalised to the chromatographic signal of an unweathered compound present in both injections (normaliser compound, H)
C_{AB}	Correlation matrix between the chromatographic signals of compounds A and B
C_{AB}'	Pseudo-correlation matrix composed of Pearson correlation coefficients between the chromatographic signals of compounds A and B , reduced as low as possible to allow the Cholesky factorization of the covariance matrix
DR	Diagnostic ratio
$\overline{DR}_1$	Mean value of the diagnostic ratio determined in the sample 1
DR_2	Single value of the diagnostic ratio determined in the sample 2
$\overline{DR}_2$	Mean value of the diagnostic ratio determined in the sample 2
$\overline{DR}_d$	Mean value of the diagnostic ratio means determined in the sample x and sample y (used in Chapter 3), or in the spill sample and suspected source sample (used in Chapters 4 and 5)
$\overline{\overline{DR}}_d$	Mean value of the mean values of three consecutive simulated diagnostic ratio means determined in the spill sample and in the suspected source sample
$\overline{DR}_i$	Mean value of the diagnostic ratio i
DR_{Sp}	Single value of the diagnostic ratio determined in the spill sample
$\dot{DR}_{Sp}$	Real value of the diagnostic ratio in the spill sample
$\overline{DR}_{Sp}$	Mean value of the diagnostic ratio determined in the spill sample
$\overline{\overline{DR}}_{Sp}$	Mean value of three consecutive simulated diagnostic ratio means determined in the spill sample

DR_{SS}	Single value of the diagnostic ratio determined in the suspected source sample
$\dot{D}R_{SS}$	Real value of the diagnostic ratio in the suspected source sample
$\overline{DR}_{SS}$	Mean value of the diagnostic ratio determined in the suspected source sample
$\overline{\overline{DR}}_{SS}$	Mean value of three consecutive simulated diagnostic ratio means determined in the suspected source sample
DR_x	Single value of the diagnostic ratio determined in sample x
$\overline{DR}_x$	Mean value of the diagnostic ratio determined in sample x
DR_y	Single value of the diagnostic ratio determined in sample y
$\overline{DR}_y$	Mean value of the diagnostic ratio determined in sample y
$(\dot{D}R_{Sp} - \dot{D}R_{SS})$	Difference between the real diagnostic ratio values of the spill sample and the suspected source sample
$(\overline{DR}_{Sp} - \overline{DR}_{SS})$	Difference between the diagnostic ratio means determined in the spill sample and in the suspected source sample
$(\overline{\overline{DR}}_{Sp} - \overline{\overline{DR}}_{SS})$	Difference between the mean values of three consecutive simulated diagnostic ratio means determined in the spill sample and in the suspected source sample
$\overline{(\overline{DR}_{Sp} - \overline{DR}_{SS})}$	Mean value of three consecutive simulated differences between the diagnostic ratio means determined in the spill sample and in the suspected source sample
$(\overline{DR}_x - \overline{DR}_y)$	Difference between the diagnostic ratio means determined in the sample x and in the sample y
E	Evidence
F	Matrix of simulated chromatographic signals of compounds A and B or multiple compounds, with a certain correlation and dispersion, adjusted to the central value
H	Chromatographic signal of an unweathered compound (normaliser compound)
H_d	Defence hypothesis
H_p	Prosecutor hypothesis
K_{AB}	Covariance matrix between the chromatographic signals of compounds A and B or signals of multiple compounds
L	Matrix generated by Cholesky decomposition of the covariance matrix between the chromatographic signals of compounds A and B or signals of multiple compounds
LR	Likelihood ratio

LR^{1T}	Likelihood ratio determined with the probabilities of true and false compositional equivalence claims between the spill sample and the suspected source samples known to be and not to be the source of the spill, respectively, both estimated considering the outcomes of a single diagnostic ratio comparison trial
LR^{2T}	Likelihood ratio determined with the probabilities of true and false compositional equivalence claims between the spill sample and the suspected source samples, known to be and not to be the source of the spill, respectively, both estimated considering the outcomes of the combined effect of two diagnostic ratio comparison trials
LR^{3T}	Likelihood ratio determined with the probabilities of true and false compositional equivalence claims between the spill sample and the suspected source samples, known to be and not to be the source of the spill, respectively, both estimated considering the outcomes of the combined effect of three diagnostic ratio comparison trials
m	Number of injection replicates of sample 2 (used in Chapter 2); number of chromatographic signals needed to define each diagnostic ratio to be simulated (used in Chapter 3)
M	Number of diagnostic ratios from a set of ratios that defines the fingerprint of a sample
$\mathbf{M}$	Matrix of simulated chromatographic signals of compounds A and B or multiple compounds with observed correlation and dispersion, and mean value equal to zero
m/z	Ratio between the mass and charge of a fragment of a mass spectrum
n	Number of injection replicates of sample 1
N	Number of injection replicates of sample 1 that is equal to the number of injection replicates of sample 2
n_{Sp}	Number of injection replicates of spill sample
n_{SS}	Number of injection replicates of suspected source sample
n_x	Number of injection replicates of sample x
n_y	Number of injection replicates of sample y
$\mathbf{O}$	Matrix composed by rows with repeated mean values of each chromatographic signal observed experimentally
$O(H_p)$	Prior odds
$O(H_p E)$	Posterior odds
P	Confidence level

$P1$	Percentile associated to a cumulative probability of 1%
$P2.5$	Percentile associated to a cumulative probability of 2.5%
$P50$	Percentile associated to a cumulative probability of 50%
$P50_i$	Percentile associated to a cumulative probability of 50% of the probability distribution of the diagnostic ratio i
$P97.5$	Percentile associated to a cumulative probability of 97.5%
$P99$	Percentile associated to a cumulative probability of 99%
$P(E)$	Probability of observing the evidence independently of the prosecutor or the defence hypothesis
$P(E H_d)$	Probability of observing the evidence given the defence hypothesis being true
$P(E H_p)$	Probability of observing the evidence given the prosecutor hypothesis being true
$P(H_d)$	Prior probability of the defence hypothesis occurring without the influence of any evidence (used in Chapter 1); prior probability of a misdetection of the oil spill origin (used in Chapter 5)
$P(H_d E)$	Probability of defence hypothesis being true given the evidence (used in Chapter 1); probability of the oils in the spill sample and suspected source sample being different given the findings of the chemical analysis (used in Chapter 5)
$P(H_p)$	Prior probability of the prosecutor hypothesis occurring without the influence of any evidence (used in Chapter 1); probability of a reliable detection of the oil spill origin (used in Chapter 5)
$P(H_p E)$	Probability of prosecutor hypothesis being true given the evidence, also known as posterior probability (used in Chapter 1); probability of the oils in the spill sample and suspected source sample being the same given the findings of the chemical analysis (used in Chapter 5)
P^M	Exponential with grade M of the confidence level
$P_{Sp SS_\alpha}$	Probability of compositional equivalence claim between the spill sample and the suspected source sample most likely to be the source of the spill
$P_{Sp SS_\beta}$	Probability of compositional equivalence claim between the spill sample and the second suspected source sample most likely to be the source of the spill
$P_{Sp SS_\gamma}$	Probability of compositional equivalence claim between the spill sample and the alternative suspected source sample of the spill

$P_{Sp SS_i}^{jT}$	Probability of compositional equivalence claim between the spill sample and the suspected source sample i , estimated considering the outcomes of the combined effect of j diagnostic ratio comparison trials
$P_{Sp SS_\alpha}^{jT}$	Probability of compositional equivalence claim between the spill sample and the suspected source sample most likely to be the source of the spill, estimated considering the outcomes of the combined effect of j diagnostic ratio comparison trials
$P_{Sp SS_\beta}^{jT}$	Probability of compositional equivalence claim between the spill sample and the second suspected source sample most likely to be the source of the spill, estimated considering the outcomes of the combined effect of j diagnostic ratio comparison trials
$P_{1-\chi}[\overline{DR}_{Sp} - \overline{DR}_{SS}]$	$(1-\chi)^{th}$ percentile of the difference between the diagnostic ratio means determined in the spill sample and in the suspected source sample, both simulated by Monte Carlo Method
$P_\chi[\overline{DR}_{Sp} - \overline{DR}_{SS}]$	χ^{th} percentile of the difference between the diagnostic ratio means determined in the spill sample and in the suspected source sample, both simulated by Monte Carlo Method
P_χ^{th}	χ^{th} percentile of the simulated diagnostic ratio determined in sample 1 (used in Chapter 2), in sample x (used in Chapter 3), in the difference between the simulated diagnostic ratio means determined in sample x and sample y (used in Chapter 3), or in the difference between the simulated diagnostic ratio means determined in spill sample and suspected source sample (used in Chapters 4 and 5)
s	Standard deviation of three consecutive simulated differences between the diagnostic ratio means determined in the spill sample and in the suspected source sample
SC_{LL}	Lower confidence limit defined by the single criterion method/approach
SC_{UL}	Upper confidence limit defined by the single criterion method/approach
s_d	Standard deviation of the difference between a diagnostic ratio means determined in sample x and sample y (used in Chapter 3), or in spill sample and suspected source sample (used in Chapters 4 and 5)
s_{DR}	Standard deviation of a diagnostic ratio calculated when the standard deviations of the diagnostic ratio replicates determined in sample 1 and sample 2 are statistically equivalent
s_{DR_1}	Standard deviation of a diagnostic ratio replicates determined in sample 1

S_{DR_2}	Standard deviation of a diagnostic ratio replicates determined in sample 2
S_{DRi}	Standard deviation of replicates of diagnostic ratio i determined in a certain sample
$S_{DR_{Sp}}$	Standard deviation of a diagnostic ratio replicates determined in the spill sample
$S_{DR_{SS}}$	Standard deviation of a diagnostic ratio replicates determined in the suspected source sample
S_{DR_x}	Standard deviation of a diagnostic ratio replicates determined in the sample x
S_{DR_y}	Standard deviation of a diagnostic ratio replicates determined in the sample y
S/N	Signal to noise ratio
$SpG_{15.65/15.65}$	Specific gravity with oil and water densities determined at 15.65 °C
t_1	t -value of the Student's t distribution considering 95% or 98% confidence level and $(n - 1)$ degrees of freedom
$t((1 - P); 2)$	t -value of the Student's t distribution considering the confidence level P and two degrees of freedom
$t((1 - P); \lfloor \xi \rfloor)$	t -value of the Student's t distribution considering the confidence level P and $\lfloor \xi \rfloor$ degrees of freedom
T	Matrix of random and independent one-tailed t -values of Student's t distribution, with cumulative probabilities ranging 0 to 1 and certain degrees of freedom
t_A	t -value of the Student's t distribution considering 95% or 98% confidence level and $(N - 1)$ degrees of freedom
t_{cr}	Critical value of the Student's t distribution for 95% confidence level
t_{exp}	Estimated t -value as the ratio between the absolute difference of the mean value of the probability (total risk) of true or false compositional equivalence claims between the spill sample and the suspected source sample and the standard deviation of the difference estimated from statistically equivalent or different standard deviations of compared probabilities of true or false compositional equivalence claims
t_x	t -value of the Student's t distribution considering 95% or 98% confidence level and $(n_x - 1)$ degrees of freedom
γ	Probability (specific risk) of true acceptance of diagnostic ratio equivalence observed in two samples

γ_{95}	Probability (specific risk) of true acceptance of diagnostic ratio equivalence observed in two samples, estimated by the Monte Carlo Method or Student's t approaches considering 95% confidence level
γ_{98}	Probability (specific risk) of true acceptance of diagnostic ratio equivalence observed in two samples, estimated by the Monte Carlo Method or Student's t approaches considering 98% confidence level
γ_{SC}	Probability (specific risk) of true acceptance of diagnostic ratio equivalence observed in two samples, estimated by the single criterion approach
δ	Probability (total risk) of true acceptance of the compositional equivalence between two samples (used in Chapter 3); probability of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill (used in Chapters 4 and 5)
$\bar{\delta}$	Mean value of the probability (total risk) of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill
$\delta_{1^{st}T}$	Probability of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill, estimated using the outcomes from the first diagnostic ratio comparison trial
δ^{1T}	Probability of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill, estimated considering the outcomes of a single diagnostic ratio comparison trial
$\delta_{2^{nd}T}$	Probability of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill, estimated using the outcomes from the second diagnostic ratio comparison trial
δ^{2T}	Probability of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill, estimated considering the outcomes of the combined effect of two diagnostic ratio comparison trials (used in Chapter 5)
$\delta_{3^{rd}T}$	Probability of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill, estimated using the outcomes from the third diagnostic ratio comparison trial
δ^{3T}	Probability of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill, estimated considering the outcomes of the combined effect of three diagnostic ratio comparison trials

δ_{95}	Probability (total risk) of true acceptance of the compositional equivalence between two samples, estimated by the Monte Carlo Method or Student's t approaches considering 95% confidence level
δ_{98}	Probability (total risk) of true acceptance of the compositional equivalence between two samples, estimated by the Monte Carlo Method or Student's t approaches considering 98% confidence level
δ_{MCM}	Probability (total risk) of true acceptance of the compositional equivalence between two samples, estimated by the Monte Carlo Method approach
$\bar{\delta}_{\text{MCM}}$	Mean value of the probability (total risk) of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill, estimated by the Monte Carlo Method approach
δ_{SC}	Probability (total risk) of true acceptance of the compositional equivalence between two samples, estimated by the single criterion approach
$\bar{\delta}_{\text{SC}}$	Mean value of the probability (total risk) of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill, estimated by the single criterion approach
$\bar{\delta}_{\text{S-t}}$	Mean value of the probability (total risk) of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill, estimated by the Student's t approach
Δ	Amplitude between confidence limits estimated for the diagnostic ratio of sample x or for the difference between diagnostic ratio means determined in sample x and sample y
Δ_{95}	Amplitude between confidence limits estimated for the diagnostic ratio of sample x or for the difference between diagnostic ratio means determined in sample x and sample y , by the Monte Carlo Method or Student's t approaches considering 95% confidence level
Δ_{98}	Amplitude between confidence limits estimated for the diagnostic ratio of sample x or for the difference between diagnostic ratio means determined in sample x and sample y , by the Monte Carlo Method or Student's t approaches considering 98% confidence level

Δ^N	Amplitude between confidence limits estimated for the diagnostic ratio of sample x or for the difference between diagnostic ratio means determined in sample x and sample y , normalised with the percentile associated to a cumulative probability of 50% of the simulated data from the Monte Carlo Method approach
Δ^{N95}	Amplitude between confidence limits estimated for the diagnostic ratio of sample x or for the difference between diagnostic ratio means determined in sample x and sample y , by the Monte Carlo Method or Student's t approaches considering 95% confidence level, normalised with the percentile associated to a cumulative probability of 50% of the simulated data from the Monte Carlo Method approach
Δ^{N98}	Amplitude between confidence limits estimated for the diagnostic ratio of the sample x or for the difference between diagnostic ratio means determined in the sample x and in the sample y , by the Monte Carlo Method or Student's t approaches considering 98% confidence level, normalised with the percentile associated to a cumulative probability of 50% of the simulated data from the Monte Carlo Method approach
Δ^{NSC}	Amplitude between confidence limits estimated for the diagnostic ratio of sample x or for the difference between diagnostic ratio means determined in sample x and sample y , by the single criterion approach, normalised with the percentile associated to a cumulative probability of 50% of the simulated data from the Monte Carlo Method approach
Δ^{SC}	Amplitude between confidence limits estimated for the diagnostic ratio of sample x or for the difference between diagnostic ratio means determined in sample x and sample y , by the single criterion approach
ε	Probability of false compositional equivalence claim between the spill sample and the suspected source sample known not to be the source of the spill
$\bar{\varepsilon}$	Mean value of the probability of false compositional equivalence claim between the spill sample and the suspected source sample known not to be the source of the spill
$\varepsilon_{1^{st}T}$	Probability of false compositional equivalence claim between the spill sample and the suspected source sample known not to be the source of the spill, estimated using the outcomes from the first diagnostic ratio comparison trial
ε^{1T}	Probability of false compositional equivalence claim between the spill sample and the suspected source sample known not to be the source of the spill, estimated considering the outcomes of a single diagnostic ratio comparison trial

$\varepsilon_{2^{\text{ndT}}}$	Probability of false compositional equivalence claim between the spill sample and the suspected source sample known not to be the source of the spill, estimated using the outcomes from the second diagnostic ratio comparison trial
ε^{2T}	Probability of false compositional equivalence claim between the spill sample and the suspected source sample known not to be the source of the spill, estimated considering the outcomes of the combined effect of two diagnostic ratio comparison trials
$\varepsilon_{3^{\text{rdT}}}$	Probability of false compositional equivalence claim between the spill sample and the suspected source sample known not to be the source of the spill, estimated using the outcomes from the third diagnostic ratio comparison trial
ε^{3T}	Probability of false compositional equivalence claim between the spill sample and the suspected source sample known not to be the source of the spill, estimated considering the outcomes of the combined effect of three diagnostic ratio comparison trials
$\bar{\varepsilon}_{\text{MCM}}$	Mean value of the probability of false compositional equivalence claim between the spill sample and the suspected source sample known not to be the source of the spill, estimated by the Monte Carlo Method approach
$\bar{\varepsilon}_{\text{SC}}$	Mean value of the probability of false compositional equivalence claim between the spill sample and the suspected source sample known not to be the source of the spill, estimated by the single criterion approach
$\bar{\varepsilon}_{\text{S-t}}$	Mean value of the probability of false compositional equivalence claim between the spill sample and the suspected source sample known not to be the source of the spill, estimated by the Student's t approach
η	Overlapping percentage of confidence intervals defined by the Monte Carlo Method and by the Student's t method
θ	Probability of two compositionally equivalent samples not producing all equivalent diagnostic ratio pairs that define the oil fingerprints; probability of falsely rejecting equivalence between samples (estimation by simulation method)
ξ	Degrees of freedom of the difference between diagnostic ratio means determined in the sample x and sample y (used in Chapter 3), or in the spill sample and suspected source sample (used in Chapters 4 and 5)
$\lfloor \xi \rfloor$	Nearest integer of the degrees of freedom of the difference between diagnostic ratio means determined in the sample x and sample y (used in Chapter 3), or in the spill sample and suspected source sample (used in Chapters 4 and 5)

τ	Percentage of non-equivalent diagnostic ratios in a set of diagnostic ratios compared, determined in the spill sample and in the suspected source sample
φ	Probability of the confidence limits estimated by the Student's t method falsely rejecting equivalence between compared diagnostic ratios; fraction of the total area below the probability density function of the simulated data by Monte Carlo Method that is beyond the limits defined by the Student's t model for a certain confidence level
$\bar{\varphi}$	Mean value of the probability of the diagnostic ratio confidence limits, estimated by the Monte Carlo Method and Student's t methods, falsely do not include the diagnostic ratios determined in an independent analysis of the same sample (estimation by experimental method)
ω	Probability (total risk) of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill, estimated considering the outcomes of two diagnostic ratio comparison trials (used in Chapter 4)
$\bar{\omega}$	Mean value of the probability (total risk) of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill, estimated considering the outcomes of two diagnostic ratio comparison trials
$\bar{\omega}_{\text{MCM}}$	Mean value of the probability (total risk) of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill, estimated by the Monte Carlo Method approach considering the outcomes of two diagnostic ratio comparison trials
$\bar{\omega}_{\text{SC}}$	Mean value of the probability (total risk) of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill, estimated by the single criterion approach considering the outcomes of two diagnostic ratio comparison trials
$\bar{\omega}_{\text{S-t}}$	Mean value of the probability (total risk) of true compositional equivalence claim between the spill sample and the suspected source sample known to be the source of the spill, estimated by the Student's t approach considering the outcomes of two diagnostic ratio comparison trials

Units outside the International System of Units

$^{\circ}\text{API}$	American Petroleum Institute degrees; used to express the API gravity
% w/w	Percentage of mass fraction; used to express the concentration

cP	Centipoise; used to express the dynamic viscosity
cSt	Centistokes; used to express the kinematic viscosity
mb	Million barrels; used to express the crude oil reserve
mb/d	Million barrels per day; used to express the crude oil production
mg/mL	Miligrams per millilitre; used to express the concentration
mm ² /s	Square millimetre per second; used to express the kinematic viscosity
mN/m	MilliNewtons per meter; used to express the interfacial tension
mPa.s	Millipascal-second; used to express the dynamic viscosity

Introductory Note

The research presented in this PhD thesis was conducted over the course of the last four years as part of cooperation between the *Instituto Hidrográfico* (IH) and the *Faculdade de Ciências da Universidade de Lisboa* (FCUL). Two supervisors oversaw the work, namely Doctor Ricardo Jorge Neves Bettencourt da Silva from FCUL and Doctor Carla Maria Ferreira Mesquita Palma from IH.

This thesis presents and discusses the results of papers published in international journals with peer review and relevant impact factor in accordance with the paragraph a) of the no. 2 of the Article 25 of the *Regulamento de Estudos de Pós-graduação da Universidade de Lisboa*, published as Despacho n.º 8631/2020 (2020)¹.

As the papers were written in collaboration with the supervisors, the candidate states that she was fully and actively involved in the idea conceptualisation, research design, development of the computational tools, laboratory work, analytical data acquisition and processing, outcomes analysis and their critical discussions, as well as manuscript production.

The thesis is written in English and contains a **Preface** followed by six chapters. In the **Preface**, the candidate mentions the motivation behind the research topic of this thesis, as well as its main objective and sub-objectives.

The **Chapter 1** introduces the topic under research, pointing not only the evolution of spills in Portugal and worldwide but also their main causes and sources. It also addresses the chemical composition of crude oils and their derivatives, as well as the processes that occur and change the chemical composition when they are spilt in the marine environment. The chapter concludes with the presentation of the state of the art of the processes applied to the forensic chemical analysis that are essential to determine the source of an oil spill, as well as a brief theoretical introduction to the statistical approaches employed in the investigations detailed in this thesis.

Chapters 2 to 5 outline the four published studies, each of which provides an abstract with keywords sorted alphabetically, a brief introduction, the description of the materials and methods used, the presentation and discussion of the study's results, and ends with the main findings.

¹ Despacho n.º 8631/2020, de 8 de setembro. (2020). *Diário da República n.º 175, Série II, 2020-09-08*. Available at <https://files.diariodarepublica.pt> (accessed on March 18, 2024).

Chapter 6 highlights the final remarks of the overall research conducted in this PhD, as well as the future research.

Except for **Chapter 6**, every chapter ends with a list of references. The lists of references are organised alphabetically by author surname. The multiple references with the same surname are presented in ascending order by year of publication. Furthermore, when studies by the same first author published in the same year are cited, the reference is distinguished by adding lowercase letters in alphabetical order after the year of publication. The thesis's citation and reference list presentation were made uniform, deviating from the format assumed by the journal that published the studies in certain instances.

A list of abbreviations and chemical structures of the compounds was not provided considering the high number of compounds analysed and the use of more than one abbreviation for the same compound in different chapters. In return, the list of abbreviations of the compounds analysed in the study presented in each chapter is provided in the corresponding annex, when necessary, except for the compounds referred in the chapters' text, with these being mentioned in the list of abbreviations. The abbreviations and symbols adopted in the published versions of the studies provided in **Chapters 2 to 5** have been retained unchanged to faithfully reproduce the original papers, even if the same designation is referred to different acronyms or symbols across chapters. However, the list of abbreviations and symbols provides the chapter in which each acronym or symbol is used.

An annex is mentioned for each of **Chapters 2 to 5** and contains additional information not covered in the main text, corresponding to the supplementary material made available in each paper published.

The various computational tools produced in Microsoft Excel during this PhD were made available for download in both this thesis and the published versions of the studies it presents.

The studies performed during the four years of this PhD was disseminated in one national and four international scientific journals with peer review, as well as in five national and nine international scientific events. The candidate also integrated various training activities, which contributed not only to instruct students and operators in the area but also to disseminate the research conducted for this PhD. A list of indicators presents all the participations and is available in the annexes.

Preface

The examination of oil samples collected from oil spills plays an important role for identifying the pollution source, the extent of contamination, and the behaviour and fate of the spilt oil. It was in the 1970s, after greater awareness of environmental preservation and protection and the consequent increase in regulation, that forensic analysis of oil samples from illegal pollution began. These analyses are grounded on the premise that each crude oil and derivative product has a distinct chemical pattern. Thus, the forensic scientists take this advantage to correlate oil patterns from collected samples in the spill and in suspected sources of the spill to identify the responsible parties of the pollution act and assign legal liability. Essentially, the methodologies employed focus primarily on sample analysis by gas chromatography, which extensively characterises the oil samples by abundance ratios of oil-discriminating compounds, *i.e.*, diagnostic ratios. A comparative analysis of the diagnostic ratios is next performed, involving statistical and/or chemometric tools to assess similarities and identify the potential polluting source with a reliable, solid, and defensible foundation. Some of the current oil pattern comparison approaches, *i.e.*, the Student's *t* statistics and a maximum relative difference between diagnostic ratios, adopt approximations, such as the assumption of the normality of the probability distribution of diagnostic ratios and a likely dispersion of the diagnostic ratios replicates, respectively. These assumptions may result in highly uncertain assessments of the oil patterns equivalence and, consequently, weak and unreliable evidence. Therefore, to ensure the quality of an oil spill origin claim it is essential to adjust the statistical tools used in the data evaluation as closely as possible to the probabilistic reality of the diagnostic ratios, as well as to assess and reduce the uncertainty of the spill source identifications.

In Portugal, the *Instituto Hidrográfico* is responsible for performing the chemical analyses aiming to identify the sources of oil spills in the marine environment, supporting the *Autoridade Marítima Nacional* in solving illegal pollution acts. Since 2010, these analyses have been carried out according to an internal analytical method, implemented and optimised by the candidate, that follows international guidelines and was improved by in-house research and development studies. The candidate also delivers courses to provide the officers of *Polícia Marítima*, from the *Autoridade Marítima Nacional*, with the knowledge and technical skills required to collect oil samples for expert analysis. In addition, the candidate participates in the annual exercises to combat sea pollution promoted by the *Direção de Combate à Poluição do Mar* of the *Autoridade Marítima Nacional* and joined, since 2015 to 2023¹ the Oil Spill

¹ Due to sustainability factors, in 2023 the network was restructured and limited to laboratories nominated by the governments of the nations covered by the Bonn Agreement. For this reason, the *Instituto Hidrográfico* is no longer a member since Portugal is not a contracting party to the Bonn Agreement.

Identification Network of Experts within Bonn Agreement, known as Bonn-OSINet. All these activities enable to find vulnerabilities in different facets of the forensic process, one of them being the reliability and robustness of the findings obtained by the chemical analyses presented to the court.

The needs identified and cited above motivated the investigation of procedures and tools that could result in relevant improvement and streamlining for the processes of oil spill source identification, namely the data examination and the evidence presentation. In this sense, this PhD thesis's research aimed to assess and optimise the uncertainty in identifying the source of oil spills in the marine environment. To attain this purpose, it is proposed a novel and innovative approach to compare oil patterns that is more objective, statistically sound and employs optimised comparison conditions. The new approach also allows estimating the probabilities of compositional equivalence claim between different pairs of spill and suspected source samples to determine likelihood ratios, enabling the assessment of the oil spill source identification uncertainty. Both processes result in an upgrading in the quality of the spill source identifications. Some intermediate objectives were defined in accordance with the overall goal of this PhD, namely:

- To develop a new approach to compare oil patterns that describes the real probabilistic behaviour of the diagnostic ratios;
- To create and validate user-friendly computational tools to compare oil patterns using the developed approach and other standard methodologies that can be applied to different comparison conditions, as well as to estimate probabilities of composition equivalence claim between two samples considering outcomes from only one or more diagnostic ratios comparison trials;
- To verify the existence of deviations from the normality of the probability distributions of diagnostic ratios at different comparison conditions and evaluate the impact that these deviations have on the comparisons of the ratios through the quality of compositional equivalences claims of compared sample pairs;
- To apply the created computational tools to samples from oil spill scenarios reproduced in international proficiency tests in order to evaluate and compare the performance of different oil pattern comparison approaches, both the developed and the standard ones, obtained under different comparison conditions and using more than one diagnostic ratio comparison trial;

- To assess the uncertainty of the oil spill source identifications by calculating likelihood ratios using probabilities of compositional equivalence claim between distinct sample pairs, which are estimated by both the proposed approach and the standard methodologies;
- To formulate and propose a strategy to identify the most probable origin of an oil spill that will improve the strength of the evidence from the chemical analysis to be presented in court.

During the first year of the PhD, a novel approach for comparing the chemical compositions of two oils was conceived and implemented into a user-friendly computational tool. This tool works for the replicated analysis of one of the oils to compare and the single analysis of the other, along with the comparison conditions proposed by one of the recommended conventional methodologies, *i.e.*, the Nordtest method. The application of the novel approach, that simulates diagnostic ratios applying the Monte Carlo Method, allowed to evaluate not only the probabilistic behaviour of diagnostic ratios, but also the quality of oil compositional equivalence claims. The study, described in **Chapter 2**, was published in the research paper mentioned below, where the developed spreadsheet was also made available.

- Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N. (2022). Development and validation of statistically sound criteria for the match of unweathered GC-MS fingerprints in oil spill forensics. *Chemosphere*, 289, 133085. DOI: [10.1016/j.chemosphere.2021.133085](https://doi.org/10.1016/j.chemosphere.2021.133085). (IF 8.8; CS 13.3; Q1; Candidate contribution statement: conceptualization, methodology, software, validation, formal analysis, investigation, data curation, writing (original draft), visualization)².

In the second year, the computational tool created was adapted to include the requirements for comparing chemical compositions specified by the current standard methodology applied to oil spill source identification, *i.e.*, the EN 15522-2 standard method. A broader range of compounds was set to determine, and the tool became more flexible by facilitating the selection of different comparison conditions, particularly the number of replicated analyses to be considered for each compared oil sample. Furthermore, an adaptation of the tool was made for estimating the probability of true compositional equivalence claim of two oils compared. This improved tool was validated by its application to sample data from an international proficiency test. The results also enabled an assess of the probabilistic behaviour of the variables that characterise

² The concept and its definition are listed at Brand, A., Allen, L., Altman, M., Hlava, M., Scott, J. (2015). Beyond authorship: Attribution, contribution, collaboration, and credit. *Learned Publishing*, 28, 151–155. DOI: [10.1087/20150211](https://doi.org/10.1087/20150211).

the chemical composition of the samples when different replicates of each sample are employed, as well as the impact that different comparison conditions applied to the new and conventional approaches induce on the performance and quality of the oil composition equivalence claims. This work is detailed in **Chapter 3** and was published, along with the optimised and upgraded computational tool, in the following research paper:

- Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N. (2022). Optimisation of the uncertainty of oil spill identification from replicate comparative analyses: Comparison of standardised and novel identification methods. *Chemosphere*, 308, 136201. DOI: [10.1016/j.chemosphere.2022.136201](https://doi.org/10.1016/j.chemosphere.2022.136201). (IF 8.8; CS 13.3; Q1; Candidate contribution statement: conceptualization, methodology, software, validation, formal analysis, investigation, data curation, writing (original draft), visualization)³.

The studies conducted in the third year of the PhD were focused on the applicability of the new and the conventional approaches for comparing the chemical compositions of different oil types, as well as the evaluation of their performance in claiming the oils compositional equivalence. The number of diagnostic ratios used to characterise each oil, as well as the combination of results from two comparison trials with different analytical data of the same oil samples, were also assessed. This work, presented in **Chapter 4**, was published in the following paper:

- Rocha, A.C., Bettencourt da Silva, R.J.N., Palma, C. (2023). Statistically sound comparison of standardized and simulation methods for oil spill source identification in real spill scenarios. *Science of the Total Environment*, 887, 163930. DOI: [10.1016/j.scitotenv.2023.163930](https://doi.org/10.1016/j.scitotenv.2023.163930). (IF 8.2; CS 17.6; Q1; Candidate contribution statement: conceptualization, methodology, software, validation, formal analysis, investigation, data curation, writing (original draft), visualization)³.

The research activities performed in the final year of the PhD were entirely centred on evaluating the compositional equivalence or difference between oil samples, estimating the probabilities of a true and a false oil compositional equivalence claim, and assessing the strength of the expert analysis findings obtained by all the oil pattern comparison approaches under investigation. During the research, additional computational tools were created to estimate the probability of a false composition equivalence claim between oil samples. The outcomes of the studies supported the establishment of a strategy to identify the origin of spilt

³ The concept and its definition are listed at Brand, A., Allen, L., Altman, M., Hlava, M., Scott, J. (2015). Beyond authorship: Attribution, contribution, collaboration, and credit. *Learned Publishing*, 28, 151–155. DOI: [10.1087/20150211](https://doi.org/10.1087/20150211).

oils, which, being based on uncertainty, may more effectively assist the judgement on the guilt or innocence of the suspect for the pollution act. The **Chapter 5** presents the mentioned strategy and the studies that support it, which was published in the research paper:

- Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N. (2025). Sound uncertainty-based strategy for oil spill source identification. *Chemometrics and Intelligent Laboratory Systems*, 256, 105275. DOI: [10.1016/j.chemolab.2024.105275](https://doi.org/10.1016/j.chemolab.2024.105275). (IF 3.7; CS 7.5; Q2; Candidate contribution statement: conceptualization, methodology, software, validation, formal analysis, investigation, data curation, writing (original draft), visualization)⁴.

The research presented in this thesis aim to contribute to a substantial improvement in the resolution of oil pollution cases in Portugal, where the presentation of the likelihood ratio and/or verbal equivalent can be an integral part of the technical reports emitted by the *Instituto Hidrográfico*, thus assisting the decision on the legal responsibility of the pollution act. Furthermore, the studies presented in this thesis constitute a valuable scientific contribution to the area. They not only provide the first objective evaluation of the performance of oil pattern comparison approaches, which is required for a well-founded assessment of the validity of the developed approach but also reveal the vulnerabilities of conventional approaches. Ultimately, the studies demonstrate the enhanced effectiveness of the new approach and the relevance of its use.

⁴ The concept and its definition are listed at Brand, A., Allen, L., Altman, M., Hlava, M., Scott, J. (2015). Beyond authorship: Attribution, contribution, collaboration, and credit. *Learned Publishing*, 28, 151–155. DOI: [10.1087/20150211](https://doi.org/10.1087/20150211).

1. General introduction

1.1. Oil spills in the marine environment

1.1.1. Overview of oil spills worldwide and regionally

The pollution of the marine environment is, by definition, "the introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of seawater, and reduction of amenities" (GESAMP, 1993). Among numerous contaminants that may pollute the marine environment, contamination by crude oil (*i.e.*, liquid petroleum) and its derivatives has long been an important worldwide problem due to its harmful impacts and challenges in the fight for its mitigation. This contamination is either natural or anthropogenic (*i.e.*, a consequence of human activities), and it is mostly caused by seepage of natural origin from petroleum reservoirs as well as petroleum extraction, production, transportation, and consumption. As a result of human activities, oil can be introduced in the marine environment accidentally or by deliberate discharges, either operational or illegal discharges, accomplishing or violating the laws and regulations. Among the various sources, those related to fuel transfer operations, oil and gas exploration and production, operational discharges from vessels and the oil and gas industry, as well as incidents involving vessels and aircraft are particularly noteworthy (NRC, 2003; Stout and Wang, 2007; Stout *et al.*, 2016a; Zhang *et al.*, 2019). Concerning the future, as well as the growing importance today, the National Research Council of United States National Academy of Sciences (NRC) has recently identified other potential sources of oil pollution in the marine environment. These include sunken wrecks, aged and decommissioned infrastructures located in the sea and along the coasts, as well as extreme weather events (*e.g.*, earthquakes, hurricanes, severe storms) whose intensity and frequency are increasing due to climate change (NRC, 2022). The first two sources can be damaged by corrosion, submarine landslides, tectonic displacements, and even by collisions with vessels in transit, while the last one can cause significant damage to extraction and production platforms as well as difficulties in vessel navigation that may result in equipment failure and grounding.

The most recent estimates of the amount of crude oil and derivatives released into the global marine environment were provided for the period of 1988 to 1997 by the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) and for the period of 1990 to 1999 by the NRC (NRC, 2003; GESAMP, 2007).

The NRC estimated an average oil intake into the marine environment of more than 1,300,000 tonnes/year, with 45% of the total petroleum input worldwide due to natural seeps (600,000 tonnes/year) and the remain 55% due to anthropogenic activities related to oil and gas exploration and production activities, oil transportation and refining, oil consumption, and other sources (NRC, 2003). GESAMP published similar statistics, estimating an average oil input into the marine environment of 1,245,200 tonnes/year, with anthropogenic activities being responsible for 52% of total oil released and 48%, corresponding to 600,000 tonnes/year, owed to natural oil seeps (GESAMP, 2007). **Figure 1.1** shows the distribution of oil inputs into the marine environment from man-made sources identified by NRC and GESAMP.

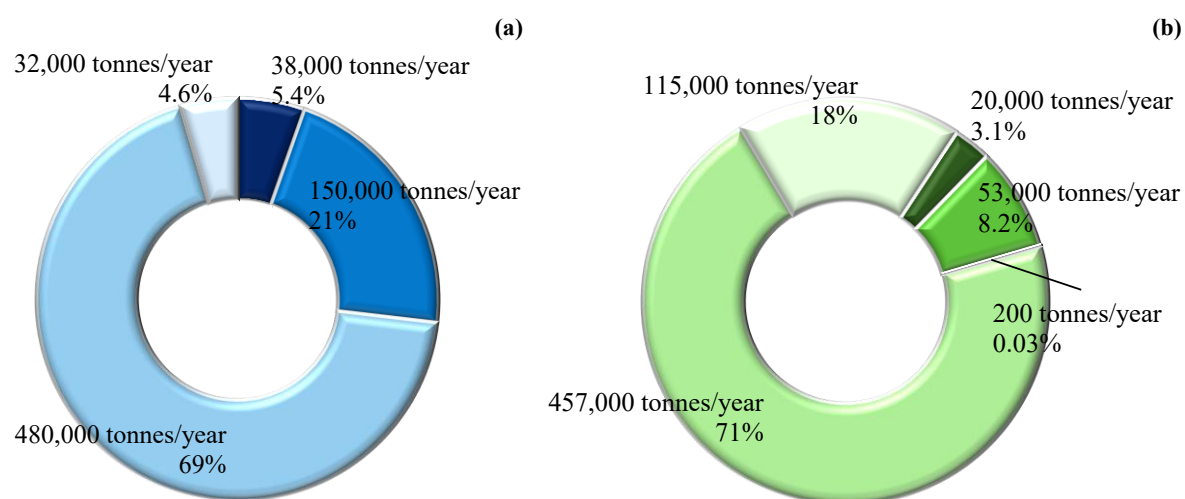


Figure 1.1. Distribution of oil inputs into the marine environment by anthropogenic activities identified by (a) National Research Council of United States National Academy of Sciences and (b) Group of Experts on the Scientific Aspects of Marine Environmental Protection. ● Oil and gas exploration and production; ● Oil transportation and refining; ● Oil consumption; ● Other sources; ● Oil and gas exploration and production; ● Small craft activities; ● Shipping activities; ● Coastal facilities; and ○ Unidentified sources (adapted from NRC (2003) and GESAMP (2007)).

According to the NRC, oil consumption is the primary source of oil contamination, followed by oil transportation and refining and GESAMP identified maritime operations and coastal infrastructures as the most significant contributors to oil input into marine environment. In addition, the operational discharges and accidents from vessels contribute with 45% (207,900 tonnes/year) and 36% (163,200 tonnes/year) of the total amount of spilt oil from vessels, respectively, with the bilge and sludge waster oils being the main spilt oil products from operational discharges (188,000 tonnes/year).

According to the estimates presented in the most recent NRC report, for the region of North America and the period from 2010 to 2019, there was a decrease in the oil input into the marine

environment from 9,209 tons/year to 818 tons/year as a result of activities related to oil transportation and distribution. Nevertheless, there was an increase from 2,980 tonnes/year to 9,500 tonnes/year for oil extraction and production activities and from 83,520 tonnes/year to 1,200,399 tonnes/year for oil consumption, with the latter being mostly due to land-based runoff (NRC, 2022).

The European Maritime Safety Agency (EMSA) conducted a periodic assessment of maritime accidents and incidents in the territorial sea or inland waters of the member states of the European Union (EU) for the period 2014 to 2022 (EMSA, 2023). The assessment shows that there is not much variation in the number of occurred incidents, with cargo vessels suffering the most occurrences when compared to passengers, fishing, and service vessels. When all vessel types are included, the total amount of occurrences is 51.5% in internal waterways, 24.3% in territorial seas, and 20.8% in open seas (both inside and beyond the Economic Exclusive Zone (EEZ)). Although, the frequency of pollution-related incidents has decreased since 2014, the spills of fuel, cargo residues, lubricants, and hydraulic oils still accounting for 64.2% of all pollution caused by bunker vessels.

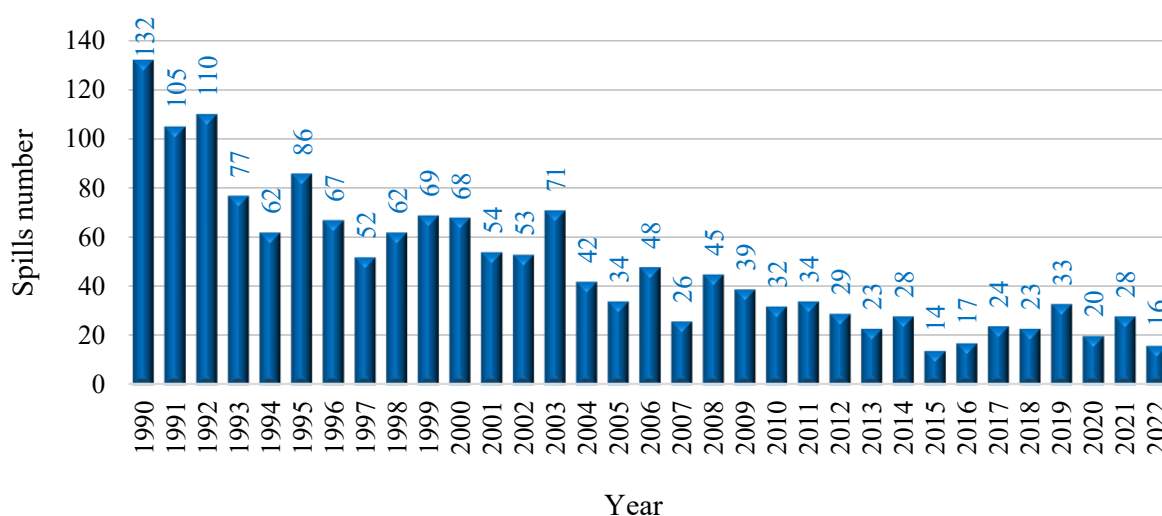
Statistics from 2002 to 2021 of the United States of America (USA) Coast Guard also revealed a decreasing trend in the number of incidents and volume of oil released into USA waters (Ramseur, 2023). The same decline was also reported by the Baltic Marine Environment Protection Commission, known as the Helsinki Commission (HELCOM), in the Baltic Sea during aerial surveillance operations in the period of 2003 to 2022, with 292 and 64 oil discharges detected in 2003 and 2022, respectively, and discharges of less than 1 m³ being the most representative (HELCOM, 2023).

The International Tanker Owners Pollution Federation Limited (ITOPF) maintains a global record of oil spills caused by tanker vessels. Despite the increase in oil exploration, production, and transportation since the 1970s, ITOPF has also reported a decrease in the number of oil spills (ITOPF, 2024). However, there has been no apparent change in the statistics for the most recent periods of 2010 to 2019 and 2020 to 2023, with averages of 6.3 and 6.8 occurred spills, respectively. According to ITOPF, medium-rated spills (7 to 700 tonnes of oil spilt) occur more frequently than large spills (> 700 tonnes of oil spilt), but the rare occurrence of major pollution accidents may lead to a single event accounting for more than half of the total spilt oil that year (**Table 1.1**).

Table 1.1. Amount of spilled oil from major tanker vessels accidents related to the total oil spilled in the year of the event (adapted from ITOPF (2024)).

Year	Vessel	Spill location	Amount of spilled oil by the vessel (tonnes)	Total amount spilled oil in the year of the incident (tonnes)	Amount of spilled oil by the vessel relative to the total of spilled oil (%)
1978	<i>Amoco Cadiz</i>	Off Brittany (France)	223,000	393,000	57
1983	<i>Castillo de Bellver</i>	Off Saldanha bay (South Africa)	252,000	384,000	66
1985	<i>Nova</i>	Off Kharg Island (Gulf of Iran)	70,000	85,000	82
1988	<i>Odyssey</i>	700 nautical miles off Nova Scotia (Canada)	132,000	190,000	70
1991	<i>Abt Summer</i>	700 nautical miles off Angola	260,000	431,000	60
1996	<i>Sea Empress</i>	Milford Haven (United Kingdom)	72,000	80,000	90
2002	<i>Prestige</i>	Off Galicia (Spain)	63,000	66,000	96
2007	<i>Hebei Spirit</i>	Off Taean (South Korea)	11,000	15,000	76
2018	<i>Sanchi</i>	Shanghai (China)	113,000	116,000	97

According to data shared by the *Direção de Combate à Poluição do Mar* (DCPM) of the *Autoridade Marítima Nacional* (AMN), the number of oil spills reported by the *Comandos Locais da Polícia Marítima* (CLPM) that occurred between 1990 and 2022 in waters under Portuguese jurisdiction has shown the same downward trend observed throughout the world (Figure 1.2).

**Figure 1.2.** Evolution of the number of oil spills reported to the *Direção de Combate à Poluição do Mar* of the *Autoridade Marítima Nacional* by the *Comandos Locais da Polícia Marítima* in the period of 1990 to 2022 (data unpublished shared by the *Direção de Combate à Poluição do Mar* of the *Autoridade Marítima Nacional*).

During this period, 78% of pollution cases reported to DCPM were caused by oil spills, followed by 17% by unidentified substances or other type of pollution, 3.8% by hazardous and noxious substances (HNS), and 0.74% by vegetable oils (**Figure 1.3 (a)**). Furthermore, the most spilt oil typology was oily mixtures/residues (33%), *i.e.*, waste oils from vessel machinery rooms, diesel (31%), and fuel oil (24%), with naphtha, gasoline, and crude oil accounting for the remaining 12% (**Figure 1.3 (b)**).

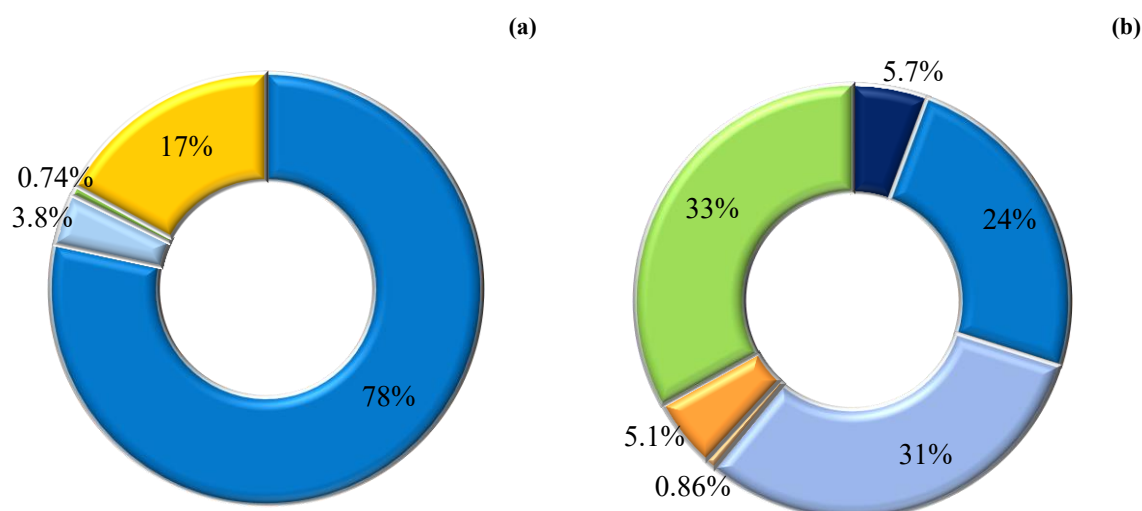


Figure 1.3. Spilt substances reported to the *Direção de Combate à Poluição do Mar* of the *Autoridade Marítima Nacional* by the *Comandos Locais da Polícia Marítima* in the period of 1990 to 2022: (a) by type of substance, ● oil, ● hazardous and noxious substances, ● vegetable oils and ● unidentified substances or other type of pollution; (b) by type of oil product, ● crude oil, ● fuel oil, ● diesel, ● gasoline, ● naphtha and ● oily mixtures/residues (data unpublished shared by the *Direção de Combate à Poluição do Mar* of the *Autoridade Marítima Nacional*).

Out of all the pollution events with incident type reported (66%), the spilt of the aforementioned substances occurs mostly from failures in refuelling or transfer operations (24%), in loading or unloading cargo operations (19%), and in equipment (15%) (**Figure 1.4**). However, in 20% of cases the officers of *Polícia Marítima* (PM) were unable to identify the incident's cause.

The PM officers confirmed the presence of pollution *in loco* in 98% of the 1,623 pollution notifications received by DCPM from 1990 to 2022, with the remaining 2.0% cases involving a lack of verification. However, only 11% of confirmed spills were sampled for expert analysis. The CLPM with the most cases of pollution identified in their jurisdiction area were the CLPM of Lisboa (655 spills), Setúbal (141 spills), Leixões (132 spills), Sines (108 spills), and Aveiro (88 spills) due to proximity to the country's major harbours and oil industry (**Figure 1.5**). Compared to the rest of continental Portugal, the CLPM of Funchal (77 spills) and Ponta

Delgada (56 spills) on the Madeira and Azores archipelagos recorded a significant number of spills.

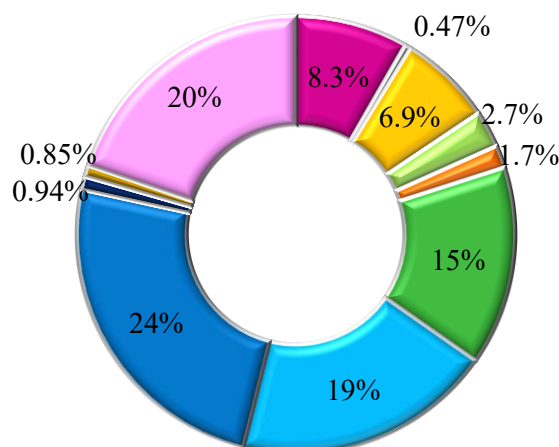


Figure 1.4. Type of occurrence that caused the spill reported to the *Direção de Combate à Poluição do Mar* of the *Autoridade Marítima Nacional* by the *Comandos Locais da Polícia Marítima* in the period of 1990 to 2022: ● sinking, ● collision, ● illegal discharge/washing tanks, ● grounding, ● runoff originating on land, ● equipment failure, ● failure in loading/unloading cargo operations, ● failure in refuelling/transfer operations, ● fire/explosion, ● breach in the hull and ● unidentified cause (data unpublished shared by the *Direção de Combate à Poluição do Mar* of the *Autoridade Marítima Nacional*).

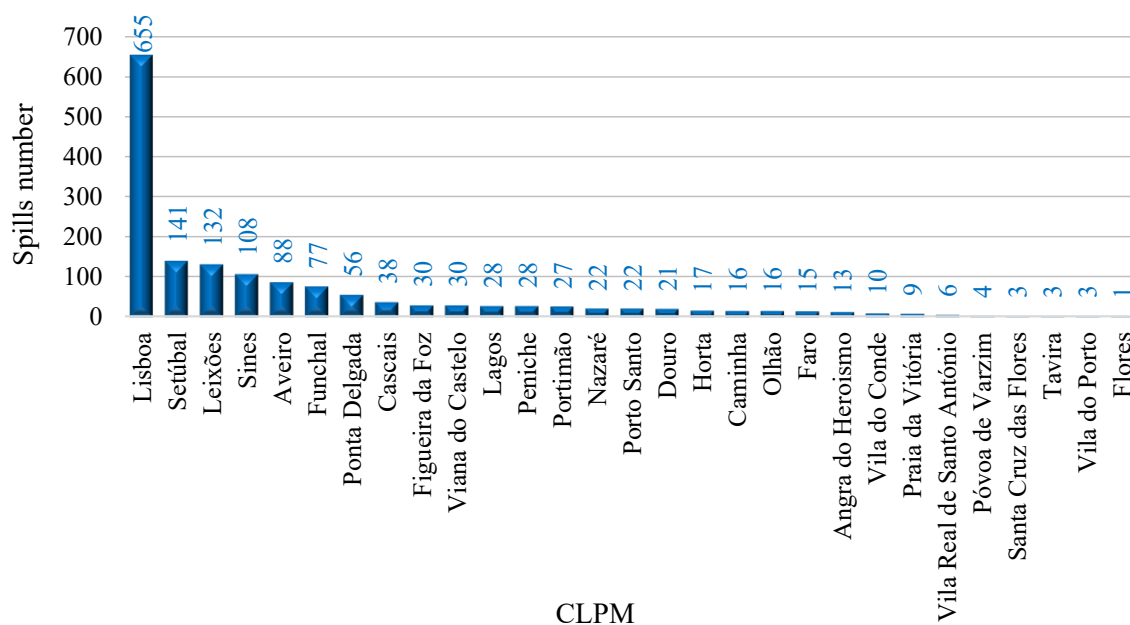


Figure 1.5. Number of spills reported to the *Direção de Combate à Poluição do Mar* of the *Autoridade Marítima Nacional* by each *Comando Local da Polícia Marítima* in the period of 1990 to 2022 (data unpublished shared by the *Direção de Combate à Poluição do Mar* of the *Autoridade Marítima Nacional*).

A European satellite-based oil spill and vessel detection service operated by EMSA since 2007, *i.e.*, CleanSeaNet (CSN), provides synthetic aperture radar (SAR) satellite images to detect and track oil pollution on the sea surface, to monitor unintentional pollution during emergencies, and to assist the identification of potential polluters (EMSA, 2024). Once a slick is detected in European waters, the coastal States are notified, and the national authorities and contact points receive an alert report with the SAR images and some important information, such as slick location, area and length, as well as potential origin (*e.g.*, vessels). Records of oil pollution detection by CSN on the sea under national jurisdiction were also made available by DCPM. **Figure 1.6** presents the number of slicks detected by CSN between 2008 and 2022 (2,180 slicks), with the observed different trends resulting from greater surveillance and control of maritime space, the number of satellites operating, and the improvements made to the CSN (*e.g.*, increase of the monitored area and detection of the smaller spills). During this period, most slicks were found in the CLPM jurisdiction regions of Lagos and Funchal (290 and 249 slicks, respectively) (**Figure 1.7**).

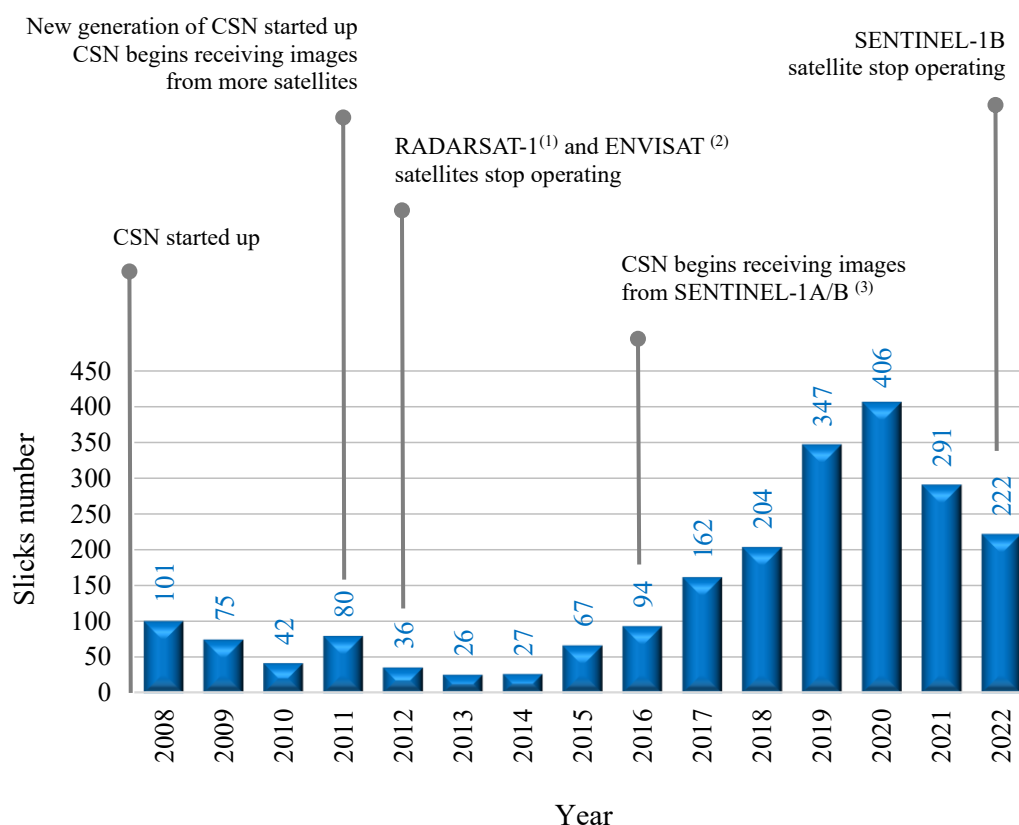


Figure 1.6. Evolution of the number of slicks detected by satellite for the period of 2008 to 2022. (1) Earth observation satellite operated by Canadian Space Agency; (2) Earth observation satellite operated by European Space Agency; (3) Earth observation satellite constellation (A and B satellites) operated by European Space Agency (data unpublished shared by the *Direção de Combate à Poluição do Mar* of the *Autoridade Marítima Nacional*; Sawyer and Khabarov, 2022).

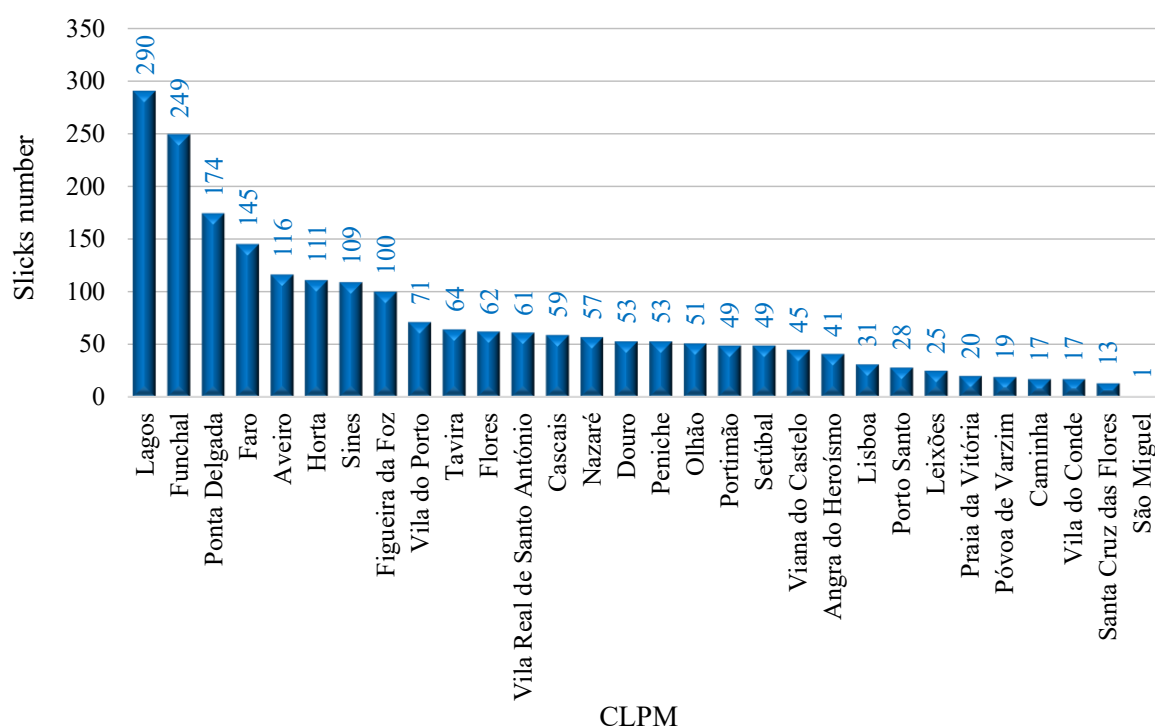


Figure 1.7. Number of slicks detected by satellite in the jurisdiction area of each *Comando Local da Polícia Marítima* for the period of 2008 to 2022 (data unpublished shared by the *Direção de Combate à Poluição do Mar* of the *Autoridade Marítima Nacional*).

The global decline in the number of spills and the volume of spilt oil is mostly related to the implementation of the environmental management culture in the industry, changes in the operating regulations of vessels and offshore platforms, advancements in processes and techniques for monitoring, controlling, and detecting oil spills, and improvements in maritime traffic monitoring and management systems, oil pipelines, and cargo and fuel tanks of vessels (Homan and Steiner, 2008; Yip *et al.*, 2011; Ranasinghe *et al.*, 2021; NRC, 2022). However, oil spills continue to have a probability of occurrence that should not be neglected as the conservation of wildlife and the marine environment, especially the sensitive areas in inland and coastal waters, becomes more vital.

1.1.2. Behaviour, fate and impacts of oil spills

Spilt oil into the marine environment tends to float, producing a layer at the water surface whose thickness is influenced by several factors. The multiple interactions of a spilt oil will change the chemical and physical attributes of the oil, influencing its behaviour and fate, and impacting

the environment where it was released. These interactions are determined by the environmental conditions, including climate and conditions of the spill site, the original chemical and physical features of the oil, and the physical, chemical, and biological processes that the oil may experience (Rogowska and Namieśnik, 2010; ITOPF, 2014). Along with the physical properties of the oil (*e.g.*, viscosity), the marine hydrodynamic conditions, such as currents and wave action, will favour the drift of oil slicks, their spread over the surface of the water, their dispersion in the water column, and their emulsification affecting the split oil behaviour and fate (NRC, 2003; Rogowska and Namieśnik, 2010; Chang *et al.*, 2014; ITOPF, 2014; Zhang *et al.*, 2019; Péquin *et al.*, 2022). The path of the oil slick can be shifted by routing it toward the open sea or sensitive coastal regions, resulting in different repercussions and cleanup actions. The dispersion of the oil in the aquatic system increases the area of oil exposure to water and the atmosphere, increasing the chance of occurring processes that modify the chemical and hence physical properties of the spilt oil. In addition, it promotes the oil interaction with particulate material suspended in the water column, forming the oil particle aggregates, which can enhance the oil transport in the water and accelerate the oil particle aggregates deposition on the seabed due to the rise in density (Rogowska and Namieśnik, 2010; ITOPF, 2014; Péquin *et al.*, 2022). The oil emulsification, which results of the incorporation of small water droplets into oil, produces an emulsion which, due to their larger volume, density, and viscosity, behave differently on water than oil, influencing the selection of the cleaning procedures (NRC, 2003).

Wind is another factor that influences the drift of an oil slick, and, like wave action, it could make cleaning operations at sea difficult or even impractical. The wind, along with the higher temperature, promotes evaporation, *i.e.*, the loss of the more volatile components and the solvent portion of the spilt oil, and therefore alters the behaviour of the oil in the water owing to changes in viscosity, density, and preference to emulsify (ITOPF, 2014). Moreover, this mechanism releases hazardous compounds into the atmosphere that might endanger marine life and human health, particularly sea birds and oil spill response workers, respectively. Other mechanisms that affect the marine environment, causing adverse effects on marine fauna and flora, are the dissolution, photo-oxidation, and biodegradation, which are discussed in more detail in **Section 1.3.3**, along with other physical and chemical processes. These processes depend on both oil type and biological, chemical, and physical characteristics of the environment in which the oil was discharged (NRC, 2003; Rogowska and Namieśnik, 2010; ITOPF, 2014; Zhang *et al.*, 2019). On the one hand, dissolution introduces harmful chemicals from petroleum into the marine environment with the potential to become bioavailable, on the

other hand, biodegradation and photo-oxidation processes produce byproducts that may be more hazardous than the original substances.

Because of their physical and chemical features, distinct oils react and end up differently in marine environment (GESAMP, 2009). Heavy oils, which are more viscous and have a higher density, are more persistent in the marine environment because they are easily retained and difficult to remove from the surfaces located on banks, beaches and harbours (*e.g.*, rocks and quays). Furthermore, these oils are less likely to spread to the water surface but more likely to mix with water and thus more likely to emulsify and disperse in the water column. On the contrary, the light oils are less viscous as they are richer in volatile components. As a result, these oils are less persistent because they easily and rapidly evaporate and spread in the water, making their removal from the marine environment faster.

The impacts of oil pollution in the marine environment could be characterised as chronic or acute. Chronic pollution has reduced release rates and has a long-term impact on wildlife populations (NRC, 2003; Rogowska and Namieśnik, 2010; Stout *et al.*, 2016a). An example of chronic pollution is urban runoff, which is the most significant source of petroleum contamination of waterways, resulting from oil consumption that is primarily carried out on land (NRC, 2003, NRC, 2022). Acute pollution, such as major oil spill accidents or illegal discharges, has a faster rate of release, forcing more oil to enter in the marine environment in a shorter period of time and resulting in harmful effects in a short-term (NRC, 2003; Stout *et al.*, 2016a).

The assessment of impacts is complex as they depend on a variety of factors such as the oil type, the spill size, the oil release rate, and the spill location, with the last one being the most important variable (Ramseur, 2023). Oil spills deteriorate natural resources due to the oil behaviour, as well as the toxicity, bioaccumulation, and biomagnification of the oil chemical components, resulting in known impacts for the environment, wildlife populations and human health (Rogowska and Namieśnik, 2010; Chang *et al.*, 2014; Li *et al.*, 2016; Zhang *et al.*, 2019; Asif *et al.*, 2022). The sediments fouled by oil particle deposition can release the oil chemical components into the water, becoming a chronic contamination source (Hong *et al.*, 2012; Nemirovskaya and Glyaznetsova, 2024). Even when cleaning measures are employed to eliminate the oil from the polluted site, the oil is not entirely removed, leaving residues that might cause chronic contamination until bioremediation is carried out. Besides, the cleaning techniques, such as manual or mechanical oil removal from water (*e.g.*, using absorbents and skimmers), pressurised hot water to remove oil from surfaces, application of chemical

dispersants, and *in situ* oil combustion, disrupt and damage marine ecosystems (Chang *et al.*, 2014; Asif *et al.*, 2022). In respect to wildlife, the oil layer formed on the water surface acts as a barrier to light penetration, reducing the organisms and plants that thrive through photosynthesis (Rogowska and Namieśnik, 2010). Birds and marine mammals that spend time at the water surface will come into more direct contact with the oil, compromising their thermal balance, locomotion, food seeking, and, above all, their health, leading to higher mortality rates. Despite having less oil exposure, subtidal species are more sensitive to chemicals and oxidation products that migrate from oil to water, as well as by ingestion of oily particles and contaminated food (Chang *et al.*, 2014; Zhang *et al.*, 2019). Human health is also put at risk not only by the ingestion of contaminated food but also by skin contact and inhalation of vapours from spilt oil, particularly during cleaning operations (Suarez *et al.*, 2005; Na *et al.*, 2012; Chang *et al.*, 2014; Jung *et al.*, 2017). To those previously mentioned, we may add the tremendous socioeconomic impacts caused by remediating the contaminated site, interrupting activities that rely on the affected natural resources, and the loss of the region's reputation (Chang *et al.*, 2014; Zhang *et al.*, 2019; Ramseur, 2023). The costs of cleaning the contaminated site and disposing its waste are determined not only by the location of the incident (more sensitive areas/ lower hydrodynamic conditions vs. less sensitive areas/ higher hydrodynamic conditions), but also by the quantity and oil type spilt (heavy oil/ greater volume spilt vs. lighter oil/ less volume spilt). Activities that are dependent on affected natural resources, such as commercial and recreational fishing, aquaculture industry, harbour activities, commercialised product transport, and maritime industries, may be severely harmed by the interruption of their exercise (Chang *et al.*, 2014; Ramseur, 2023). Furthermore, an oil spill in a tourist location or one that promotes recreational pursuits will lead to important impacts on the tourism sector, not only through restriction of the access to the site, but also by the effects on the region's reputation that is, in a certain way, correlated with media coverage of the incident (Chang *et al.*, 2014; Zhang *et al.*, 2019). A quick response to pollution accidents is critical to avoid catastrophic effects. However, it is not always feasible due to difficulties with the access of the contaminated site, logistics, and even unfavourable environmental conditions for the cleaning activities. The behaviour, fate and impacts assessment of spilt oil are critical parts of the extensive list of tasks that must be conducted following an oil pollution incident, as they facilitate decision-making and the development of appropriate contingency plans (Chang *et al.*, 2014; ITOPF, 2014; Jung *et al.*, 2017; Wegeberg *et al.*, 2024). In addition, appropriate warning of the dangers of oil contact to inhabitants, as well as proper usage of individual protective equipment by cleaning staff members, are required to reduce major public health risk.

Over the years, the modelling of the trajectory and the physical, chemical, and biological processes has been studied to predict the evolution of an oil spill (Lehr *et al.*, 2002; Mishra and Kumar, 2015; Keramea *et al.*, 2021; Chen *et al.*, 2023). This information is relevant not only to select the most effective measures to combat the oil spill, but also to evaluate the behaviour and fate of the spilt oil, as well as the environmental and socioeconomic consequences of the spill.

Above all and at last, the environment has the ability to heal itself and reestablish balance with the best self-remediation mechanisms being evaporation, biodegradation, and higher hydrodynamic conditions of the affected place (GESAMP, 2009; Rogowska and Namieśnik, 2010; Chang *et al.*, 2014; ITOPF, 2014; Barron *et al.*, 2020; Asif *et al.*, 2022).

As pointed out, the behaviour, fate, and impacts of spilt oil are a game of many interconnected factors, although the resulting effects of a spill decline with time as documented in various studies (Morales-Caselles *et al.*, 2008; Kahkashan *et al.*, 2019; Barron *et al.*, 2020; Choueri *et al.*, 2024).

1.1.3. National and international legal frameworks

Over time, a reduction in the number of oil spills in the marine environment has been noted around the world, but they are still a concern due to their impacts. This reduction is mainly due to the policies and regulations that have been implemented and updated as a result of greater attention to environmental problems and the culture for preserving the natural resources at a global scale. The international conventions, regional treaties, and national legislation manage the legal framework related to marine pollution with the goal of protecting the marine environment and ensuring prevention, control, response, liability, and compensation to parties affected.

To internationalise standard measures for maritime safety, navigation efficiency, and prevention of marine pollution, the United Nations created in 1948 the Intergovernmental Maritime Consultative Organization, which entered into force in 1958 and was renamed to International Maritime Organization (IMO) in 1982. The IMO aims to increase maritime navigation safety and efficiency, as well as to prevent, combat, and regulate ship-caused marine pollution, being the most relevant international entity that coordinates and develops regulations and conventions in these domains. Currently, it comprises 176 member states and has developed 50 conventions and protocols (IMO, n.d.–a).

The international legal framework with respect to marine pollution is governed by several of IMO conventions (IMO, n.d.–b), namely those related to liability and compensation for affected parties, as well as those concerning to pollution prevention and combating.

Three conventions stand out when deciding culpability and attributing compensation: the International Convention on Civil Liability for Oil Pollution Damage (CLC), the International Convention on the Establishment of an International Fund for Compensation for Oil Pollution Damage (FUND), and the International Convention on Civil Liability for Bunker Oil Pollution Damage (BUNKER). The CLC was established in 1969 and has been amended a few times, with the most recent of which became effective in 1992. This convention addresses the liability for damages caused by oil pollution in 140 nations, including IMO members. Except for rare exceptions, shipowners are held liable for their actions, regardless of their guilt. Furthermore, with the support of the International Oil Pollution Compensation Fund (IOPC), it ensures that victims of pollution incidents are compensated. The IOPC was established with the entry into force of the Protocol 1992, which resulted from the revision of the FUND, which was adopted in 1971 and entered into force in 1976. This agreement aims to compensate parties that incurred damage from oil pollution where the compensation provided by CLC is insufficient. Furthermore, it can assist member states that have been or may be injured by the oil spill. More recently, the Protocol 2003 enter into force providing a supplementary fund to complement the compensation supplied by the IOPC and CLC. All these funds are obtained by contributions made by people from member states, considering the total amount of oil they receive by maritime way. The BUNKER, which was established in 2001 and went into action in 2008, gives compensation to parties who have been affected by spills of fuel from bunker vessels, that are not covered by the CLC. However, BUNKER follows the CLC 1969 as a reference and applies to damage committed within member nations' territorial seas and exclusive economic zones.

The prevention and combating of marine pollution are addressed by the International Convention for the Prevention of Pollution from Ships (MARPOL 73/78), the International Convention Relating to Intervention in the High Seas in Cases of Petroleum Pollution Casualties (INTERVENTION), and the International Convention on Oil Pollution Preparedness, Response and Co-operation (OPCR). The MARPOL 73/78, established in 1973 and amended by the Protocol 1978, went into force only in 1983, and it is the main worldwide treaty for preventing oil pollution in the marine environment caused by vessel operations and accidents. This convention currently includes six annexes that entered into effect on different

timescales, with measures to prevent, control, and minimise pollution from different types of substances:

- Annex I: Prevention of pollution by oil (in force since 1983);
- Annex II: Control of pollution by noxious liquid substances in bulk (in force since 1983);
- Annex III: Prevention of pollution by harmful substances carried by sea in packaged form (in force since 1992);
- Annex IV: Pollution by sewage from ships (in force since 2003);
- Annex V: Pollution by garbage from ships (in force since 1988);
- Annex VI: Prevention of air pollution from ships (in force since 2005).

Annex I is one of the most relevant, which presents regulations for the oil pollution prevention, whether accidental or from operational discharges, establishing oil discharge areas and criteria, as well as, requiring that all vessels carry oil record book and have emergency plans to deal with oil spills. Additionally, it contributed to the implementation of structural improvements in vessels by requiring oil tankers to have double hulls as a protective and preventive measure against oil spills.

Currently, the MARPOL 73/78 – Annexes I and II has 164 member states (IMO, n.d.–c) which are required to guarantee compliance with the regulations on their own vessels and on foreign vessels. Moreover, the convention defines special areas of greater ecological sensitivity and emission control areas (ECA), where stricter discharge regulations are in place, and the atmospheric emissions are more tightly controlled, imposing the use of fuels with lower sulphur content, respectively.

The INTERVENTION, adopted in 1969 and in force since 1975, grants a state the right to take preventive measures, mitigate, and eliminate the risk of oil spills in its coastal zone as a result of maritime accidents in the open sea. This convention is applicable to all vessels, apart from those owned by a state and operated by it for non-commercial purposes (*e.g.*, warships). With the increased transportation of other substances that can put at risk the environment if released, INTERVENTION adopted the Protocol 1973, which went into effect in 1983, granting member states the right to act in maritime accidents on the high seas that involve certain listed hazardous materials, such as noxious compounds (*e.g.*, acids, pesticides, organometallic compounds,

organic solvents), liquefied gases (*e.g.*, chlorine, methane, sulphur dioxide), and radioactive substances (*e.g.*, the isotopes cobalt-60, radium-226, uranium-235).

When it comes to respond and to combat oil pollution in the marine environment, the OPRC is one of the most relevant conventions. This agreement, established in 1990 and entered into effect in 1995, requires that parties have national systems capable of responding to oil spills caused by major pollution accidents, cooperation systems with third parties that focus on providing assistance in emergency situations, material and human resources to provide, as well as specialised technical knowledge. In this sense, the parties must designate national authorities to communicate the oil spill incidents and manage the oil spill response, as well as prepare national contingency plans that include emergency guidelines, and measures and resources to combat oil pollution and reduce environmental damage. Furthermore, harbours, vessels, and offshore production units that are under the jurisdiction of the parties must have emergency procedures established to deal with oil pollution in a timely and effective manner. Therefore, it is required to build up reserves of pollution-fighting equipment (*e.g.*, blooms and skimmers) and to train teams to respond to incidents, which is carry out, in part, by the OPRC's obligation to conduct incident and pollution combat exercises at the regional, national, and international scale. OPRC further requires vessels to report any oil spill to the authorities with jurisdiction over the affected region and parties to report any oil pollution that may impact neighbouring nations. Recently, and like INTERVENTION, the OPRC broadened its application to HNS through the OPRC-HNS Protocol 2000, improving the response to the mitigation of pollution caused by these compounds.

Portugal's commitment to protecting the marine environment, imposing legal responsibility on polluters, and compensating parties impacted by, can be witnessed in the agreement of the CLC in 1976 (Decreto n.º 694/76, 1976), INTERVENTION in 1979 (Decreto n.º 88/79, 1979), FUND in 1985 (Decreto do Governo n.º 13/85, 1985), MARPOL 73/78 in 1987 (Decreto do Governo n.º 25/87, 1987), OPRC and OPRC-HNS in 2006 (Decreto n.º 8/2006, 2006; Decreto n.º 12/2006, 2006), as well as BUNKER in 2015 (Resolução da Assembleia da República n.º 62/2015, 2015). To meet the requirements of the conventions, it was adopted maritime traffic monitoring measures (*e.g.*, Automatic Identification System (AIS), Vessel Traffic Service (VTS) and the European Maritime Surveillance System (SafeSeaNet), as well as vessel inspection proceedings through the process of Port State Control (PSC)). In addition, it was developed a national contingency plan designated by *Plano de Emergência para o Combate à Poluição das Águas Marinhas, Portos, Estuários e Trechos Navegáveis dos Rios, por*

*Hidrocarbonetos e Outras Substâncias Perigosas*¹, commonly called in Portugal as *Plano Mar Limpo* (PML). The PML (Resolução n.º 25/93, 1993) establishes a quick and efficient way of responding to threats or pollution of oil and other hazardous substances in order to prevent and mitigate the impacts caused, as well as setting the responsibilities of the entities involved in resolving and coordinating environmental disasters (e.g., AMN, *Marinha Portuguesa*², *Força Aérea Portuguesa*³, *Agência Portuguesa do Ambiente*⁴). This applies to incidents occurred in marine waters, harbours, estuaries, and navigable waterways (e.g., rivers). The PML requires, among others, the development of intervention and communication plans among entities, the acquisition and maintenance of pollution-fighting equipment, the training of technicians involved in this, and the execution of simulated pollution exercises (e.g., ATLANTIC POLEX.PT, carried out annually and promoted by the DCPM of the AMN (AMN, 2024)).

The identification of the polluting source is an essential part of the pollution combat management provided by the PML as the polluter must, whenever possible, be held liable. However, it is not always easy to identify the polluter given due, for example, to the challenge of recognising the potential origin of the pollution among multiple suspected sources, the late detection of the spill and the absence of the pollutant source at the spill site (e.g., deliberate discharge by a vessel ongoing). Suggested by the PLM, some procedures may be helpful to identify the spill source, such as the evaluation of information from maritime traffic monitoring and from the harbour inspections, as well as the analysis of spilt oil samples and oil collected in spill suspected sources to establish a correlation between the sample's chemical compositions. Even if the potentially polluting vessel is ongoing, international cooperation among member states allows the sample collection in the harbour when the vessel docks. When requested, samples are collected by the AMN (Decreto-Lei n.º 192/98, 1998) in accordance with a guideline from the *Direção-Geral da Autoridade Marítima*⁵ (Circular n.º 123/2007-P, 2007) and must be kept in a chain of custody. These samples are delivered to a laboratory with recognised competence to perform the required chemical analyses, such as the IH (Decreto-Lei n.º 235/2000, 2000), and the resulting technical report serves as evidence in criminal proceedings.

¹ Emergency Plan for Pollution Response of Marine Waters, Harbours, Estuaries, and Navigable River Sections by Hydrocarbons and Other Hazardous Substances.

² Portuguese Navy.

³ Portuguese Air Force.

⁴ Portuguese Environmental Agency.

⁵ General Directorate of the Maritime Authority.

1.2. Petroleum, crude oil and refined products

The term “petroleum” is derived from the Latin words *petra* and *oleum*, which literally mean rock oil (Gary *et al.*, 2007; Speight, 2014). The definition of petroleum has varied over time but is currently described as a mixture of hydrocarbons that occur naturally in gas, liquid, and solid states (Speight, 2014; Vassiliou, 2018). Although petroleum is often used as a synonym for crude oil, the crude oil is considered as the liquid fraction of petroleum, whereas natural gas and bitumen refer to the gaseous and solid fractions, respectively (Speight, 2002; Gary *et al.*, 2007; Wang *et al.*, 2016; Vassiliou, 2018).

Unless clearly stated, the term "oil" is used in this study to refer, in a generalised way, to any crude oil, a derivative of it, and mixtures of any of these and with biodiesel, as the substances spilt may be any of the aforementioned.

1.2.1. Petroleum formation

Petroleum is found underground, beneath land or ocean, and derives from ancient plants and animals that died hundreds of millions of years ago. For this reason, petroleum is commonly classified as a fossil fuel. The organic matter from the remains of organisms accumulated in layers and combined with sand, mud, and other sediments leads to the formation of sedimentary rocks. Over time, geological processes caused by temperature, pressure, and microorganisms lead to the transformation of organic matter of these accumulations into simpler chemical components, such as hydrocarbons, which form petroleum. Upon encountering permeable and porous beds, petroleum formed in gaseous and liquid states migrated until it became trapped in accumulations surrounded by non-permeable material. These accumulations, known as reservoirs, remain subject to different geological conditions depending on the depth and surrounding material. Over time, these conditions influence petroleum maturation. The same rock structure can contain several separated and neighbouring reservoirs, which forms the so-called oil field. In turn, a sedimentary basin or province refers to a set of oil fields that share the same geological environment (Robbinson, 2006; Speight, 2014; Speight, 2017).

Petroleum deposits exist in numerous places of the world, but they can only be located where sedimentary rock has formed. **Figure 1.8** presents the five countries with the major crude oil reserves and production.

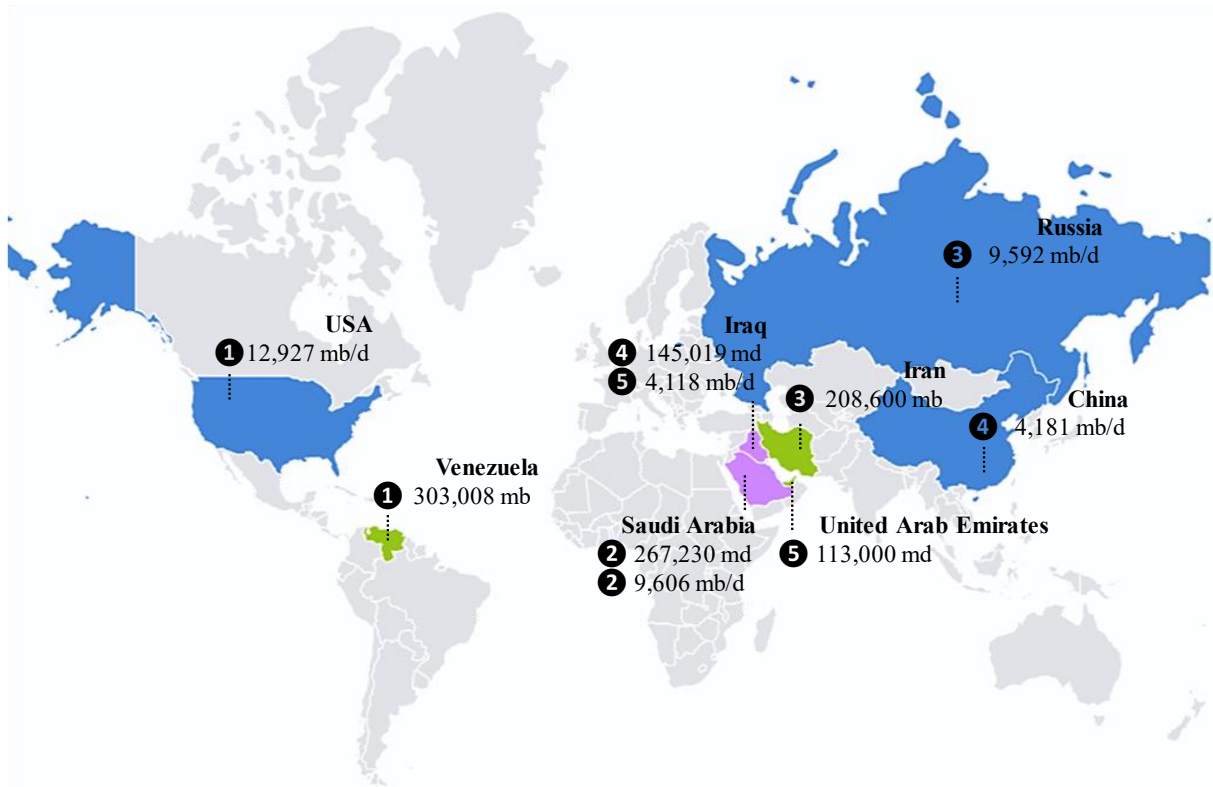


Figure 1.8. Five major crude oil producers, expressed as million barrels per day (mb/d), and crude oil reserves, expressed as million barrels (mb) worldwide (adapted from OPEC (2024)): ● oil producer; ● oil reserve; ● oil reserve and producer; ranking from largest reserve/ producer (1) to smallest reserve/producer (5).

Obtaining petroleum (gas and liquid) is an arduous task and essentially involves three steps:

- 1) Exploration: identification of reservoirs based on preliminary underground investigations conducted by geologists;
- 2) Drilling: drilling the soil after identifying the reservoir in the exploration phase, with the intention of confirming the presence of petroleum and estimating the extent of the reservoir and field. At this stage, the economic and commercial potential of extracting from the indicated oil field is also assessed;
- 3) Extraction: removal of petroleum from reservoirs with proper equipment.

Following extraction, petroleum is transported to refineries by pipelines and sea or land transportation, where it is transformed into more valuable products.

1.2.2. Crude oil and refined products

Petroleum is vital to modern society since it provides the raw ingredients needed for the manufacture of a large variety of high-consuming products, such as natural gas, liquid fuels,

lubricating oils, waxes, asphalts, plastics, synthetic fibres and rubber, among others (Speight, 2017). The liquid petroleum, *i.e.*, crude oil, has low value as it is found in the environment, but when it is subjected to refining gives rise to a wide variety of refined products, also known as crude oil derivatives, which have high utility and commercial value (Speight, 2002; Speight, 2017). A wide variety of refined products are produced nowadays at refineries, including fuels for automobiles (gasoline and diesel), aviation (jet fuels), vessels (marine diesel and heavy fuel oil), heat and energy production for domestic and industrial furnaces (fuel oils), lubricants for machinery (lubricating oil), asphalt for road construction, solvents, among others (Robinson, 2006; Gary *et al.*, 2007; Stout *et al.*, 2016a). Therefore, refineries are the primary destination for crude oil used as refining feedstock material. Its quality, determined by its physical and chemical properties, affects its commercial value based on the products it will yield, and the refining processes it must undergo to meet market demands (Speight, 2002; Speight, 2017). This means that not all the crude oils are appropriated for refining, and, for this reason, each refinery has preferences for certain crude oils in order to manufacture specific refined products. Thus, knowing the crude oil chemical composition is important to select the most suitable refining feedstock to obtain certain products, to determine the way of a particular crude oil can be processed, to optimise the refining processes in order to maximise the refining yields, as well as to expand the variety of the ultimate products and enhance their quality (Speight, 2002; Speight, 2017).

Refining is a set of processes that starts with the separation of crude oil into fractions, defined by their molecular weight and boiling points (**Table 1.2**), with these fractions treated by different operations to produce the various refined products (Robinson, 2006; Speight, 2014).

Table 1.2. Boiling and carbon ranges of refined fractions and ultimate products.

	Boiling range (°C)		Carbon range ⁽¹⁾	
	Speight (2002)	Stout and Wang (2007)	Speight (2002)	Stout and Wang (2007)
Refined fractions				
Light naphtha	15.5 to 149	25 to 90	–	C5 to C6
Heavy naphtha	–	85 to 190	–	C6 to C10
Atmospheric gas oil	–	250 to 425	–	C13 to C27
Gas oil	232 to 343	–	–	–
Vacuum gas oil	343 to 566	370 to 575	–	C22 to C45
Vacuum residue	> 566	> 540	–	> C40
Refined products				
Gas and LPG ⁽²⁾	-160 to -1	-160 to 0	C1 to C4	C1 to C4
Aviation gasoline	–	25 to 175	–	C4 to C10
Gasoline	-1 to 216	25 to 215	C4 to C12	C4 to C12
Volatile solvents/Naphtha	36 to 302	70 to 250	C5 to C17	C6 to C14
Commercial jet fuel	126 to 287	80 to 290	C8 to C16	C7 to C16
Kerosene (Fuel oil #1) ⁽³⁾	126 to 258	200 to 290	C8 to C18	C11 to C16
Fuel oil #2 ⁽³⁾	216 to 421	150 to 400	C12 to >C20	C9 to C25
Diesel fuel #2 ⁽³⁾	126 to 258	150 to 425	–	C9 to C27
Heavy fuel oils (residual)	–	150 to 575	–	C9 to C45
Lubricating oils	> 343	270 to 525	> C20	C15 to C40
Wax	302 to > 343	–	C17 to C20	–
Asphalt	> 343	–	> C20	–

(1) Carbon range defined as *n*-alkanes range (Cx; with *x* as carbon number).

(2) Liquefied petroleum gas.

(3) Classification #1 and #2 denote different grades or categories of products with distinct properties, such as viscosity and volatility, and hence chemical composition. In the distillation process, product #1 is a lighter fraction while product #2 is a heavier fraction.

The refining processes are well documented in the literature and, in general, can be classified into three types (Speight, 2002; Robinson, 2006; Gary *et al.*, 2007; Speight, 2017):

- 1) Separation: distillation processes that separate crude oil into different fractions, collected along the distillation column, and characterised by ranges of molecular size and boiling point;
- 2) Conversion: processes that promote changes in hydrocarbon molecules by breaking, unifying, and rearranging molecular structures in order to achieve more appropriate products;
- 3) Finishing: additional treatments that adapt the products obtained by the separation and conversion processes into ultimate products with specific performance qualities, suited to market needs and environmentally acceptable.

Table 1.3 summarises the most widely used refining techniques, as well as the refined products produced.

Table 1.3. Overview of crude oil refining processes and products produced (Gary *et al.*, 2007; Speight, 2014; Speight, 2017).

Process	Purpose and action	Products
1) Separation		
Atmospheric distillation	Separation of desalted crude oil into fractions	Gases, naphtha, gas oil, atmospheric residue
Vacuum distillation	Distillation of atmospheric residue	Vacuum gas oil, lube stock, residue
2) Conversion		
▪ Decomposition: breaking down of large molecules into smaller ones with lower boiling points		
Thermal and catalytic cracking	Conversion of high-boiling streams into lower-boiling products by breaking down complex molecules (carbon-carbon bond rupture) into simple ones using high temperatures and low pressure, with or without a catalyst (thermal cracking and catalytic cracking, respectively)	LPG, gasoline, middle distillate products, naphtha, petrochemical feedstock
Coking	Conversion of non-distillable fractions (<i>i.e.</i> , residues) into lower-boiling products (<i>i.e.</i> , gas and distillates) and coke by thermal cracking at high temperature and low pressure	Gases, naphtha, fuel oil, gas oil, coke and petrochemical feedstock
Hydrocracking	Conversion of middle-boiling streams to lower-boiling products by thermal cracking (carbon-carbon bond rupture) using hydrogen and catalysts at relatively low temperatures and high pressures	Gases and lower-boiling products
Visbreaking	Reduction of viscosity of heavy feedstocks to acceptable levels; conversion of atmospheric residues to gas oil and naphtha by thermal cracking at moderated temperature and low pressure	Distillate products and fuel oil
▪ Unification: conversion of smaller molecules into larger ones		
Alkylation	Production of high-octane products by combining isobutane and isopentane with olefins through controlled temperature and pressure in the presence of acidic catalyst	LPG-grade propane, liquid butane, C ₅₊ alkylate and tar, high octane number products (alkylates) to be blended with others (<i>e.g.</i> , motor and aviation gasoline) to improve the antiknock fuel value
Catalytic oligomerisation	Conversion of light olefin gases (<i>e.g.</i> , propylene and butylene) into products with higher molecular weight and octane number by creating linkages among molecules, in the presence of a catalyst at low temperature, maintaining the atomic arrangement of the basic molecule	Olefins with unleaded octane numbers are used as a gasoline blendstock
▪ Reforming: rearrangement of molecular structures in different orientations		
Thermal and catalytic reforming	Improvement of the octane number of the streams, by dehydrogenation and dehydrocyclisation reactions, at high temperatures, with or without catalysts (thermal reforming and catalytic reforming, respectively)	High-octane products (reformate) used as gasoline blend stock and a source of aromatics
Isomerisation	Conversion of straight-chain paraffins (<i>e.g.</i> , <i>n</i> -butane, <i>n</i> -pentane and <i>n</i> -hexane) into isoparaffins (<i>e.g.</i> , isobutane, isopentane and isohexane) with higher octane number by the rearrangement of atoms in the molecules	High-octane products
3) Finishing		
Drying	Removal of trace water using dry adsorbents (<i>e.g.</i> , activated charcoal, iron sponge, zinc oxide, alumina, silica, molecular sieve)	Dried products or with trace water content
Sweetening	Removal of sulphur and odour (<i>e.g.</i> , using copper, alkaline sodium plumbite, hypochlorite, among others)	Products odourless, without or with lower content in sulphur
Hydrotreating	Removal of contaminants (<i>e.g.</i> , sulphur, oxygen, nitrogen and metals compounds) from liquid streams, saturation of olefins and conversion of aromatics into naphthenes by hydrogenation without simultaneous occurrence of thermal cracking	Improved and valuable products that meet market specifications, new products, existing products with new uses
Treating	Improvement of odour, colour, and stability of the products that come from the separation and conversion processes by acid, caustic, clay/lime, oxidative, and other treating processes	Improved ultimate products and feedstocks used in other processes (catalytic polymerisation and reforming)
Product blending	Mixture of different liquid products to produce the ultimate product with desired features, improved stability and to accomplish certain requirements (<i>e.g.</i> , additives to enhance octane number, antioxidants, antiknock agents, among others)	Gasoline, distillates, jet fuel and kerosine with a required properties

The chemical composition of refined products is determined by the crude oil that generated them, as well as the refining operations that the crude oil and its fractions underwent. As result, the refined products have less constituents than crude oils and their chemical and physical properties are more particular and less variable in each product type. Still, the compositional analysis of these products is complex.

The global demand for crude oil and its derivatives drives up exploration and transportation across the world, raising the possibility of oil spills. A broad understanding of the chemistry of crude oil and its derivatives, as well as refining operations, may assist the characterisation and the discrimination of these substances in investigations of potential pollution sources and environmental and biological impacts.

1.2.3. Classification of crude oil and refined products

There are several ways to classify crude and derivatives. These are based on the physical and chemical features of substances, with the latter influencing the first. Thus, given the crude oils' diverse chemical compositions, it is expected a large variation of their physical characteristics. Of a wide range of properties used to classify oils, the most commonly used are the American Petroleum Institute (API) gravity and related features, viscosity, interfacial tension, flash and pour points, sulphur content and carbon distribution. Refined products can also be classed based on the distillation ranges. **Table 1.4** shows the oil classifications based on some of the mentioned properties.

Table 1.4. Oil classification according to physical and chemical properties.

Property	Oil classification	Classification intervals	Unit	Reference
Physical properties				
API gravity	Light	> 31.1	°API	Fingas (2022)
	Medium	22.3 to 31.1		
	Heavy	10 to 22.3		
	Extra heavy	< 10		
Density	Very light	< 0.80	g/cm	Yashchenko and Polishchuka (2019)
	Light	0.80 to 0.84		
	With medium density	0.84 to 0.88		
	Heavy with increased density	0.88 to 0.92		
	Extra heavy	0.92 to 0.96		
	Bituminous	> 0.96		
Kinematic viscosity (at 20 °C)	Low viscosity	< 10	mm ² /s	Yashchenko and Polishchuka (2019)
	Medium viscosity	10 to 35		
	Viscous with increased viscosity	35 to 100		
	Highly viscous	100 to 500		
	Extra viscous	> 500		
Chemical properties				
Sulphur content	Low sulphur	< 0.5	% w/w	Yashchenko and Polishchuka (2019)
	Medium sulphur	0.5 to 1		
	Sour	1 to 3		
	Hight sulphur	> 3		
Hydrocarbons classes percentage (250 °C to 300 °C fraction)	Paraffin	46 > Paraffin > 61	%	Speight (2014)
		22 > Naphthene > 32		
		12 > Aromatic > 25		
		Wax < 10		
		Asphalt < 6		
	Paraffin-naphthene	42 > Paraffin > 45		
		38 > Naphthene > 39		
		16 > Aromatic > 20		
		Wax < 6		
		Asphalt < 6		
Naphthene	15 > Paraffin > 26			
	61 > Naphthene > 76			
	8 > Aromatic > 13			
	Wax = 0			
	Asphalt < 6			
Paraffin-naphthene-aromatic	27 > Paraffin > 35			
	36 > Naphthene > 47			
	26 > Aromatic > 33			
	Wax < 1			
	Asphalt < 10			
Aromatic	Paraffin < 8			
	57 > Naphthene > 78			
	20 > Aromatic > 25			
	Wax < 0.5			
	Asphalt < 20			

The API gravity is one of the most often used qualities for classifying oils, and the API has presented it as an indicator of oil quality. This attribute is derived from specific gravity, which in turn depends on density. The density of an oil is the mass of oil per unit volume, expressed in grams per millilitre (g/mL), and is influenced by the oil's temperature and chemical composition. Tendentially, an increase in temperature and saturated hydrocarbon content correlates to a decrease in density (Hollebone, 2011; Speight, 2014). The specific gravity is defined as the ratio of the oil and water densities at a given temperature (*e.g.*, specific gravity with oil and water densities both determined at 15.65 °C, $SpG_{15.65/15.65}$). In meantime, the API gravity, expressed in API degrees (°API), is calculated using **Equation 1.1**, and it is a function of $SpG_{15.65/15.65}$. Thus, a drop in the $SpG_{15.65/15.65}$ implies a rise in the API gravity.

$$API\ gravity = \frac{141.5}{SpG_{15.65/15.65}} - 131.5 \quad (1.1)$$

According to API gravity, oils are classified as light, medium, heavy, or extra heavy (**Table 1.4**) (Hollebone, 2011; Yang, *et al.*, 2022). The API gravity and related properties are also used to determine whether an oil spilt in water will float or have more propensity to sink.

Viscosity (dynamic or kinematic) and pour point are attributes that characterise oils based on their flow. The dynamic viscosity is force required to flow an oil and is measured in millipascal-second (mPa·s) or the equivalent centipoise (cP). The kinematic viscosity, expressed as square millimetre per second (mm²/s) or the equivalent centistokes (cSt), is the ratio of the dynamic viscosity and the specific gravity, and it describes how quickly a fluid spreads under gravity (Speight, 2014). Hence the less viscous the oil, the easier and faster it flows. Viscosity, like density, is affected by the oil's temperature and chemical composition, rising with the decrease of temperature and oil richness of higher molecular weight compounds (Hollebone, 2011; Watt and Roussis, 2006). The pour point is defined as the temperature at which no oil flow is observed, *i.e.* when the oil no longer has the ability to flow freely (Hollebone, 2011; Speight, 2002). This feature is important for pipeline oil transportation (Watt and Roussis, 2006).

The interfacial tension is defined as the tension in the border region between two liquids (*e.g.*, oil and water) and is measured in milliNewtons per meter (mN/m) (Hollebone, 2011; Speight, 2014). The value of this property rises with the decrease of the temperature and a higher content of high molecular weight components. A reduced interfacial tension of a spilt oil into the marine environment leads the slick to spread more widely.

The flash point is the temperature at which the vapour of a liquid ignites. Oils rich in low-boiling constituents are more combustible than heavy oils that contains more high-molecular weight components. However, the losses of the volatile compounds by evaporation turns a spilt light oil less flammable (Hollebone, 2011).

The sulphur content, expressed in weight of sulphur per weight of oil (% w/w), is another property that, together with API gravity, assists in determining the value of a crude oil as a refining feedstock (Gary *et al.*, 2007; Speight, 2014). The main reasons are that the presence of sulphur in crude oils and fuels produced can cause corrosion of refining equipment and contribute to atmospheric pollution by forming sulphur oxides during combustion (Speight, 2002). Nevertheless, in recent years, there has been an effort for regulating the sulphur content in fuels in order to minimise pollution emissions. Based on their sulphur content, in general derived from hydrogen sulphide, thiophenes, benzothiophenes, and dibenzothiophenes constituents, oils are classified as sweet or sour, with a distinction criterion of 0.5% w/w (**Table 1.4**) (Gary *et al.*, 2007). Additionally, the sulphur content is related to the odour of the crude oils (Speight, 2002).

A classification of the oil in terms of its chemical composition can also be made by distributing the carbon among the main classes of oil components, resulting in five categories: paraffinic, paraffinic-naphthenic, naphthenic, paraffinic-naphthenic-aromatic, and aromatic oil (**Table 1.4**) (Speight, 2002; Speight, 2014). In addition, the classification of light and heavy oil is employed based on the predominance of low- or high-boiling compounds, respectively (Speight, 2002).

In wider terms, crude oils can be classified as conventional crude oils and heavy crude oils, considering that the first ones are recovered from the reservoir using regular pumping methods and the latter requiring more specialised apparatus (Speight, 2014). These needs are consistent with the physical and chemical characteristics of each crude oil type. Conventional crude oils are classified as light or medium, with API gravity $> 20^\circ$, viscosity under reservoir conditions < 100 cP, sulphur content below 3% w/w and a preponderance of low-boiling and paraffin wax components. In contrast, heavy oils have an API gravity $< 20^\circ$, viscosity in reservoir conditions > 100 cP, sulphur content above 5% w/w and are rich in higher-boiling, aromatic, and heteroatom-containing compounds (Speight, 2002; Stout and Wang, 2007; Speight, 2017).

The need for an oil classification is related to its purpose of its use. Although each feature can be assigned an oil classification, a classification based on a single parameter seems to be insufficient for an adequate assessment (Speight, 2014; Yashchenko and Polishchuk, 2019).

For example, the chemical composition and structural characteristics of the molecules that comprise it, particularly those considered molecular fossils that carry genetic information from the sedimentary rock, are essential for geochemists to understand the formation and maturation processes of a specific crude oil. However, to assess the value and feasibility of using a crude oil as a feedstock of the refining process is equally important a classification of the crude oil in terms of its constituents (*e.g.*, sulphur content, distribution of the largest classes of hydrocarbons) and a classification by some physical properties (*e.g.*, boiling point, API gravity and viscosity), since they will be used to determine the products to be produced, the apparatus and the processes necessary to obtain them, and their yields. A categorisation of spilt oil based on physical properties, such as density, viscosity, and flash point, is important to choose the most effective equipment and techniques for removing the spilt oil, as well as ensuring the safety of cleaning activities. Oil spill response and resource organisations are particularly interested in characteristics that allow them to evaluate the behaviour and impacts of spilt oil in the marine environment, such as density, specific gravity, viscosity, interfacial tension, pour point, and oil composition. In turn, the detailed characterisation of the oil pattern in samples collected in the spill and its suspected sources is fundamental and indispensable in spilt oil investigations for the purpose of deciding the legal culpability for the pollution act.

Several assays are used to determine the oil physical and chemical characteristics summarised by Speight (2002). Data from these characteristics can also be accessed through the open access crude oil assays reports provided by oil and gas companies (*e.g.*, British Petroleum, ExxonMobile, Equinor), as well as through databases provided by government entities, such as the Environment Canada Crude Oil and Petroleum Product Database from the Environment and Climate Change of the Canada Government, and the ADIOS Oil Database from the National Oceanic and Atmospheric Administration (NOAA) of the USA Government (NOAA, 2021; Environment and Climate Change Canada, 2022; British Petroleum, 2024; Equinor, 2024; ExxonMobile, 2024).

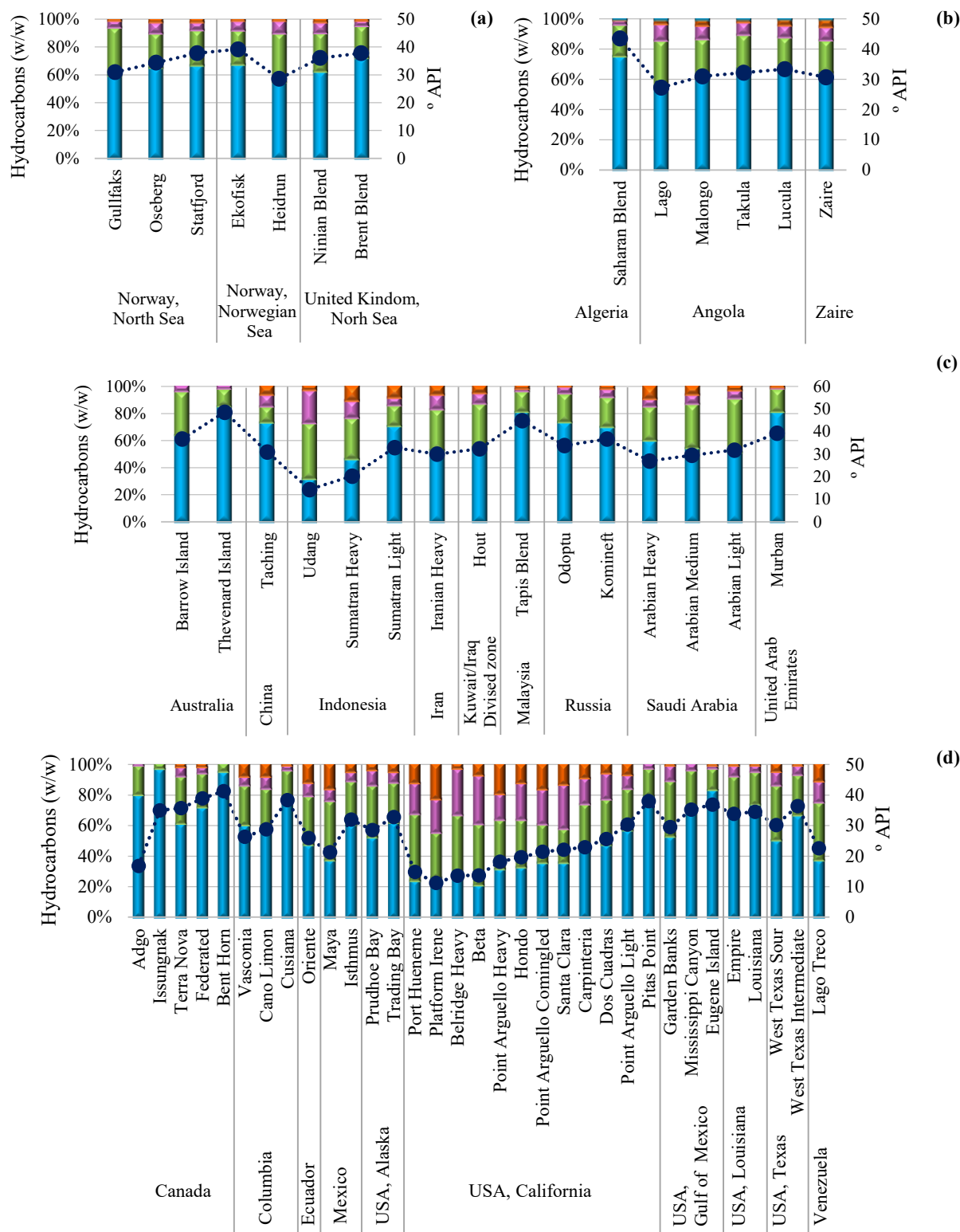
1.2.4. Composition of crude oil and refined products

Crude oil is a complex mixture of carbon and hydrogen molecules, referred as hydrocarbons, with small amounts nitrogen, oxygen, and sulphur heteroatom components, as well as trace levels of metals, such nickel and vanadium (Robinson, 2006; Gary *et al.*, 2007; Stout and Wang, 2007; Speight, 2014; Wang *et al.*, 2016; Fingas, 2022). In general, the majority of these

components are present in all crude oils, but their proportions vary widely (Speight, 2017; Fingas, 2022). These compositional differences are related to (Speight, 2002; Robinson, 2006; Gary *et al.*, 2007; Stout and Wang, 2007; Fingas, 2011; Speight, 2014):

- the unique attributes of the geographic location and the circumstances of the geological formation, depending on the source rock of ancient organic matter;
- the conditions of the depositional environment (*e.g.*, temperature and pressure);
- the kinetic conditions in the formation and expulsion of crude oil that promote the maturation through cracking, isomerisation and aromatisation reactions;
- the migration of crude oil to other depositional environments that stimulates compositional changes, *e.g.*, due to biodegradation (degradation by microorganisms), water-washing (effect due to contact with flowing water in the subsurface) or addition of chemicals from the carrier beds or reservoirs rocks.

For this reason, crude oils are geographically specific and, normally, its identification is accompanied by the place where it was found. The variations in chemical characteristics of crude oils result in changes in their physical properties, including colour, odour, density, viscosity and boiling point (Speight, 2002; Fingas, 2011; Speight, 2016; Wang *et al.*, 2016). **Figure 1.9** presents the variation of the API gravity and the content of hydrocarbons' classes for several crude oils.



Crude oil and origin

Figure 1.9. API gravity and hydrocarbon's content of several crude oils from different geographical areas (data from Environment and Climate Change Canada (2022) and NOAA (2021)): (a) Europe, (b) Africa, (c) Asia and (d) America; ● saturated hydrocarbons, ● aromatic hydrocarbons, ● resins, ● asphaltenes, ... API gravity.

The crude oil's constituents have a huge diversity of chemical structures and range from simple, low molecular weight and volatile compounds to compounds with a larger molecular structure, high molecular weight and stability (Stout and Wang, 2007; Fingas, 2011; Wang *et al.*, 2016). These constituents can be categorised into three classes (Gary *et al.*, 2007; Fingas, 2011; Speight, 2014; Wang *et al.*, 2016):

- Saturated: normal alkanes with straight chains (*n*-alkanes or paraffins), branched alkanes and mono and polycyclic alkanes with at least one cyclic saturated chain (naphthenes or cycloparaffins);
- Aromatics: hydrocarbons with at least one benzene ring;
- Polar compounds: hetero-atoms hydrocarbons that contain nitrogen, oxygen or sulphur in a small or large molecular structure.

Another class of compounds, namely olefins or alkenes, *i.e.*, unsaturated hydrocarbons with at least one double bond between carbon atoms, is rarely present in crude oils but abundant in the refined products (Gary *et al.*, 2007; Fingas, 2011; Speight, 2014). Together, saturates and olefins constitute the aliphatic fraction of hydrocarbons (**Figure 1.10**) (Hollebone, 2011). The main variation in the molecular structure of naphthenes (sesqui-, di-, tri-, tetra-, and pentacyclic terpanes, as well as steranes) is the ring number, with the polycyclic structures having all rings with six carbons or a combination of rings with five and six carbons (**Figure 1.10**).

The aromatic fraction of hydrocarbons (**Figure 1.11**) is composed by monoaromatics, like benzene, toluene, ethylbenzene, and the isomers *o*-, *m*- and *p*-xylenes known as BTEX, polyaromatics (PAH), such as parental (pPAH) and alkylated (alkyl-PAH) polycyclic aromatic hydrocarbons, and naphthenoaromatics, *i.e.*, compounds containing both saturated and aromatic rings (*e.g.*, monoaromatic and triaromatic steranes) (Stout and Wang, 2007; Fingas, 2011; Hollebone, 2011). A special attention is attributed to alkylated homologous series (monoalkyl-substituted- (C1-), dialkyl-substituted- (C2-), trialkyl-substituted- (C3-), and tetraalkyl-substituted- (C4-)) of naphthalene, fluorene, phenanthrene/anthracene, fluoranthene/pyrene and chrysene, particularly useful for the characterisation of crude oils and derivatives due to these aromatics being found in greatest abundance (Fingas, 2011; Wang *et al.*, 2016).

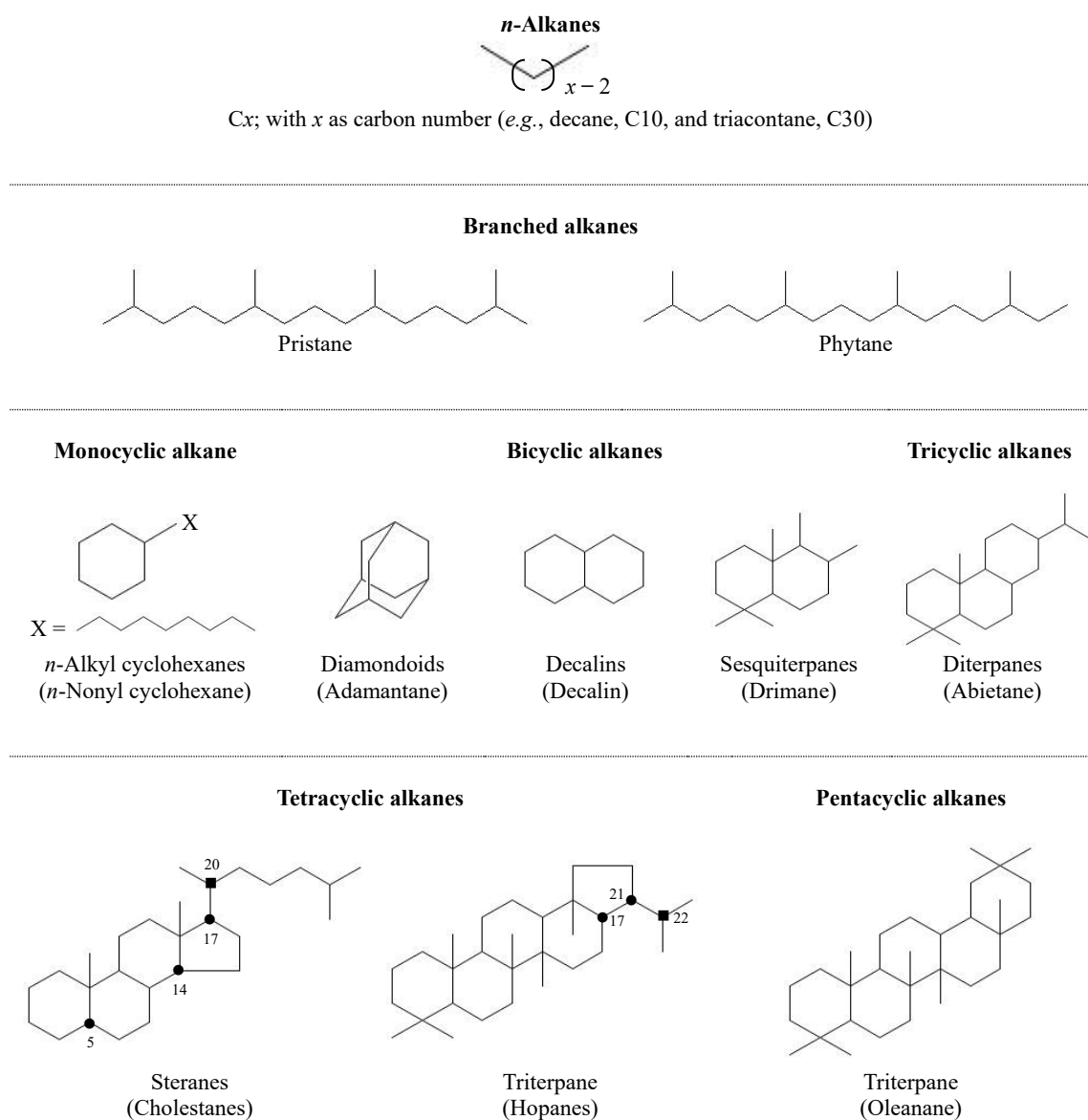


Figure 1.10. Chemical structures of representative aliphatics present in crude oils and refined products: ● α or β (H) stereoisomerism; ■ R or S (C) stereoisomerism. The compound(s) exemplified are indicated in parenthesis, while the class of compounds is stated outside of them.

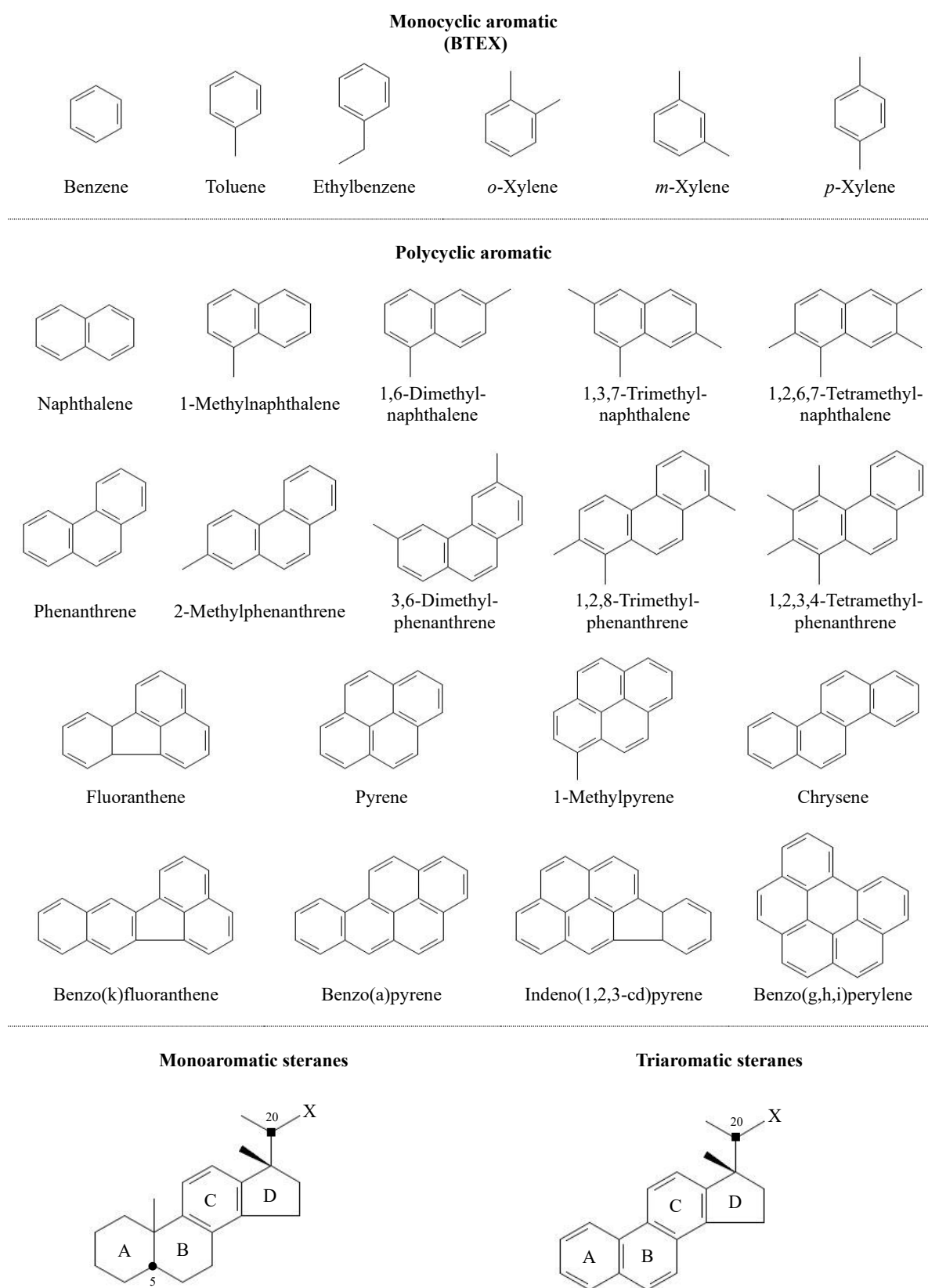


Figure 1.11. Chemical structures of representative aromatics present in crude oils and refined products: ● α or β (H) stereoisomerism; ■ R or S (C) stereoisomerism.

The presence of nitrogen, oxygen, and sulphur heteroatoms in some compounds confers polarity, positive or negative charge, to the molecular structure (Stout and Wang, 2007; Fingas, 2011; Wang *et al.*, 2016). These compounds are referred to as polar resins or asphaltenes based on their small or large molecular structure dimensions, respectively (Wang *et al.*, 2016). Examples of these substances include alcohols and acids with oxygen atoms, thiols (also known as mercaptans) and mono and polynuclear aromatic thiophenes with sulphur atoms, and pyridines, amides, and quinolines with nitrogen atoms (**Figure 1.12**) (Stout and Wang, 2007; Speight, 2014).

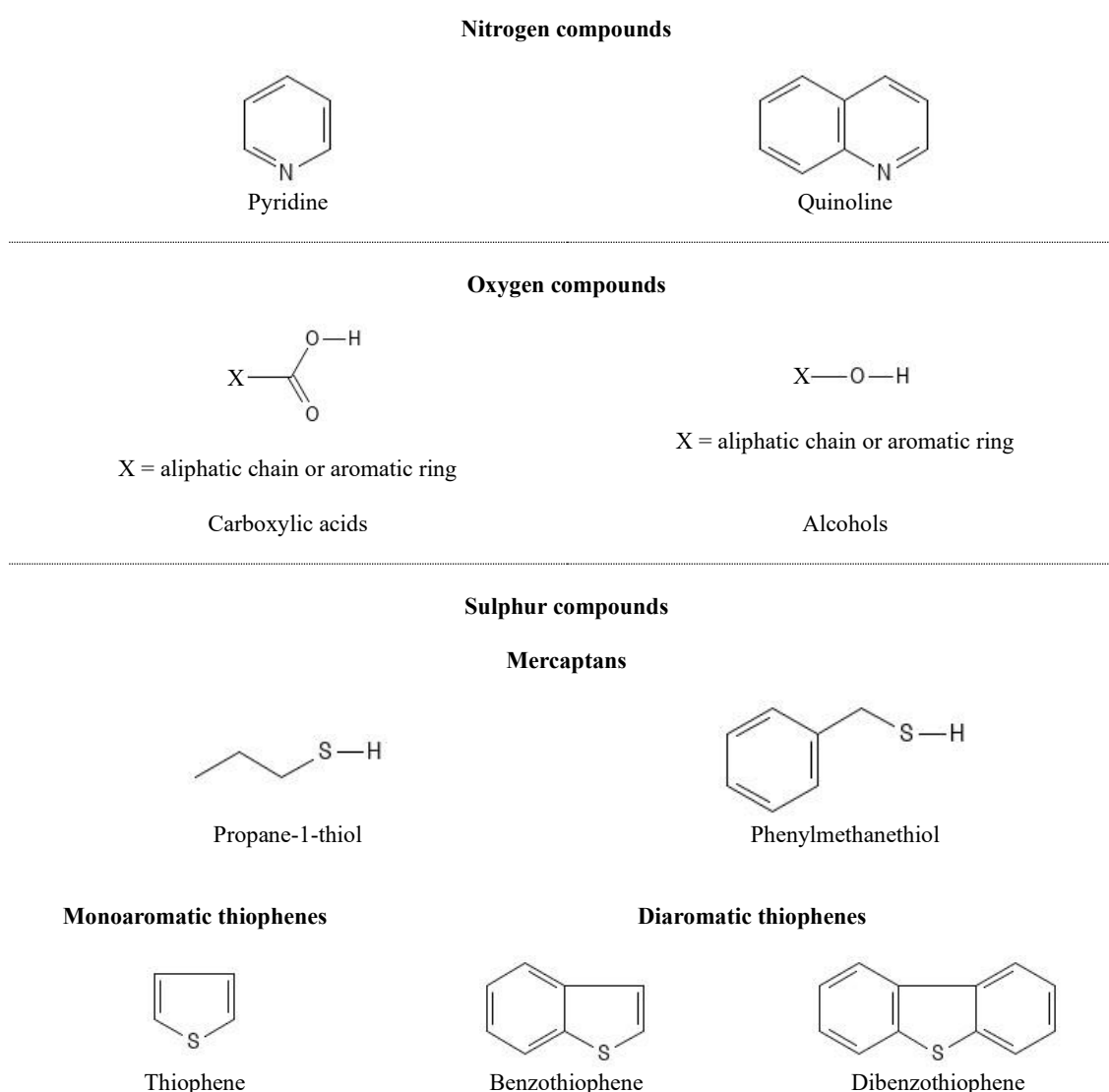


Figure 1.12. Chemical structures of representative polar compounds present in crude oils and refined products.

Refined derivatives, which consist of different fractions of crude oil based on boiling point ranges, exhibit distinct compositions due not only to the refining processes and the fraction to which they correspond, but also to the compositional variability of the crude oil subjected to distillation. In general, as the boiling point of the petroleum fraction rises, the proportion of paraffins decreases while the percentage of naphthenic and aromatic compounds increases. Petroleum fractions with a higher boiling range are richer in naphthenic aromatic compounds (*e.g.*, mono- and triaromatic steranes), whereas fractions with a lower boiling range tend to have more aromatics, such as alkyl-PAH (Speight, 2014). In addition to the compositional diversity of refined derivatives given by the refining techniques and the feedstock subjected to them, the final products may contain additional substances added during manufacturing, such as additives to enhance the octane number (alcohols, *e.g.*, methanol and ethanol), anti-icing substances (surfactants, alcohols and glycols), antioxidants (aromatic amines), corrosion inhibitors (carboxylic acids and carboxylates), and antiknock agents (*e.g.*, the banned tetraethyl lead, isooctane) (Speight, 2014).

Fuelled by increased interest in the application of reusable and more ecologically friendly fuels, the biodiesel has been used as an emerging energy resource across the world. It may be used individually (biodiesel at 100%) or blended with conventional fossil diesel in different proportions (*e.g.*, biodiesel at 20%) (DeMello *et al.*, 2007; Murugesan *et al.*, 2009). Biodiesel is mostly composed of fatty acid methyl esters (FAME), which are formed by the transesterification reaction of triglycerides found in vegetable oils (*i.e.*, alcoholysis of triglycerides using an alcohol, such as methanol, in the presence of a catalyst, such as a base) (Murugesan *et al.*, 2009; Yang *et al.*, 2016). Its chemical composition is thus determined by the raw materials used in its production, which may include edible vegetable oils (*e.g.*, rapeseed, soybean, palm, coconut oil), non-edible vegetable oils (*e.g.*, karanja, algae), animal fats (*e.g.*, tallow, chicken fat), and waste and recycled vegetable oils (Thiruvengadaravi *et al.*, 2012; Boffito *et al.*, 2013; Issariyakul and Dalai, 2014; Altikriti *et al.*, 2015; Gupta *et al.*, 2016; Olubunmi *et al.*, 2022; Pravin and Baskar, 2024). **Figure 1.13** shows the general structure of FAME that results from transesterification of the most common vegetable oils with methanol in an alkaline medium, while **Table 1.5** lists the designations and acronyms for the most abundant ones.

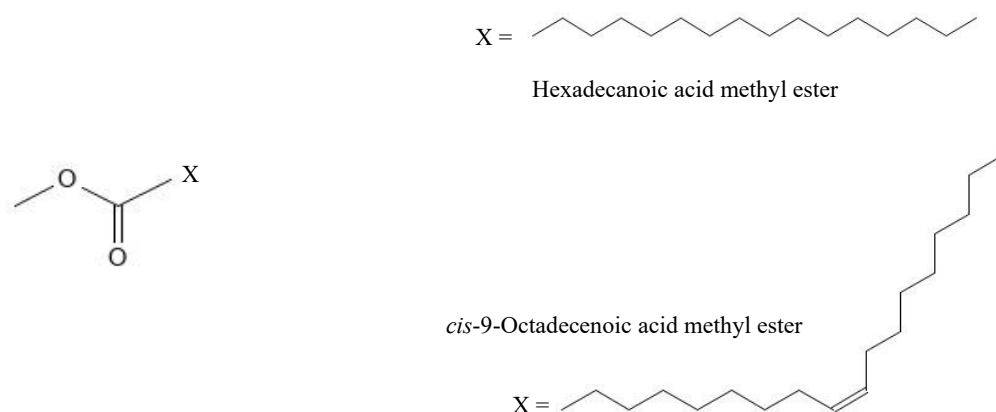


Figure 1.13. General and two representative chemical structures of fatty acid methyl esters present in biodiesel and biodiesel and diesel fuel blends.

Table 1.5. Designations and acronyms of the most common fatty acid methyl esters present in biodiesel and biodiesel and diesel fuel blends (adapted from Yang *et al.* (2016)).

Identification	Formula	Acronym (FAME Cx:y) ⁽¹⁾
Dodecanoic acid methyl ester	C ₁₂ H ₂₄ O ₂	FAME C12:0
Tetradecanoic acid methyl ester	C ₁₄ H ₂₈ O ₂	FAME C14:0
Hexadecanoic acid methyl ester	C ₁₆ H ₃₂ O ₂	FAME C16:0
<i>cis</i> -9-Hexadecenoic acid methyl ester	C ₁₆ H ₃₂ O ₂	FAME C16:1
Octadecanoic acid methyl ester	C ₁₈ H ₃₆ O ₂	FAME C18:0
<i>cis</i> -9-Octadecenoic acid methyl ester	C ₁₈ H ₃₄ O ₂	FAME C18:1
<i>cis</i> -9, <i>cis</i> -12-Octadecadienoic acid methyl ester	C ₁₈ H ₃₂ O ₂	FAME C18:2
<i>cis</i> -9, <i>cis</i> -12, <i>cis</i> -15-Octadecatrienoic acid methyl ester	C ₁₈ H ₃₀ O ₂	FAME C18:3
Eicosanoic acid methyl ester	C ₂₀ H ₄₀ O ₂	FAME C20:0
<i>cis</i> -11-Eicosanoic acid methyl ester	C ₂₁ H ₄₀ O ₂	FAME C20:1

(1) With *x* being the carbon number in the chain and *y* being the number of double bonds in the chain.

The knowledge gained all over time on the composition of crude oils and derivatives has contributed to investigations into oil pollution accidents by allowing for a more suitable compositional comparison of samples. Several studies have been conducted to identify components that best differentiate and characterise each oil type aiming the application in forensic identification of spill source (Wang *et al.*, 2005; Wang *et al.*, 2006a; Wang *et al.*, 2013; Yang *et al.*, 2014; Alexandrino *et al.*, 2019; Malmberg *et al.*, 2021; Filewood *et al.*, 2022a; McCallum *et al.*, 2023; Yang *et al.*, 2024). One of the sets of compounds that best characterise crude oils and refined derivatives are the biological markers, commonly called biomarkers. Biomarkers are molecules with complex chemical structures whose carbon skeletons are unequivocally linked to the chemical structures of chemicals found in live organisms, *i.e.*, their biogenic precursors (Stout *et al.*, 2007; Speight, 2014; Philp and Connock, 2022). In this sense,

these hydrocarbons act like chemical fossils, attesting to the organic matter of origin, geologic age, depositional environments, as well as oil maturation and formation conditions (Stout *et al.*, 2007; Speight, 2014; Philp and Connock, 2022). Furthermore, biomarkers are stable making them valuable in degradation assessments, and their diversity, both in character and relative abundance, enabling a high degree of differentiation among crude oils and derivatives (Wang *et al.*, 2007). Because of these features, identifying and quantifying the relative content of biomarkers in samples of illegal oil pollution, namely sesquiterpanes, diamondoids, terpanes, steranes, and mono and triaromatic steranes, is a crucial part of the expert examination.

1.3. Oil spill source identification

The assessment of the extent and nature of a pollution incident is the primary step after an oil spill, which includes examining the location and area impacted, the amount and type of spilt oil, and the potential polluting source. Following that, spill response activities begin, which involve assessing the security of the spill area for the operational personnel, establishing sampling plans, and containing, recovering, and treating the spilt oil (Owens *et al.*, 2007; Owens *et al.*, 2016). Within the framework of a forensic inquiry, it is imperative to collect samples that are intended for laboratory analyses with different objectives, such as:

- determining the oil nature in order to assess the type of health risk (*e.g.*, flammable substance, toxic by inhalation or skin contact) to define appropriate safety conditions for response operations, to help in the selection of the suitable recovery equipment, and to assist the identification of the potential source of the spill (*e.g.*, bunker fuel, oil from cargo tanks, bilge or slops tanks, pipelines, offshore platforms);
- assessing the level of degradation of the spilt oil due to exposure to environmental conditions, which is useful for evaluating the behaviour and fate of the spilt oil in the environment;
- environmental monitoring to assess the impact and persistence of the oil in the environment;
- identifying the potential polluting source in order to assign legal responsibility for the illicit pollution act, including setting costs related to response operations, cleaning and waste treatment, property damage, and impact on local activities (*e.g.*, fishing, aquaculture, recreational activities).

Given the nature of the study provided, the following points solely address sample collection and expert analysis to identify the polluting source. Sample collection and analysis for other uses indicated above can be found in the literature (Yender *et al.*, 2002; Environment Agency of United Kingdom Government, 2004; ITOFP, 2012; IPIECA and IOGP, 2020; Klasing *et al.*, 2020).

1.3.1. Sampling

To conduct a forensic investigation aiming to identify the potential source of an oil spill, representative samples of the pollution evidenced must be collected, *i.e.*, spill samples (Sp), as well as samples from the points presumed to be the spill origin, *i.e.*, suspected source samples (SS). An appropriate number of samples adequately preserved, collected in critical points of the spill and its potential sources by qualified technicians, is vital to the quality of the expert analysis results that are presented as evidence in court (Bonn Agreement, 2007; Daling *et al.*, 2016; Owens *et al.*, 2016; CEN, 2023a). Thus, sampling plans are established by the assessment of the polluted area and must define the sampling objectives (*e.g.*, environmental impact assessment and spill source identification), the suitable points for sample collection, the sequence of sampling, the number of samples to collect, the techniques, procedures, material and equipment for sampling, the conditions for sample preservation and transportation, the information for sample documentation, labelling and tracking the samples, as well as the site's safety risks and measures (Daling *et al.*, 2016; Owens *et al.*, 2016). The use of digital or video cameras is highly recommended in order to document not only the sampling but also other information from the spill that is considered relevant to the process (Bonn Agreement, 2007; Daling *et al.*, 2016; CEN, 2023a).

The priority is to collect the Sp, which easily degrades when exposed to adverse environmental conditions. In these instances, time is critical due to sample compositional change which makes the expert analysis more challenging. Typically, the Sp are collected from surface water of the sea, rivers and lakes, on the seashores and beaches, as well as on piers and vessels quay walls. It is particularly important to collect samples from several slicks of the polluted area, even if they are thin and especially if they reveal a distinct visual aspect, in order to rule out the possibility of more than one spill (CEN, 2023a).

The origin of a spill can be evident or unknown but, in both circumstances, samples should be collected from the potential sources (Bonn Agreement, 2007; Daling *et al.*, 2016; Owens *et al.*,

2016; CEN, 2023a). All points suspected of being the origin of pollution must be sampled, which might include any vessel tank, offshore and land-based facilities, pipelines, fuel supply or cargo units, among others. In more confined maritime areas, such harbours, it may be easier to recognise suspected sources of a spill. However, in coastal or open waters, this task may become a challenge and, most of the time, require crossing data of the spill location and type of spilt oil with the information from the maritime traffic monitoring systems, such as VTS, AIS, and SafeSeaNet⁶ to determine which vessels navigated in the area and vicinities of the spill, their paths, and their cargo. This procedure is not only useful to identify possible sources of the spill but also to shorten the number of suspects (Daling *et al.*, 2016). Collecting samples from a vessel can be tough since it may have multiple tanks (*e.g.*, fuel, cargo, bilge, slops, sludge tanks) that could be potential sources of a spill, and samples from all vessel tanks must be obtained unless there is an acceptable explanation not to (Daling *et al.*, 2016). For the sampling technician, collect SS inside a vessel is not always straightforward because it requires some knowledge of the vessel's structure, machines, and pumping and cargo systems (Bonn Agreement, 2007). Even though the technician should be accompanied by vessel staff to assist in recognising the potential pollution sources and paths, the vessel staff will deviate the technician away from the true pollution origin avoiding the sample from being collected and, therefore, being incriminated for the pollution act. However, the technician can consult the vessel logbooks that contain some useful information about the oils transported and the operations capable of leading to discharges (CEN, 2023a).

Other samples that must be obtained are the reference samples which are intended to indicate the background distribution of chemical compounds in the spill area. Therefore, these samples are collected close to the spill but free of spilt oil, and they are especially vital not only when it is suspected that the Sp contains contaminants from the environment, but also to ensure that the spill observed is not a normal contamination for the site (Bonn Agreement, 2007; Daling *et al.*, 2016; CEN, 2023a). The latter scenario may occur in harbour waters, which always have a greater level of hydrocarbons than coastal and oceanic waters, whereas the first scenario is more frequent when Sp are obtained, for instance, on beaches.

Several guidelines for collecting samples with the intent of identifying the source of an oil spill are available, but in general, the suggested techniques are similar across procedures (IMO, 1998; Bonn Agreement, 2007; INTERPOL, 2007; Daling *et al.*, 2016; HELCOM, 2021;

⁶ System employed in European Union waters operated by EMSA.

Kneeland *et al.*, 2022; CEN, 2023a). Mostly, the type of samples collected from the sites mentioned above are neat, weathered or emulsified oil, oil mixtures, oily water, sorbents or other materials soaked in oil, tar balls and oiled animals. The sampling equipment and materials are clean and disposable to avoid contamination, except for a few (*e.g.*, extension handles, ropes, chains) that must be properly cleaned before storage and use between sampling points (CEN, 2023a). In general, the sampling material are nitrile gloves, glass bottles or flasks, wooden spatulas, and ethylene tetrafluoroethylene (ETFE) or polytetrafluoroethylene (PTFE) net used as oil adsorbent (**Figure 1.14 (a)**). Other sampling materials can be used to apply specific sampling techniques, like PTFE conical cornet attached to a metal ring and an extension handle (**Figure 1.14 (b)**).

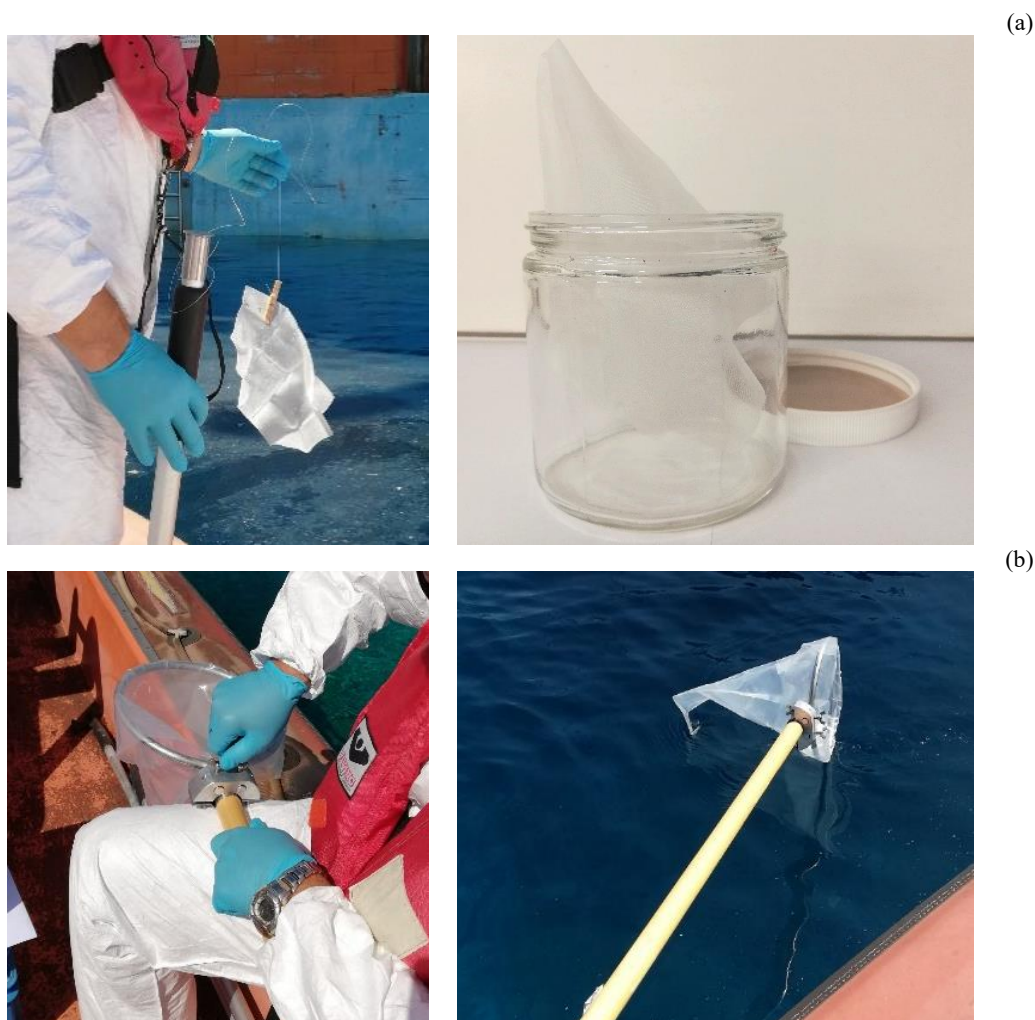


Figure 1.14. Sampling techniques to collect spilt oil from surface water: (a) ethylene tetrafluoroethylene net attached to an extendable cable and (b) polytetrafluoroethylene conical cornet attached to an extendable cable.

Although sampling techniques are relatively simple, they are mostly dependent on the form in which the spilled oil is present (*e.g.*, tar balls, emulsified oil, fresh oil in a slick), its viscosity and the necessity to separate the oil from the environment in which it was found (Kneeland *et al.*, 2022). For instance, sweeping the oil slick using an ETFE or PTFE net is the adequate sampling technique to collect low viscous oils which form a thin layer on the water surface. On the contrary, the direct-to-bottle sampling method can be used to collect viscous oils that form a thick layer on the water surface without compromising the amount of oil in the sample. Last, collecting an oil sample from a beach without substrate is challenging unless the sand is also taken, but from contaminated animals the sampling should, whenever possible, only gather the oil, avoiding collecting the animal or any of its parts. The quantity of samples needed varies according to the spill, and it may be important to collect replicate samples for administrative motives, such as conducting counterevidence requested by the defence⁷ (CEN, 2023a). The location and timing of the sampling are other variable of the utmost importance. The collection of several samples from the impacted sites throughout the relevant time frame allows for a characterisation of both temporal and spatial spill distribution, which may be helpful in evaluating the spill evolution, level of oil degradation, and locating the pollution source (Bonn Agreement, 2007; Daling *et al.*, 2016). The loss of an oil original identity as a result of exposure to environmental conditions can be avoided or mitigated by collecting samples rapidly, sampling the spilled oil in the thickest region of the slick in the water, or sampling the oil at the main points of a coastal area affected (*e.g.*, beach) where the oil amount is higher (Daling *et al.*, 2016). In this last situation, complications in characterising the spilled oil composition will also be minimised because the contamination of the oil with background chemical components present in the environment is decreased. Contaminated animal or its feathers or fur also contain compounds that can be added to the oil chemical composition, thus it is preferred collecting an oil portion that coats an animal, using appropriate sampling material (*e.g.*, ETFE or PTFE net or wooden spatula to collect viscous oil directly to flask). Furthermore, contamination of the spilled oil may also occur if samples are collected after certain clean up actions, such dispersants application or *in situ* burning.

As part of the process of assigning legal responsibility, all samples collected must be handled as evidence and kept in a chain of custody, *i.e.*, with rigorous surveillance or guarding of samples by authorized personnel. Hence, each sample is sealed and identified with a unique

⁷ CEN (2023a) does not impose the collection of replicated samples. However, collecting replicated samples may be mandated as part of each country's forensic processes.

number which allows to track the sample and check whether it has been tampered by opening the flask (Bonn Agreement, 2007; Daling *et al.*, 2016). Each sample's label is filled with process-relevant information such as sample identity, seal number, sampling date, time and location (*e.g.*, sampling site registered using Global Positioning System coordinates), meteoceanographic conditions (*e.g.*, air and water temperature, wind direction and velocity, ocean agitation and currents), description of the sample, sampling team and other sampling relevant information. Some of this information is also provided in a letter of request, which formally requests the analyses of the samples as well as their purpose and accompanies the delivery of samples to the laboratory. The transport of oil samples to laboratory should be quick and must comply with applicable regulations, namely the International Air Transport Association regulations in case of transport by air (CEN, 2023a). The samples must be stored in a system protected from light and refrigerated ($< 4\text{ }^{\circ}\text{C}$, except if the samples are animals, which, in this case, must be frozen, $< 0\text{ }^{\circ}\text{C}$) in order to preserve their identity.

In Portugal, the collection of samples from an oil pollution incident is assigned to the AMN (Decreto-Lei n.º 192/98, 1998; Decreto-Lei n.º 235/2000, 2000). Therefore, sampling is performed by PM officers from the CLPM with jurisdiction in the area of the pollution incident and, in more particular, complex and serious cases, by forensic divers of PM or experts from the *Unidade Central de Investigação Criminal* of PM⁸. All sampling personnel have recognised technical skills for this purpose through appropriate specialised training.

The sampling is performed using appropriate material and equipment, present in a kit distributed among the various CLPM, and according to established procedures and techniques. Those, as well as the number of samples and locations to be sampled, the measures for sample preservation and transport to the laboratory, and all the information necessary for the proper identification of the samples are described in detail in a document from the AMN (Circular n.º 123/2007-P, 2007). After sampling, the samples are transported to a laboratory recognised to perform analysis aiming identifying the pollution source, namely the IH (Decreto-Lei n.º 235/2000, 2000).

1.3.2. Analysis

The compositional characterisation of an oil is carried out by identifying a variety of compounds capable of demonstrating the uniqueness of each oil's chemical composition, *i.e.*, by

⁸ Central Criminal Investigation Unit of the Maritime Police.

determining oil-discriminating constituents that are both resistant and non-resistant to degradation. A set of relative contents of these components defines the commonly referred oil fingerprint (Wang and Fingas, 2003). Thus, by comparing oil fingerprints of Sp and SS, it is feasible to determine a likely source of spilt oil in marine environment. To accomplish this goal, proper sampling and chemical analysis of samples combined with the determination of chemical metrics treated by suitable result processing approaches, are required to reach a solid, objective, and reliable conclusion about the pollution source.

The oil constituents commonly determined in samples with the objective of identifying a potential polluting source are (Alimi *et al.*, 2003; Wang and Fingas, 2003):

- Aliphatics, *i.e.*, *n*-alkanes from octane (C8) to tetracontane (C40) and the isoprenoids, *e.g.*, pristane, phytane and norpristane;
- Single-ring aromatic hydrocarbons, *e.g.*, BTEX and the alkylbenzenes;
- pPAH, *e.g.*, priority substances defined by United States Environmental Protection Agency (US EPA) and other, such as dibenzothiophene, as well as their alkylated homologous series;
- Biomarkers such as sesquiterpanes, diamondoids, terpanes (triterpanes, tetraterpanes and pentaterpanes), methylated hopanes, steranes, methylated steranes, diasteranes, triaromatic steranes, and unique geologically rare biomarkers (*e.g.*, 18 α (H)-oleanane, gammacerane, and 17 α (H),18 α (H),21 β (H)-28,30-bisnorhopane);
- Nitrogen and oxygen heterocyclic hydrocarbons.

Oils have been characterised over time using several specific and non-specific analytical techniques, including gravimetry, gas chromatography, high-performance liquid chromatography, supercritical fluid chromatography, thin-layer chromatography, ultraviolet spectroscopy, infrared spectroscopy, fluorescence spectroscopy, and isotope ratio mass spectrometry (Wang and Fingas, 1997; Alimi *et al.*, 2003; Wang and Fingas, 2003). Among the several techniques mentioned, the most popular for identifying an oil fingerprint are the gas chromatography with flame ionization detection (GC-FID) or mass spectrometry detection (GC-MS) (Wang and Fingas, 1997; Stout and Wang, 2016). In particular, the GC-MS used with selected ion mode for spectra recording (SIM) is highly useful in obtaining the sensitivity and selectivity required for the purpose of these chemical analyses. **Figure 1.15** shows the

combined SIM chromatograms obtained from GC-MS analysis of six oil types demonstrating the differences in the oil distribution patterns.

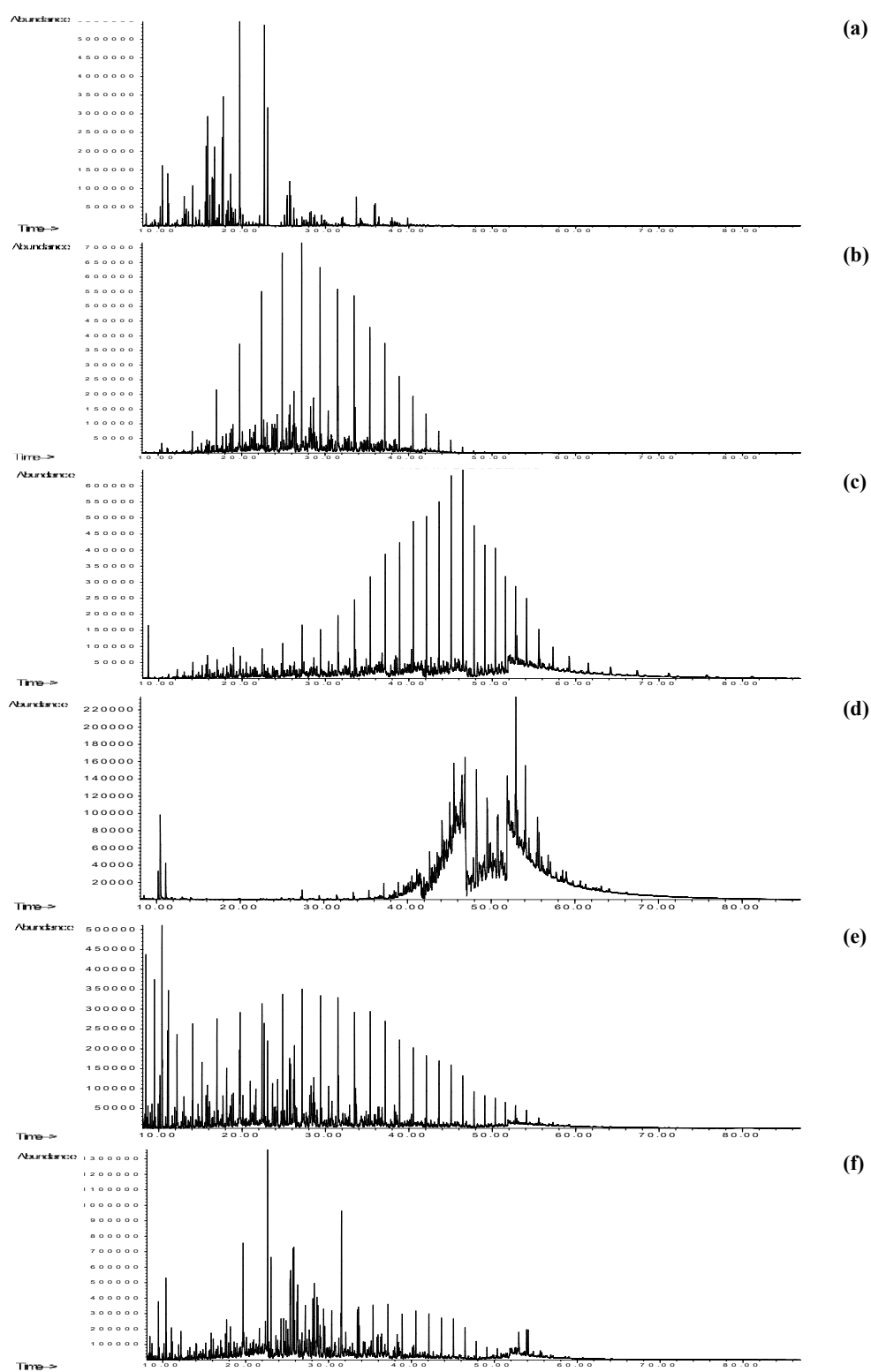


Figure 1.15. Combined SIM chromatograms, obtained by gas chromatography-mass spectrometry analysis with spectrum recording in selected ion monitoring mode, of six distinct oil types: (a) Gasoline Super (1.5 mg/mL); (b) Diesel S-43 (0.8 mg/mL); (c) Heavy fuel oil (8 mg/mL); (d) Lubricating oil (2 mg/mL); (e) Ekofisk crude oil from North Sea (1.5 mg/mL); (f) Bonny Medium crude oil from Nigeria (4 mg/mL). The oils belong to the petroleum products database of *Instituto Hidrográfico* and were analysed at *Instituto Hidrográfico* according to acquisition conditions described in Chapter 4.

The analysis by GC-FID and GC-MS demands the application of sample preparation methods that are, generally, simple and only require to perform an organic solvent extraction (*e.g.*, with dichloromethane) followed, if needed, by an extract cleaning procedure (*e.g.*, using florisil, silica gel, alumina or a combination of silica gel and alumina) (Wang and Fingas, 1997; Kienhuis *et al.*, 2016). Nowadays, and taking advantage of the petroleum geochemists' knowledge, specific ratios between the abundances of oil-discriminating compounds, known as diagnostic ratios (*DR*), are employed to characterise the compositional oil patterns. Several studies have been conducted throughout the years with the aim of finding and implementing new *DR* that could enhance the oil characterisation and differentiation (Wang *et al.*, 2005; Wang *et al.*, 2006a; Yang *et al.*, 2006; Yang *et al.*, 2008; Yim *et al.*, 2011; Wang *et al.*, 2013; Yang *et al.*, 2014; He *et al.*, 2016; Malmborg *et al.*, 2021; Filewood *et al.*, 2022b; McCallum *et al.*, 2023). The application of *DR* not only allows for oil discrimination, but it also minimises the impacts caused by concentration discrepancies, variances in analytical equipment and technicians, as well as matrix effects (Wang and Fingas, 2003). Nevertheless, the accuracy and precision of analytical data must be monitored, which are guaranteed by a variety of quality assurance and control measures, such as the analysis of solvent blanks and control standards, the evaluation of peak resolution, retention time drift, and mass discrimination, as well as the analysis of replicates. These measures enable the assessment of instrumental performance, contamination, and baseline variations during chromatographic analysis, as well as the estimation of the variance of *DR* and percentage of normalised compound abundances (Wang and Fingas, 2003; CEN, 2023b). With computational advances, the analytical data processing has improved, and conventional or multivariate statistical tools are now used to help achieve an objective and well-founded conclusion about the similarity of oil fingerprints from compared samples. The chemometric tools that have been used to characterise oils and identify the source of an oil spill, among other purposes, are the principal component analysis (PCA), the hierarchical component analysis, the cluster analysis, the parallel factor analysis (PARAFAC), and the Kohonen and convolutional neural networks (Stout *et al.*, 2001; Christensen *et al.*, 2004; Christensen *et al.*, 2005; Fresco-Rivera *et al.*, 2007; Fernández-Varela *et al.*, 2008; Lobão *et al.*, 2010; Corilo *et al.*, 2013; Chua *et al.*, 2020; Oliveira *et al.*, 2021; Wang and Wang, 2022; Wang *et al.*, 2024). However, these chemometric methods should not be used as a substitute for more direct statistical comparisons of *DR*, since multivariate statistical methods do not recognise variations caused by weathering, which result in the exclusion of *DR* from the *DR* set to be compared, but rather as a supplement to compare and/or reduce the number of suspected sources of the pollution incident by comparing the sample fingerprints with oil fingerprints

from a database (*e.g.*, the database named Computerised Oil Spill Identification, COSIWeb (Dahlmann and Kienhuis, 2016; CEN, 2023b)).

Some standardised methods developed in USA by the American Society for Testing and Materials (ASTM), published since the 1970s and updated over time, have been used to identify the source of spilt oil, such as:

- ASTM D3650 – Standard test method for comparison of waterborne petroleum oils by fluorescence analysis (ASTM, 2011);
- ASTM D3414 – Standard test method for comparison of waterborne petroleum oils by infrared spectroscopy (ASTM, 2017a);
- ASTM D5037 – Standard test method for comparison of waterborne petroleum oils by high performance liquid chromatography (ASTM, 2017b);
- ASTM D3328 – Standard test method for comparison of waterborne petroleum oils by gas chromatography (ASTM, 2020a);
- ASTM D5739 – Standard practice for oil spill source identification by gas chromatography and positive electron impact low resolution mass spectrometry (ASTM, 2020b).

Furthermore, studies based on pollution incidents have also been used to develop alternative methodologies to identify sources of pollution (Fresco-Rivera *et al.*, 2007; Fernández-Varela *et al.*, 2008; Stout, 2016; Han and Clement, 2018; Wang and Wang, 2022).

In Europe, the Scandinavian countries created the Nordtest method in 1983 that was revised in 1991 (NORDTEST, 1983; NORDTEST, 1991). The revised method uses GC-FID and GC-MS to obtain the fingerprint of the Sp and SS but compare them by visual inspection of the chromatograms. The method was endorsed in the Bonn Agreement⁹ Counter Pollution Manual, therefore Scandinavian and other European laboratories adopted it as a guideline for oil spill source identification (Bonn Agreement, 2007). Over the years, and due to the advances in instrumental techniques, as well as data processing and results interpretation, the European oil spill source identification method has been optimised, becoming more quantitative and considerably more reliable, objective, and legally defensive. Additionally, the method was converted into a guideline of the European Committee for Standardization (CEN) in 2006 and in a CEN standard in 2023. The advancement of the methodology over time is briefly depicted in **Figure 1.16**, and Kienhuis *et al.* (2016) provide a detailed description of its evolution.

⁹ The Bonn Agreement is the structure by which ten governments and the EU collaborate in order to address the pollution issue by oil and other hazardous materials in the North Sea (Bonn Agreement, 2024a).

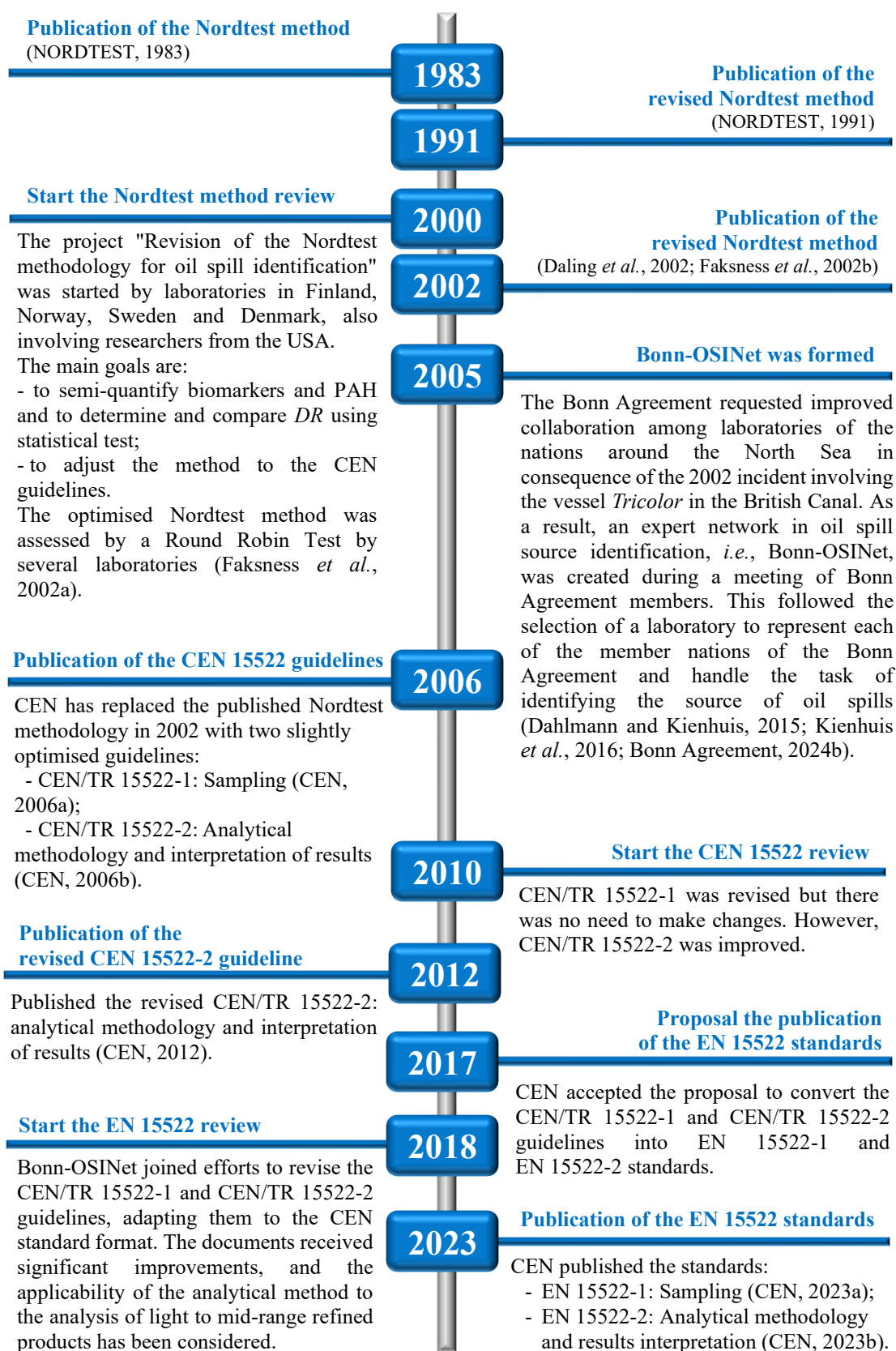


Figure 1.16. Evolution of the methodology for identifying oil spill sources in Europe.

The most significant differences among the versions of the methodology are:

- Analytical techniques;
- Compounds analysed;
- Qualitative vs. quantitative analysis of analytical data;
- Weathering check;
- Requirements and criteria for evaluating outcomes;
- Final conclusion.

The two versions of the Nordtest (published in 1991 and 2002) and CEN/TR 15522-2 (published in 2006 and 2012) methodologies were intended for the analysis of oil samples containing a substantial proportion of hydrocarbons with boiling point above 200 °C (NORDTEST, 1991; Daling *et al.*, 2002; Faksness *et al.*, 2002b; CEN, 2006b; CEN 2012). However, between 2018 and 2020, the Bonn Agreement expert body for oil spill identification and guidance in the analytical method, *i.e.*, Bonn-OSINet, committed to updating the CEN/TR 15522-2 methodology to its third edition, *i.e.*, EN 15522-2 (CEN, 2023b). The main goal was to extend the method applicability to the analysis of oil samples and refined products containing large proportions of hydrocarbons with boiling point above 150 °C. To accomplish this, a set of new *DR*, determined with abundant and oil-discriminating compounds from light and mid-range refined oil products, were selected by a study that involved the participation of 18 laboratories from 14 countries (Malmberg *et al.*, 2021).

The Nordtest and EN 15522-2 methodologies addressed in this study use both GC-FID and GC-MS analysis to obtain the samples' fingerprints, to compare the *Sp* and *SS* chromatograms and *DR* in order to identify differences, to perform weathering checks, and to produce the final conclusion. The last one is based on all evaluations of the results carried out with the same sentences based on match definitions between *Sp* and *SS*, although the EN 15522-2 also allows reporting an evaluative report format using likelihood ratios (Daling *et al.*, 2002; Faksness *et al.*, 2002b; CEN 2023b). However, both methodologies differ considerably in the structure of the decision protocol for oil spill identification and especially in the number of replicates required to evaluate the precision of the method, the compounds analysed, the way of weathering is assessed, the inputs and format of *DR*, and the *DR* comparison approach (Table 1.6).

Table 1.6. Main differences between the Nordtest and EN 15522-2 methodologies.

Method requirement	Nordtest methodology	EN 15522-2 methodology
Replicate analysis	Triplicate analysis, preferable for one Sp, to assess the sample preparation and instrumental analysis precision	Duplicate analysis of one sample extract, to assess the instrument analysis precision, since sample preparation is minimal: - two duplicates in investigations with two samples - duplicate analysis in 10% of samples in investigations of several samples.
Compounds analysed	<i>n</i> -Alkanes, isoprenoids (pristane and phytane), decalins, benzothiophenes, pPAH and alkyl-PAH homologues (<i>i.e.</i> , including sulphur-containing PAH), norhopanes, hopanes, methylhopanes, homohopanes, steranes, diasteranes and triaromatic steranes	<i>n</i> -Alkanes, isoprenoids (farnesane, norpristane, pristane and phytane), branched alkanes, <i>n</i> -alkyl cyclohexanes, decalins, adamantanes, sesquiterpanes, diamantanes, benzothiophenes, alkylbenzenes, alkyltoluenes, hydro-PAH, pPAH and alkyl-PAH homologues (<i>i.e.</i> , including sulphur-containing PAH), triterpanes, norhopanes, hopanes, homohopanes, steranes, diasteranes, triaromatic steranes and FAME
Weathering check	Bar chart with semi-quantitative distribution (<i>i.e.</i> , normalised abundances) for Sp and SS of: - <i>n</i> -alkanes and isoprenoids (data from GC-FID analysis) - PAH (data from GC-MS analysis in SIM mode) Assessment by trends in the compounds' distributions	Percentage of weathering plots to assess depletion percentage of normalised compound abundance in the Sp relatively to SS: - of <i>n</i> -alkanes and isoprenoids (data from analysis by GC-FID or GC-MS in full scan mode) - of all compounds analysed by GC-MS analysis in SIM mode Criteria for the depletion percentage: 85% to 118%
DR format ⁽¹⁾	$100 \cdot A/(A + B)$	A/B or $100 \cdot A/B$ dependent on the expert preference
DR character	All possible determined DR, suggested by the method using the compounds analysed	- Different sets of listed normative ratios depending on the oil type - Listed informative ratios to add robustness to oil pattern comparison
DR replicate assessment	Criterion for DR triplicates: < 5% to 10% RSD ⁽²⁾	Criterion for DR duplicates: < 5% RSD ⁽²⁾
DR comparison approach	Student's <i>t</i> statistics using the 95% and 98% confidence levels: - positive match between Sp and SS fingerprints if all DR in Sp and SS are statistically equivalent for 95% confidence level - probable match between Sp and SS fingerprints if all DR in Sp and SS are statistically equivalent for 98% confidence level - non-match between Sp and SS fingerprints if at least one DR in Sp and SS are statistically different for 98% confidence level	Single criterion of 14% ⁽³⁾ used to assess the percentage of the absolute difference of DR, observed in Sp and SS, relatively to the mean of the two DR

(1) *A* and *B* as chromatographic signals of compounds A and B.

(2) Relative standard deviation.

(3) Single criterion defined as repeatability limit for 95%, *i.e.*, $2.8 \times 5\%$ RSD.

Considering the different conditions and requirements recommended by Nordtest and EN 15522-2, those proposed by the last one are considered preferable, given that:

- its applicability is extensive to a greater variety of refined products;
- a greater number of compound classes are analysed;
- the determined *DR* are adjusted to the oil type favouring a better characterisation of the oil and an appropriate weathering assessment;
- a strict quality control of analytical data is employed.

The research conducted within the scope of this thesis intends to evaluate the performance of the conventional *DR* comparison approaches employed in the Nordtest and EN 15522-2 methodologies, and of a newly developed accurate comparison approach based on MCM simulations applying recommended comparison conditions from the standard methods.

1.3.3. Factors affecting the spilt oil fingerprint

Four factors determine the chemical composition of oils and derivatives: the genesis of crude oils, the refining processes employed to produce refined products, their degradation and their mixing in the environment (Stout and Wang, 2007). As opposed to the latter two, the first two, addressed in **Subchapter 1.2**, referred to oil composition and are unrelated to any environmental pollution event. However, when an oil spill occurs in the marine environment, the oil interacts with it, undergoing several naturally occurring processes that all contribute to its degradation, also known as weathering (Stout and Wang, 2007; Zhang *et al.*, 2019; NRC, 2022). The weathering processes starts right after the spill and persists over time, modifying the oil's physical (*e.g.*, density and viscosity) and chemical original features. Indeed, the oil compositional changes occur at different categories of compounds and at various rates caused by the distinct conditions related to each pollution incident, such oil type, spill site and environmental conditions (Wang *et al.*, 2006b; Stout and Wang, 2007; Zhang *et al.*, 2019). Additionally, when spilt, the oil can be mixed with chemicals already present in the environment, wether of natural or anthropogenic origin, resulting in what is called contamination (Stout and Wang, 2007; CEN 2023b). Thus, it becomes essential that investigations be conducted in the short term, ensuring maximum preservation of the oil's original identity, and in the long term to assess the evolution of the spill over time, allowing a proper prediction of environmental impacts as well as the behaviour and fate of weathered oil.

The predominant weathering mechanisms that occur on an oil spill in the marine environment are presented in **Figure 1.17** and divided into three categories as follows (Wang and Fingas, 1995; Wang *et al.*, 2006b; Stout and Wang, 2007; Zhang *et al.*, 2019; NRC, 2022):

- Physical processes: spreading, dispersion in the water column, emulsification, adsorption to suspended particulate matter, sedimentation;
- Chemical processes: evaporation, dissolution, photo-oxidation;
- Biological processes: biodegradation.

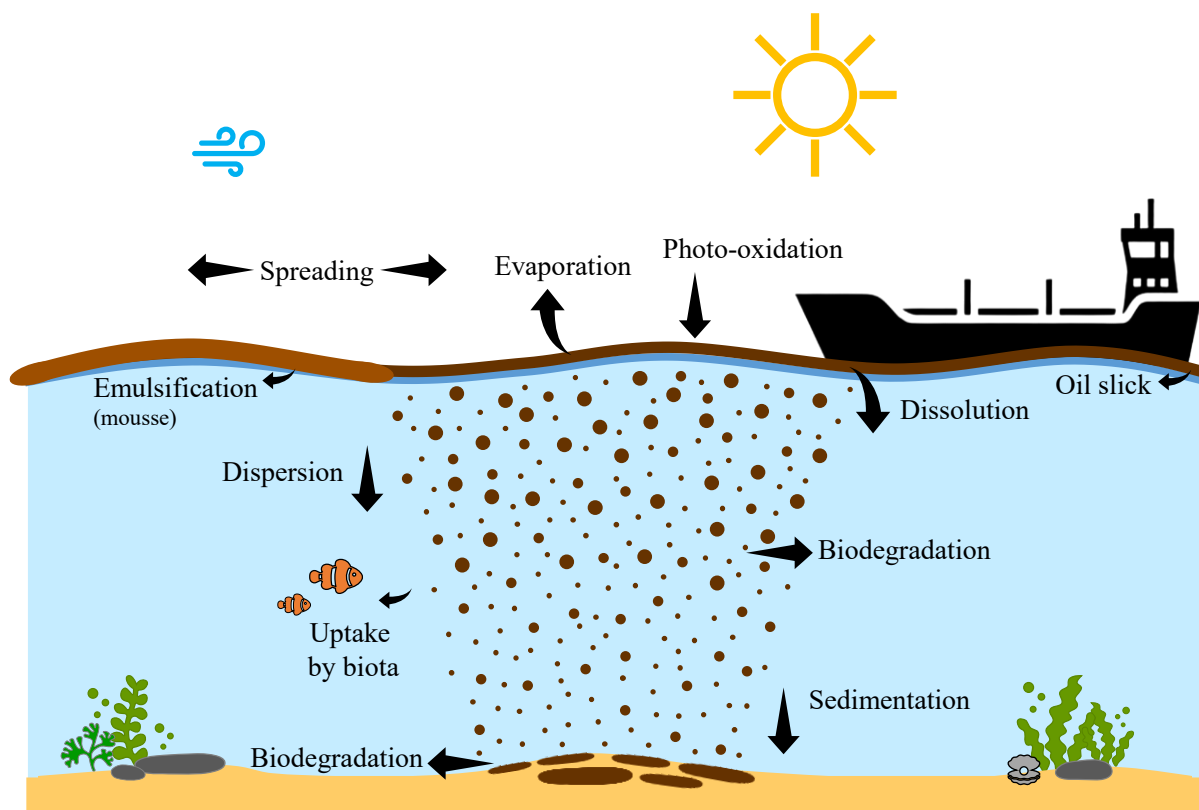


Figure 1.17. Main weathering processes that affect an oil spill in the marine environment.

The physical processes do not change the oil's chemical composition on their own, but they have an important impact on the rates at which chemical and biological processes occur (Stout and Wang, 2007). The spreading and dispersion physical mechanisms drive the oil to propagate across the surface and into the water column, respectively (NRC, 2022). These processes are boosted by the type of oil, sea turbulence, wind velocity, ocean currents as well as atmospheric and water temperature (Stout and Wang, 2007; NRC, 2022; Péquin *et al.*, 2022). Moreover, higher dispersion favours oil adsorption to suspended particulate matter, which, due to its

heavier nature, tends to deposit more quickly on the seabed, resulting in sedimentation (Zhang *et al.*, 2019; NRC, 2022). As the slick spreads and disperses, the oil contact area with the atmosphere and/or water increases, as does the degree and rate of chemical and biological processes, changing not only the chemical composition but also the oil's physical properties (*e.g.*, viscosity and density) (NRC, 2022; Péquin *et al.*, 2022). As a result of changes in density, the sedimentation of oil also takes place (Zhang *et al.*, 2019). The emulsification is the phenomenon characterised by the introduction of water droplets into the oil by turbulence and wind, forming an emulsion of water and oil, commonly called mousse (Stout and Wang, 2007; NRC, 2022). In general, the susceptibility to emulsion formation as well as the emulsion stability vary with the oil type (NRC, 2022). The water droplets inside the oil emulsion provide a physical barrier that protects the oil from environmental factors and the access of microorganisms (Stout and Wang, 2007). In addition, the oil emulsion has high viscosity and, as consequence, a lower contact area with the atmosphere and water (NRC, 2022). Thus, unlike the spreading, dispersion, and sedimentation, the emulsification slows the degradation by biological and chemical mechanisms, resulting in an emulsified oil with a similar composition to that of unweathered and non-emulsified oil (Wang *et al.*, 2021; NRC, 2022). However, the inhibition of chemical processes, such as evaporation, relies on the stability of the emulsions, with the more stable ones suffering a smaller impact (Wang *et al.*, 2021). Even at a slower rate, the degradation of the emulsified oil occurs, which results in the formation of tar mats that may crack due to wave action and, consequently, creating the tar balls (Stout and Wang, 2007).

Of the processes that change the oils' chemical composition, evaporation is the dominant one and it begins as soon as the oil is spilt, especially for the lighter oil derivatives (Wang and Fingas, 1995; Wang *et al.*, 2005; Wang *et al.*, 2006b; Yim *et al.*, 2011). This mechanism removes the low boiling range components from the oil to the atmosphere, so is determined by the vapour pressure of the compounds and impacted by the oil composition, atmospheric and water temperature, insolation, wind speed, turbulence and oil film thickness (Stout *et al.*, 2016b; Wang *et al.*, 2021; NRC, 2022). Evaporation is the process that causes the most substantial loss of oil mass and increases the viscosity, density, and emulsification of the spilt oil (Stout and Wang, 2007; Wang *et al.*, 2006b; Malmborg, 2017; Zhang *et al.*, 2019). The prediction of evaporation is quite simple, and modelling to identify its occurrence has been established in the normative reference for expert chemical analyses (CEN, 2023b). The lower molecular weight compounds are those affected in the earlier stages of the spill with the vulnerability to this mechanism being inversely proportional to chain length, number of aromatic rings and alkyl

substituent number (Wang and Fingas, 1995). Those compounds are the *n*-alkanes below Pentadecane (C15), decalins, adamantanes, alkylbenzenes and some isoprenoids that have a shorter carbon chain than pristane (He *et al.*, 2016; Stout *et al.*, 2016b; Malmborg, 2017; Alexandrino *et al.*, 2019; Filewood *et al.*, 2022a). Although on a smaller scale, dissolution occurs concurrently with evaporation and is defined by the transfer of the oil's constituents to the water in which it was spilt (NRC, 2022). The structure and polarity of molecules controls this phenomenon, which is also influenced by oil's viscosity, temperature, waves and turbulence (Malmborg, 2017; NRC, 2022). The low molecular weight *n*-alkanes have some solubility in water, which increase with the decrease of the chain length (Alimi *et al.*, 2013; He *et al.*, 2016; Stout *et al.*, 2016b). Furthermore, dissolution is increased by decreasing the number of alkyl substituents in the molecular structure of the oil constituents (Malmborg, 2017). Due to their polarity, monoaromatics (*e.g.*, BTEX and other alkylbenzenes), PAH, and hydrocarbons containing heteroatoms are the most soluble and thus more prone to dissolving in water than the other hydrocarbons (Stout *et al.*, 2016b; Malmborg, 2017). Among the PAH, naphthalene and its homologous alkylated compounds are the most susceptible to this mechanism, with the other PAH being relatively resistant (Stout *et al.*, 2016b; Malmborg, 2017). Photo-oxidation occurs with the breakdown of chemical bonds of the oil's constituents by the action of sunlight, particularly ultraviolet radiation, resulting in free radicals. Since these are quite reactive, they will undergo various chemical reactions with oxygen, resulting in the production of water-soluble polar compounds such as alcohols, peroxides, aldehydes, and ketones (Stout and Wang, 2007; Radović *et al.*, 2014; Zhang *et al.*, 2019; NRC, 2022; Li *et al.*, 2023). The photo-oxidation mechanism is thus directly dependent on the oil type and its composition in compounds with reactivity to light, as well as on the intensity of solar radiation and time of exposure, and is indirectly dependent on the environment conditions of the site where the oil was spilt (Bacosa *et al.*, 2015; CEN, 2023b; Li *et al.*, 2023). The saturated hydrocarbons are less prone to photo-oxidation than aromatic hydrocarbons, while, in the later ones, the alkylated PAH appear to be more photosensitive than their parent compounds (Bacosa *et al.*, 2015; Malmborg, 2017). Despite the reduced proneness to photodegradation of *n*-alkanes, it has been observed that the rate increases as molecular weight decreases (Li *et al.*, 2023). However, it is not clear any relationship between the photo-oxidation predisposition and the number of rings and alkyl substituents in PAH (Bacosa *et al.*, 2015; Stout *et al.*, 2016b; Li *et al.*, 2023). The benzofluorene isomers are shown to be photodegradable, as well as the 3-ring PAH, with exception of phenanthrene and its homologous alkylated family, with alkylated pyrenes being the most photosensitive (Bacosa *et al.*, 2015; Stout *et al.*, 2016b; Malmborg, 2017).

Additionally, the 4-ring monoalkyl-chrysenes were also identified as light-sensitive compounds (Radović *et al.*, 2014; CEN, 2023b). However, the compounds methylanthracene and 2,6 + 2,7-dimethylnaphthalene, from the phenanthrene/anthracene and naphthalene homologous series, respectively, have both been recognised as photo-oxidation markers (Bacosa *et al.*, 2015; Malmborg, 2017). In contrast, sulphur-containing PAH, such as naphthobenzothiophenes and dibenzothiophenes, are more recalcitrant compared to other PAH (Radović *et al.*, 2014; Stout *et al.*, 2016b). Other studies using mineral diesel and biodiesel blends revealed that only unsaturated chain FAME are photo-oxidative and, for this reason, these compounds have been set as photo-oxidation markers for this oil type (Malmborg, 2017; Alexandrino *et al.*, 2019; Filewood *et al.*, 2022a; CEN, 2023b). Among the biomarkers, the triaromatic steranes reduced their content in the oils tested when also exposed to light (Radović *et al.*, 2014; Stout *et al.*, 2016b; CEN, 2023b). The biological degradation involves the breakdown of oil's compounds into less complex molecules through the activity of microorganisms (Stout and Wang, 2007; NRC, 2022). The oil type and the characteristics of the environment where the oil was released, such as the microbial community, temperature, salinity, oxygen, pH, and nutrient availability, influence the biodegradation rate (Wang *et al.*, 2006b; Zhang *et al.*, 2019; NRC, 2022; Péquin *et al.*, 2022). Like photo-oxidation, this process is destructive and occurs more slowly than the other chemical processes. Thus, its effects require time to be noticeable in samples used to identify the polluting source, which are often collected as soon as possible after the spill (Stout and Wang, 2007). Despite being a lengthy, the mechanism is capable of naturally restoring an affected environment by minimising the presence of oil (Péquin *et al.*, 2022). Some studies have been identified the compounds most prone to biodegradation as FAME, monoaromatic compounds (alkylbenzenes and alkyltoluenes), *n*-alkanes, branched alkanes, alkylcyclohexanes, naphthalene and phenanthrene, as well as alkylated naphthalenes and methylphenanthrenes (Bacosa *et al.*, 2015; Malmborg, 2017; Alexandrino *et al.*, 2019; Malmborg *et al.*, 2021; Filewood *et al.*, 2022a). According to these findings, the susceptibility to biodegradation decreases with increasing of chain length for *n*-alkanes, number of aromatic rings for aromatic compounds and number of alkyl substituents for both compounds' classes (Wang *et al.*, 2006b; Bacosa *et al.*, 2015; Malmborg, 2017; Malmborg *et al.*, 2021). Furthermore, the biotransformation rate varies among *ortho*, *meta*, and *para* isomers and follows the trend *meta* > *para* > *ortho* (Malmborg, 2017; Malmborg *et al.*, 2021). Like other compounds, increasing chain length reduces the potential for microbial breakdown of FAME, but the preference between saturated or unsaturated chains is not clear (Malmborg *et al.*, 2021). These compounds are the most prone to biodegradation,

demonstrating the relevance of employing them as indicators of this weathering mechanism in blends of diesel and biodiesel (Alexandrino *et al.*, 2019; Malmborg *et al.*, 2021).

Over the years, numerous studies have been conducted to enhance our knowledge on the mechanisms by which spilt oil degrade and how these mechanisms affect the oil's composition (Wang *et al.*, 2005; Yim *et al.*, 2011; Radović *et al.*, 2014; Bacosa *et al.*, 2015; Stout *et al.*, 2016b; Malmborg, 2017; Alexandrino *et al.*, 2019; Chua *et al.*, 2020; Cook *et al.*, 2020; Malmborg *et al.*, 2021; Wang *et al.*, 2021; Filewood *et al.*, 2022a; Li *et al.*, 2023; Lima *et al.*, 2023). In a forensic analysis framework, the weathering assessment, as well as the identification of the main contributing processes is vital. For this purpose, some metrics have been created, such as the weathering index by evaporation, normalised compound abundances in weathered and unweathered oils presented in bar-charts to easily assess trends, and the depletion percentage of selected compounds in a weathered oil compared to an unweathered one represented as percentage of weathering plots (PW-plots) (Wang and Fingas, 1995; Daling *et al.*, 2002; Stout *et al.*, 2016b; Malmborg, 2017; Li *et al.*, 2023; CEN, 2023b). The weathering level observed have been reported using a qualitative term, for exemple as slightly/lightly, moderately, or severely weathered (Wang *et al.*, 2006b; Stout and Wang, 2007; Yim *et al.*, 2011; He *et al.*, 2016). **Table 1.7.** presents the main changes in the chemical composition of the oils that drive to each weathering degree, as well as the percentage of oil mass loss described in two studies (Wang *et al.*, 2006b; Yim *et al.*, 2011).

This classification system results in a subjective classification due the compositional changes found by experts and to various determination modes of the percentages of mass loss (Cook *et al.*, 2020). Therefore, other weathering degree classification systems, defined by stated quantitative and objective degradation stages, started to be developed and applied aiming to reduce the ambiguity in the communication of oil degradation levels (Cook *et al.*, 2020).

Table 1.7. Classification of weathering degree and the main oil compositional changes promoted by the weathering mechanisms.

Weathering degree	Mass loss	Oil compositional changes
Wang <i>et al.</i> (2006b):		
Slightly/ lightly weathered	Below 15%	Low molecular weight <i>n</i> -alkanes significantly reduced Loss of BTEX and trialkyl-substituted benzene compounds
Moderately weathered	~15% to 30%	Substantial loss of <i>n</i> -alkanes and low molecular weight isoprenoid Completely loss of BTEX and trialkyl-substituted benzene compounds Loss of naphthalene and C1-naphthalenes ⁽¹⁾ Loss of resolved hydrocarbons over the UCM ⁽²⁾ (decrease of the ratio between GC-resolved peaks and UCM)
Severely weathered	Above 30%	Heavily or completely loss of <i>n</i> -alkanes, branched alkanes and cycloalkanes Pronounced UCM Total loss of BTEX and alkylbenzenes High degradation of PAH and their alkylated homologous series showing the trend C0- < C1- < C2- < C3- < C4- ⁽¹⁾ in each alkylated PAH family
Yim <i>et al.</i> (2011):		
Initial weathering (stage I)	Average of 28.9%	Loss of saturated hydrocarbons up to dodecane (C12) and 2-ring parent PAH Weathering indices for evaporation and dissolution are distinguished from those of unweathered oil and moderately weathered oil and confirm the domination of evaporation
Moderate weathering (stage II)	Average of 37.7%	Loss of saturated hydrocarbons up to C15 Loss of C0-, C1- and C2- of 2 and 3-ring PAH Bimodal hump shape of UCM more prominent Weathering indices point out a mixed effects of evaporation and dissolution
Advanced weathering (stage III)	Average of 47.2%	Saturated hydrocarbons are reduced relatively to isoprenoids The PAH distribution pattern shows that 3-ring pPAH are mostly absent, as well as a loss of C1- and C2-phenanthrenes and dibenzothiophenes Octadecane/phytane and 4-methyldibenzothiophene/1-methyl-dibenzothiophene ratios show biodegradation occurrence
Extreme weathering (stage IV)	Average of 60.3%	Pristane and phytane dominate the saturated hydrocarbons pattern Alkylated homologous PAH have further decrease comparatively to advanced weathering level Trace amounts of naphthalene Dominance of alkylated dibenzothiophenes Weathering indices with very low values
(1) C0-, C1-, C2-, C3-, C4-: parent PAH, monoalkyl-substituted, dialkyl-substituted, trialkyl-substituted and tetraalkyl-substituted, respectively.		
(2) Unresolved complex mixture.		

1.4. Assessing the uncertainty in oil spill source identification

1.4.1. Sources of uncertainty

Chemical analysis plays an important role in identifying the origin of an oil spill source. However, the reliability of the findings obtained from such analyses is easily diminished due to the uncertainties related to the multiple processes that are associated. These sources of uncertainty can be external to the laboratory's activity or related to the analytical methodology used. The first one can be mentioned as the differentiation between competing suspected sources with only minor variations in oil patterns, which makes it difficult to distinguish between suspected sources. Additionally, the changes in the chemical composition of the oil due to degradation by environmental factors or the introduction of contaminants present in the environment where the oil was spilt also promote changes in the oil pattern. Both situations make it difficult to correlate samples and, consequently, correctly identify the polluting source. Sampling and sample conditioning processes also influence the uncertainty of the investigation. These, if not executed with caution, such as unsuitable sample preservation and/or late sample collection with contaminated material, can result in contamination and promote sample degradation. Furthermore, the identification, labelling, and transportation of the samples can introduce errors, leading to information mismatches and loss of traceability. The sampling site selection has an important effect on the success of the forensic investigation, since collecting samples in inappropriate locations decreases the representativeness of the spilt oil, making it difficult to find the potential polluter or even impossible if the real polluting source was not sampled. Another aspect that can compromise the compositional representativeness of the oil is the small amount of oil collected, which may be insufficient for the analytical methods to adequately characterise it. The analytical methods used in chemical analyses can meaningfully impact the comparison of samples, increasing the probabilities of false compositional equivalence or difference claims between oils due to the proper limitations of the analytical instruments (*e.g.*, detection and quantification limits and precision), the measurement errors arising from sample preparation, as well as the approximations and/or assumptions made when applying traditional approaches to comparing oil patterns.

To minimise these sources of uncertainty in forensic investigation and thus ensure reliable conclusions, which are fundamental for the correct identification of the polluting source and the presentation of evidence in court, it is necessary to combine rigorous and standardised protocols for sample collection, preservation, and transportation, analytical techniques with

appropriate quality control to ensure the required performance, and solid and realistic probabilistic models to assess the credibility of the identifications. Even though identifying a potential polluting source is challenging, technological and scientific developments over time have helped to reduce the uncertainty, resulting in forensic investigations that are more robust and defensible.

1.4.2. Bayes' Theorem and likelihood ratios

The uncertainty associated with a quantitative determination, *i.e.*, a measurement, can be expressed through a confidence interval, which defines the range in which the true value of the measurand sits, taking into account the dispersion of probable values (JCGM, 2023). In contrast, a qualitative analysis, *i.e.*, examination, attempts to determine the presence or absence of a substance or a specific characteristic, with the results being presented through a classification (Ellison *et al.*, 1998; Lim *et al.*, 2020; Bettencourt da Silva and Ellison, 2021). This type of analysis is commonly employed in forensic science for evaluating the hypothesis of an accusation, therefore, it is mainly the certainty of an identification that is evaluated (*i.e.*, how credible the findings of the analysis are) and, indirectly, its uncertainty (Ellison *et al.*, 1998). However, erroneous classifications in qualitative analysis, *i.e.*, false positives or false negatives, can occur and have serious implications. For example, in the absence of further evidence, a mistaken identification of an oil spill source can lead to the incrimination of an innocent party, with repercussions such as severe penalties and other sanctions, license revocation, reputation damage, and even imprisonment. Thus, it is crucial that the rates of false positives and negatives are kept as low as possible. Still, analysing and optimising uncertainty in a qualitative analysis represents a challenge distinct from that faced in a quantitative analysis.

In forensic science, Bayesian inference is used to evaluate the certainty/uncertainty of a chemical analysis-based identification. Generally, forensic scientists present the weight of the findings from the chemical analyses conducted, *i.e.*, evidence, assisting the prosecutor in updating their prior beliefs about the accusation, thereby helping in the decision regarding a suspect's guilt or innocence (Nordgaard and Rasmusson, 2012). Although the forensic scientist is responsible for presenting the strength of the evidence, the prosecutor must establish the degrees of prior belief, which are then converted to degrees of posterior belief when the evidence is introduced (Vergeer *et al.*, 2014).

Bayes' Theorem is thus a valuable statistical tool for updating the probabilities of a prior known event based on evidence. **Equation 1.2** describes this theorem in common forensic science notation (Ellison *et al.*, 1998; Nordgaard and Rasmusson, 2012):

$$P(H_p|E) = \frac{P(E|H_p) \cdot P(H_p)}{P(E)} = \frac{P(E|H_p) \cdot P(H_p)}{P(E|H_p) \cdot P(H_p) + P(E|H_d) \cdot P(H_d)} \quad (1.2)$$

where $P(H_p|E)$ is the posterior probability depicted in a conditional probability of the prosecutor hypothesis, H_p , occurring given the evidence E , $P(E|H_p)$ and $P(E|H_d)$ are the conditional probabilities of observing the evidence given the prosecutor and defence (H_d) hypothesis being true, respectively, $P(E)$ is the probability of observing the evidence independently of the prosecutor or the defence hypothesis, and $P(H_p)$ and $P(H_d)$ are the prior probabilities of the prosecutor and defence hypotheses occurring without the influence of any evidence, respectively. $P(H_p)$ and $P(H_d)$ are complementary, meaning that their sum is 100%.

In a simplified form, $P(E|H_p)$ and $P(E|H_d)$ represent the probability of a true positive/true identification and a false positive/false identification, respectively, which are often obtained during the validation of a method (Ellison *et al.*, 1998). Estimating these probabilities, however, requires conducting a large number of sample analyses and outcome assessments, in particular for lowering $P(E|H_d)$. This process is impractical in many cases, forcing the use of databases or data simulation to overcome the problem (Thompson *et al.*, 2018; Bettencourt da Silva and Ellison, 2021). As illustrated by **Equation 1.2**, the estimation of the $P(H_p|E)$ is not only influenced by the probabilities of true and false identifications but also by the prior probabilities. In general, the latter are difficult to estimate but can be determined from historical data for certain situations (Ellison *et al.*, 1998). However, when such information is not readily available, it is reasonable to assume $P(H_p) = P(H_d) = 50\%$ (Ellison *et al.*, 1998). A possible way to circumvent the assumption of prior probabilities is to employ the likelihood ratio (LR) (**Equation 1.3**) to assess the credibility of the identification, which has widespread application in forensic laboratories.

$$LR = \frac{P(E|H_p)}{P(E|H_d)} \quad (1.3)$$

The LR is derived from Bayes' Theorem and reflects how much more likely it is to observe evidence supporting the prosecutor hypothesis than the defence hypothesis. Considering the

conditional probability of the defence hypothesis occurring given the evidence provided by the forensic scientist ($P(H_d|E)$), **Equation 1.2** takes the form of **Equation 1.4**:

$$P(H_d|E) = \frac{P(E|H_d) \cdot P(H_d)}{P(E|H_p) \cdot P(H_p) + P(E|H_d) \cdot P(H_d)} \quad (1.4)$$

The ratio of the two posterior probabilities (**Equation 1.5**), expressed in **Equation 1.2** and **Equation 1.4**, demonstrates the update of the prior odds of Bayes' Theorem:

$$\frac{P(H_p|E)}{P(H_d|E)} = \frac{P(E|H_p)}{P(E|H_d)} \cdot \frac{P(H_p)}{P(H_d)} \quad (1.5)$$

with $\frac{P(H_p|E)}{P(H_d|E)}$ and $\frac{P(H_p)}{P(H_d)}$ representing the posterior ($O(H_p|E)$) and prior ($O(H_p)$) odds, respectively.

Thus, the presentation of evidence amplifies or attenuates the prosecutor's prior belief, with the LR (**Equation 1.3**) representing its weight (Ellison *et al.*, 1998; Nordgaard and Rasmusson, 2012; Vergeer *et al.*, 2014). Considering **Equation 1.3**, the value of the LR ranges from 0 to infinity, with an LR greater than one indicating that the evidence supports the prosecutor hypothesis while an LR less than one supports the defence hypothesis. Furthermore, the support for the prosecutor and defence hypotheses rises when the LR value increases or approaches zero, respectively. An LR of one reflects unbiased evidence, implying that both hypotheses have equal support (Vergeer *et al.*, 2014). Nevertheless, it is also common to define the preferred hypothesis as a numerator in the LR , which in this case the LR ranges from one to infinity (Thompson *et al.*, 2018).

After presenting the LR , the prosecutor can revise beliefs about the accusation based on the evidence. Since $P(H_p)$ and $P(H_d)$ are complementary, $P(H_d) = 1 - P(H_p)$, the **Equations 1.3** and **1.5** can be combined to form **Equation 1.6**. As mentioned above, the terms on the left and right of **Equation 1.6** reflect the $O(H_p|E)$ and the $O(H_p)$, respectively (**Equation 1.7** and **1.8**, respectively).

$$\frac{P(H_p|E)}{1 - P(H_p|E)} = LR \cdot \frac{P(H_p)}{1 - P(H_p)} \quad (1.6)$$

$$O(H_p|E) = \frac{P(H_p|E)}{1 - P(H_p|E)} \quad (1.7)$$

$$O(H_p) = \frac{P(H_p)}{1 - P(H_p)} \quad (1.8)$$

Considering **Equations 1.7** and **1.8**, the **Equation 1.6** can be simplified:

$$O(H_p|E) = LR \cdot O(H_p) \quad (1.9)$$

Rearranging $O(H_p|E)$ and $O(H_p)$ in order to convert them into probabilities obtains **Equations 1.10** and **1.11**:

$$P(H_p|E) = \frac{O(H_p|E)}{1 + O(H_p|E)} \quad (1.10)$$

$$P(H_p) = \frac{O(H_p)}{1 + O(H_p)} \quad (1.11)$$

To determine $P(H_p|E)$ as a function of LR and $P(H_p)$ (**Equation 1.12**), the variables $O(H_p|E)$ (**Equation 1.9**) and $O(H_p)$ (**Equation 1.8**) are replaced into **Equation 1.10**.

$$P(H_p|E) = \frac{LR \cdot \left(\frac{P(H_p)}{1 - P(H_p)} \right)}{1 + LR \cdot \left(\frac{P(H_p)}{1 - P(H_p)} \right)} \quad (1.12)$$

Equation 1.12 simplifies into **Equation 1.13** in the specific scenario where the prior probabilities of the prosecutor and defence hypotheses are equally plausible, *i.e.*, the prior odds are equal to one (Nordgaard *et al.*, 2012):

$$P(H_p|E) = \frac{LR}{1 + LR} \quad (1.13)$$

In this instance, the $P(H_p|E)$ is established based only on the evidence that has been provided.

To assist in the interpretation of Bayes' Theorem as applied to the identification of a suspected oil spill source, a brief overview of the terminology used in this study is provided. As previously mentioned, potential polluting sources are identified by comparing the oil patterns of the oils present in Sp and SS. The chemical analysis results are provided as a compositional equivalence or difference claim between the oils of Sp and SS. Given that the evidence is intended to support the prosecutor hypothesis, namely that the oils of the Sp and SS are the same, the LR is defined as the ratio of the probabilities of compositional equivalence claim between Sp and SS, given

that the oils in both samples are the same or distinct. These probabilities are assessed for each pollution event, as they are influenced not only by the level of characterisation of the oil patterns to be compared, which may include many or few *DR*, but also by the similarity of oils found in competing *SS*. In either cases, it is reasonable to expect that the establishment of compositional equivalence between the oils of *Sp* and *SS* will be more or less easy, directly affecting the probabilities. The $P(H_p|E)$ also depends on the prior probabilities, *i.e.*, whether the oils in *Sp* and *SS* are the same or different. Because these probabilities are unknown and difficult to obtain directly, we must assume a reasonable value for each of them.

In verdict, the certainty/uncertainty of identifying a pollution source obtained through Bayesian inference, *i.e.*, determining the *LR* and the $P(H_p|E)$, ensures that the results of the chemical analysis are communicated transparently, allowing for more reliable interpretations in the judicial context. Despite the fact that the EN 15522-2 standard recommends using *LR* to express the weight of forensic analysis as an alternative to verbal statements of positive, probable, or negative match between oil patterns, the scientific community has not directly debated the use of *LR* to express the weight of the evidence in oil spill source identification. However, it is essential to invest in reliable, rigorous, and precise examinations in order to avoid errors that could prejudice an innocent and discredit both the effectiveness of forensic investigations and the judicial system.

1.4.3. Presenting the evidence

As previously stated, forensic scientists use *LR* to convey how the evidence they provide affects the perception of the prosecutor about the accusation. However, simply presenting a numerical *LR* value may not be sufficient to indicate the strength or weakness of the evidence. For this reason, it is recommended that the degree of support for the prosecutor hypothesis be expressed not only numerically, but also by a verbal expression. This mode of presentation makes the interpretation of the evidence more objective and understandable in the judicial context. The verbal equivalents correspond to qualitative descriptions of evidence-based support and are associated with specific *LR* value ranges. When these intervals and their verbal equivalents are defined, a scale of conclusions is created to allow for a more standardised interpretation of the strength of the evidence. Two important aspects to consider when defining a scale of conclusions are resolution and terminology (Noordgaard *et al.*, 2012; Thompson *et al.*, 2018). The scale's resolution is the level of detail used to differentiate *LR* values and should be defined

in a way that balances precision and practicality. The notation of the verbal equivalents must reflect the rigour required in their area of application, ensuring clarity and objectivity in what is intended to be conveyed.

Various scales of conclusions have been proposed over time (**Table 1.8**). Despite their minor variations, the ranges of *LR* values, and particularly the terminology employed in the verbal equivalent differ among the scales. When identifying a source of an oil spill, EN 15522-2 also recommends a conclusion scale to classify the degree of evidential support based on *LR* (**Table 1.8**).

According to Noordgaard *et al.* (2012), constructing a scale of conclusions is challenging; however, defining a minimum posterior probability value based solely on the presented evidence helps in selecting the resolution of the *LR* value ranges. However, the relationship between different probabilities of true and false identifications and their impact on the *LR* can also be useful, as this approach is supported by the accuracy of the analytical methods used to obtain evidence (Thompson *et al.*, 2018). Following that, the selection and implementation of a scale is critical to ensure that the findings obtained from chemical analyses are communicated in a clear, transparent, and objective manner, allowing judges and lawyers to more readily comprehend the weight of the evidence without requiring more technical and specific knowledge.

Table 1.8. Scales of conclusions for reporting the strength of the evidence.

Range of <i>LR</i>	Verbal description
Evett and Weir (1998):	
1 to 10	Limited support
10 to 100	Moderate support
100 to 1,000	Strong support
More than 1,000	Very strong support
AFSP (2009):	
> 1 – 10	Weak support for proposition
10 – 100	Moderate support for proposition
100 – 1,000	Moderately strong support for proposition
1,000 – 10,000	Strong support for proposition
10,000 – 1,000,000	Very strong support for proposition
> 1,000,000	Extremely strong support for proposition
Noordgaard and Rasmusson (2012), and Noordgaard <i>et al.</i> (2012):	
$10^6 \leq LR$ (Scale Level: +4)	The results of the examination extremely strongly support that...
$6,000 \leq LR < 10^6$ (Scale Level: +3)	The results of the examination strongly support that...
$100 \leq LR < 6,000$ (Scale Level: +2)	The results of the examination support that...
$6 < LR < 100$ (Scale Level: +1)	The results of the examination support to some extent that...
$1/6 \leq LR < 6$ (Scale Level: 0)	The results of the examination support neither... nor...
$1/100 < LR < 1/6$ (Scale Level: -1)	The results of the examination support to some extent that... was not...
$1/6,000 < LR \leq 1/100$ (Scale Level: -2)	The results of the examination support that... was not...
$1/10^6 < LR \leq 1/6,000$ (Scale Level: -3)	The results of the examination strongly support that... was not...
$LR \leq 1/10^6$ (Scale Level: -4)	The results of the examination extremely strongly support that... was not...
ENFSI (2015):	
$1 < LR \leq 10$	Slight support/Limited support
$10 < LR \leq 100$	Moderate support
$100 < LR \leq 1,000$	Moderately strong support
$1,000 < LR \leq 10,000$	Strong support
$LR > 10,000$	Very strong support
Marquis <i>et al.</i> (2016):	
1	The results support neither propositions. This support is qualified as null
> 1 – 10	The results support the proposition that... rather than the proposition that... This support is qualified as weak or limited
> 10 – 100	The results support the proposition that... rather than the proposition that This support is qualified as moderate
> 100 – 1,000	The results support the proposition that... rather than the proposition that... This support is qualified as strong
> 1,000 – 10,000	The results support the proposition that... rather than the proposition that... This support is qualified as very strong
> 10,000	The results support the proposition that... rather than the proposition that... This support is qualified as extremely strong
Evett <i>et al.</i> (2000):	
1 to 10	Limited evidence to support
10 to 100	Moderate evidence to support
100 to 1,000	Moderately strong evidence to support
1,000 to 10,000	Strong evidence to support
> 10,000	Very strong evidence to support
CEN (2023b):	
1	The forensic findings do not support one proposition over the other
2 to 10	The forensic findings provide weak support for the first proposition relative to the alternative
10 to 100	The forensic findings provide moderate support for the first proposition rather than the alternative
100 to 1,000	The forensic findings provide moderately strong support for the first proposition rather than the alternative
1,000 to 10,000	The forensic findings provide strong support for the first proposition rather than the alternative
10,000 to 1,000,000	The forensic findings provide very strong support for the first proposition rather than the alternative
1,000,000 and above	The forensic findings provide extremely strong support for the first proposition rather than the alternative

1.4.4. Monte Carlo Method

The Monte Carlo Method (MCM) is a powerful and widely used computational technique applied to solve complex problems. Its versatility allows it to be used in a variety of domains, including chemistry, physics, engineering, medicine and even finance and risk analysis (Glasserman, 2004; Raychaudhuri, 2008; Ellison and Williams, 2012; Bindes and Heermann, 2019; Bert and Sarrut, 2022; Yang, 2022). In these subjects, the MCM has multiple applications being an extremely valuable instrument, for example, stochastic simulations, modelling intricate systems, estimating probabilities and distributions, and assessing the uncertainties associated with results (Raychaudhuri, 2008). In comparison to traditional deterministic methods, the MCM exhibits advantages, such as flexibility by adapting to practically any problem concerning to uncertainty, management of systems with interdependent variables providing a more realistic analysis, and enhancement of decision-making by avoiding conclusions based on assumptions as the tool provides probabilistic knowledge of the involved variables.

Considering the aforementioned, the oil spill source identification benefits from the application of MCM which, based on several simulated data, compares oil patterns (*i.e.*, set of selected *DR*) present in *Sp* and *SS* with criteria adapted to the probabilistic nature of each system, *i.e.*, from the realistic probability distributions of *DR*. By also estimating probabilities of compositional equivalence claim between different pairs of *Sp* and *SS*, it allows the uncertainty assessment in the decision made on the compositional similarity of each pair of samples compared (*i.e.*, *LR* determination) and, consequently, on the identification of the potential polluting source. Therefore, the MCM application to oil spill forensics involves the simulation of a large number of input variables, such as component chromatographic signals, to describe the distribution of an output variable, *i.e.*, *DR*. This allows for the determination of each output variable value using a suitable mathematical formula, such as the division between the chromatographic signals of the compounds that define each *DR* and yields as many output variable values as the values of each input variable. From the simulated output values, it is possible to represent its probability distribution and obtain several statistical parameters, such as mode, mean, standard deviation and percentiles, with the last one being used for comparison of *DR* determined in the *Sp* and *SS* (Raychaudhuri, 2008). However, in order to give the system its true nature, specific information about it must be known, notably the probability distribution of the chromatographic signals, as well as their dispersion and correlation, determined from experimental data. The simulated outputs can also be used to estimate the probability of a compositional equivalence

claim between Sp and SS, taking into account that a compositional equivalence between Sp and SS is concluded if all of the *DR* determined in the two samples are significantly equivalent at a given confidence level.

At its core, the MCM is a technique for providing valuable and powerful insights in situations where traditional methods fail due to the systems complexity, as well as overcoming the difficulty of obtaining a large volume of data required to answer certain problems when, in most cases, they are not possible to obtain experimentally. The favourable use of MCM in oil spill investigations, which allows the expert to conduct a probabilistic evaluation of the results, improves the robustness and defensibility of chemical analysis findings, resulting in reliable accountability of polluters.

1.5. References

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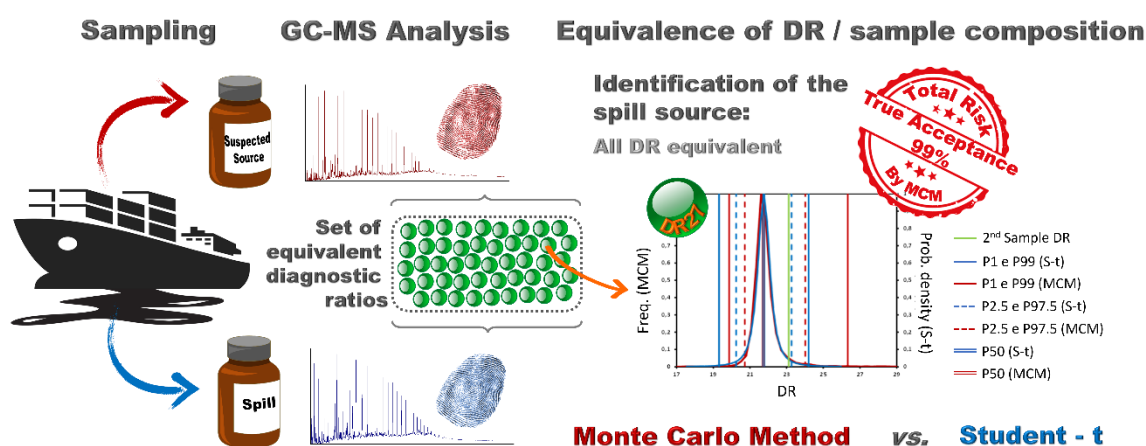
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2. Development and validation of statistically sound criteria for the match of unweathered GC-MS fingerprints in oil spill forensics



Abstract

The investigation of an oil spill's origin frequently relies on determining the equivalence of oil component patterns in samples from the contaminated environment and suspected oil source. This comparison benefits if based on the ratio of the abundance of unweathered characteristic components of the oil product, Diagnostic Ratios, *DR*. Replicate determinations of *DR* from one sample are used to set limits for the second sample's *DR*. The composition equivalence of oil patterns in both samples is indicated if all compared *DR* are statistically equivalent with a high confidence level. Some studies define *DR* limits assuming their normality and using Student's *t* statistics (S-t). However, since the ratio of correlated abundances can be not normally distributed, this criterion can drive to more false comparisons than predicted by the test confidence level. This work developed a computational tool for the reliable description of the non-normal distribution of the *DR* based on the Monte Carlo Method (MCM), aiming to allow the accurate control of the confidence of *DR* comparison. This work concluded that S-t defines 95% or 98% confidence limits with probabilities of falsely rejecting sample equivalence, ϕ , that can be up to 4.3% higher than predicted by the confidence level of the S-t test (*i.e.*, 5% and 2%). The fragilities of the S-t limits significantly reduce the probability ($1 - \theta$) of two samples with the same oil producing equivalent values of all compared *DR*. For the studied 69 *DR* from unweathered components, the ($1 - \theta$) for 98% confidence level limits, set by the MCM and S-t from triplicate injections of one sample, are 94.8% and 91.7%, respectively. These values are below the confidence level (*P*) defined for each *DR* because *DR* are correlated with a correlation coefficient lower than 1. The ($1 - \theta$) can be increased to above *P* by using MCM limits and accepting composition equivalence if at least one of two sample extract injections produces values within limits set from the other sample's replicate injection. The validated user-friendly MS-Excel file used to set and access comparison criteria is made available for download from the weblink presented in the **Annex A** and was checked experimentally. However, it is not feasible to estimate model confidence exclusively from experimentation because it would require too much independent analysis.

Keywords: Compositional match; False result rate; GC-MS; Monte Carlo Method; Nonparametric statistics; Oil spill

2.1. Introduction

Oil spills have been a concern over the years due to the growth of marine traffic and oil extraction and processing to answer present society demands. Most anthropogenic oil pollution in the marine environment comes from marine transportation or land-based sources resulting from accidental or intentional discharges (Stout *et al.*, 2001). The primary sources of such pollution are discharges from marine terminals and coastal refineries, municipal and industrial discharges, urban and river run-off, leakages from drilling operations, regular vessels operations and vessels accidents (Kennish, 1997; Stout *et al.*, 2001; Rogowska and Namiesnik, 2018; ITOPI, 2020). In contrast with the frequency and the amount of oil spilt from deliberate discharges, accidental spills occur less commonly but, in most cases, result in a substantial amount of oil spilt. Oil spills can drive to relevant socio-economic and human health impacts, and massive damage to ecosystems (Kingston, 2002; Chang *et al.*, 2014; Rogowska and Namiesnik, 2018). The magnitude and severity of impacts depend on the spill's location, and the quantity and type of product spilt (Tansel, 2014). Face to all these consequences, is crucial to identify the offender and to hold them liable under the law. Chemical analysis has been used to identify the source of the spill, interpret its behaviour and fate, assess environmental impacts, and help in selecting cleaning methods (Stout *et al.*, 2001; Wang and Fingas, 2003).

Petroleum is a complex mixture of hydrocarbons, formed over time from organic materials, that undergoes various chemical processes according to the geological conditions (Tissot and Welte, 1984). The different conditions of petroleum formation and particularities of refining processes used to generate the refined products are why crude oil and its derivatives acquire unique characteristics. The chemical fingerprints of these products can be determined from chemical analysis named fingerprinting (Wang *et al.*, 1999; Douglas *et al.*, 2016). However, after spilt, the oil is subject to numerous degradation and other transformation processes, commonly designated weathering (Wang *et al.*, 1999; Alimi *et al.*, 2003), that affect their composition. The rate and extent of the transformation depends on the oil type, and environmental (*e.g.*, sunlight and temperature) and biological conditions (*e.g.*, microbiological activity) (Wang *et al.*, 1999). The spilt oil can be subject to evaporation, dissolution, biodegradation, photo-oxidation, dispersion, water-oil emulsification and adsorption to suspended particulate matter and sediments (Wang and Fingas, 2003; Alimi *et al.*, 2003). Some of these processes make cleaning operations challenging while others promote physical and chemical changes in the oil. Chemical shifts are particularly challenging for oil source identification because different compounds can be affected differently depending on the weathering process (Wang *et al.*, 1999;

Malmborg, 2017). Therefore, oil fingerprints proven to be affected by weathering are assessed separately considering the expected composition variation with the type of weathering. Among various techniques, the most widely used to characterise the oils and identify the spill sources are gas chromatography (GC) with flame ionization detection (FID) or coupled to mass spectrometry (MS) (Wang and Fingas, 1997). The data from these instruments is subject to either multivariate or arrays of univariate statistical assessments.

Multivariate statistical tools have been used to identify the type, geographical origin or source of oil from a database of these products' compositional information. For these studies, chemometric tools, such as principal component analysis (PCA), discriminant analysis, parallel factor analysis (PARAFAC) and Kohonen self-organizing maps have been used to process signals from GC-FID, GC-MS and other analytical techniques (Stout *et al.*, 2001; Christensen *et al.*, 2004, Christensen *et al.*, 2005; Fonseca *et al.*, 2006; Borges *et al.*, 2010; Nielsen *et al.*, 2012; Corilo *et al.*, 2013). These methods can provide relevant information about the origin of a spill but do not replace the direct comparisons of the spilt oil with potential contamination sources (Daling *et al.*, 2002).

The direct assessment of the compositional equivalence of oil from the spill and of a suspected source involves performing multiple comparisons of both samples' compositional features using univariate statistical tools.

The ratio of the abundance of oil components, determined by GC-FID or GC-MS in oil or oil contaminated water or sediment, can be used to assess the equivalence of oil fingerprints on two samples. Nordtest (Daling *et al.*, 2002; Faksness *et al.*, 2002) and CEN (CEN, 2012) published methods that compare these ratios, designated Diagnostic Ratios, *DR*, using Student's *t* statistics (*S-t*) or a maximum relative difference of *DR*, respectively, assuming the normal distribution of these ratios. Triplicate *DR* determinations of a sample can be used to define the limits for the *DR* of a second sample to be considered equivalent to the first mean *DR* (Faksness *et al.*, 2002). The agreement of various characteristic *DR* observed in the contaminated environment and in suspected sources of the contamination can be used to support oil spill origin identification. The statistical comparison of *DR* requires that the ratio is not significantly affected by weathering or other chemical transformations, although both components can be depleted or concentrated in a correlated way (Faksness *et al.*, 2002; CEN, 2012). For this reason, weathering assessment is performed prior to the *DR* comparison to select the *DR* set that can be compared exclusively from the expected or modelled *DR* precision. The oil components known to be affected by weathering and that show experimental evidence of being affected by these

processes are studied separately. The CEN/TR 15522–2 proposes a methodology to identify and use compounds weathering in spill origin identification (CEN, 2012).

It is known that the ratio between independent or correlated random variables, such as oil component abundances, can deviate significantly from normality (Mielke and Flueck, 1976; Bettencourt da Silva, 2016; Dhanoa *et al.*, 2018). The deviation is more relevant when the denominator's dispersion is larger than the one of the numerators. The *DR*'s exact distribution is a complex function of ratio formula (*e.g.*, A/B or $A/(A + B)$), and input variables value, dispersion and correlation. Therefore, the use of parametric statistics to assess the agreement between a pair of *DR* can be associated with a probability of false decisions higher than the predicted from test confidence level. Even when the difference between the defined and actual confidence level of each *DR* seems negligible, the combined effects of inconsistencies in the comparison of many *DR* can make the total risk of false comparisons high. The quantification of this risk requires processing the correlation between all compositional information.

This work describes the definition of confidence limits of *DR* and the determination of the risk of false concluding about compositional equivalence of oil present in two samples from the simulation of multiple correlated abundances of chemical components using Monte Carlo Method (MCM). This identification method is compared with S-t method that assumes the normal distribution of *DR*.

The performance of MCM and S-t methods is compared by a combination of experimental information and numerical methods since it would be unpracticable to perform the high number of analyses required to quantify performance differences exclusively from this input.

2.2. Material and methods

2.2.1. Equipment

The crude oil preparation was carried out using the following equipment: Mettler PE1600 balance (Mettler, Greifensee, Switzerland) used to weigh the crude oil portion and, Heidolph Reax Top vortex stirrer (Heidolph, Schwabach, Germany) and a Thermo Heraeus Megafuge 1.0 centrifuge (Thermo Fisher Scientific Inc., Langenselbold, Germany) used to stir the crude oil with the solvent and separate the solid phase from the solvent extract.

The chromatographic analysis was performed using Agilent Technologies Gas Chromatograph (6890 N series) hyphenated with a Mass Spectrometer (5975 B series), equipped with an auto-

sampler Agilent Technologies 7683 B series and an EPC cool on-column injection port. The injection was performed by an ALS syringe of 10 μ L tapered, fixed needle, 23-26s/42/cone (Agilent Technologies, Santa Clara, USA), with a fast plunger and no pre- and post-injection dwell. The system was controlled with Mass Selective Detector Productivity ChemStation D.03.00 software (Agilent Technologies).

2.2.2. Chemicals

n-Hexane for trace analysis (Suprasolv®) obtained from Merck (Darmstadt, Germany) was used. Crude oils used belong to the petroleum products database of *Instituto Hidrográfico* and were the following: Miri Light (Malaysia), Bonny Light (Nigeria), Cabinda (Angola) and Ural (Russia).

2.2.3. Analytical data collection

A solution from a mixture of crude oil extracts (MixCrude) was prepared since some components with analytical interest may be at lower concentrations or even absent in different crude oils. 0.20 g of each crude oil was weighed into a glass centrifuge tube and dissolved in 5 mL of *n*-hexane. The solid phase was separated by centrifugation (3000 rpm for 15 min), and the supernatant subsequently transferred to a 25 mL volumetric flask. The remained solid phase inside the centrifuge tube was subjected to four more consecutive extractions. After completing the five extractions, the volumetric flask volume was adjusted with *n*-hexane and homogenized.

The MixCrude solution was prepared by mixing 0.5 mL of Miri Light, Bonny Light and Cabinda crude extract and 2 mL of Ural crude extract, further diluted to 15 mL using *n*-hexane. The mixture of crude oils extracts was analysed by GC-MS according to operational conditions presented in the **Annex A**. Eight injections of MixCrude solution were performed in a two-day interval.

2.2.4. Peak identification and quantification

n-Alkanes, isoprenoids (pristane and phytane), alkylated polycyclic aromatic hydrocarbons (alkyl-PAH), sesquiterpanes, adamantanes and, tetra and pentacyclic biomarkers (hopanes, steranes and triaromatic steranes) were identified by retention times, pattern recognition and

confirmation ions according to literature (Daling *et al.*, 2002; Faksness *et al.*, 2002; Stout *et al.*, 2005; Wang *et al.*, 2005; Wang *et al.*, 2006; Yang *et al.*, 2006; Yang *et al.*, 2009; Yang *et al.*, 2011; CEN, 2012). Ion abundances were determined from the areas of quantitation fragments peaks (**Table A.1** of the **Annex A**) where integrations were manually verified.

2.2.5. Diagnostic ratio determination

Table A.2 of the **Annex A** lists studied *DR* including the notation used in this work and in the literature for their identification. 69 *DR* were evaluated comprising various classes of compounds. 25 *DR* of alkyl-PAH described by Biscaya (1997) were evaluated, although only three of those are referred by Faksness *et al.* (2002) and in the CEN/TR 15522-2 standard (CEN, 2012). In contrast, the later two methods recommend determining all the 21 evaluated *DR* between hopanes, steranes and triaromatic steranes. The 10 *DR* among sesquiterpanes studied are described in the literature (Wang *et al.*, 2005; Yang *et al.*, 2009; Yang *et al.*, 2011) even though only some of these are considered in CEN/TR 15522-2 (CEN, 2012). Moreover, all the 12 adamantanes ratios determined are referred by Wang *et al.* (2006) and Yang *et al.* (2006) but not mentioned in the methodology described by Faksness *et al.* (2002) as in the CEN/TR 15522-2 (CEN, 2012).

Equation 2.1 presents the general formula used for the ratios where area *A* and the sum of both areas *A* and *B*, from the same GC-MS, are in the numerator and denominator, respectively.

$$DR = 100 \times \frac{A}{(A + B)} \quad (2.1)$$

This equation is recommended instead of *A/B* used in the CEN standard (CEN, 2012) since it avoids division by zero or substantial values from a comparatively low denominator (Daling *et al.*, 2002; Faksness *et al.*, 2002).

The weathering processes and their effects on chemical compounds, well discussed in literature (Wang *et al.*, 1999; Faksness *et al.*, 2002; CEN, 2012; Malmberg, 2017), produce a drift in the *DR* values making their conventional statistical control inadequate for oil pattern comparison. Some studied *DR* are known to be significantly affected by weathering. However, this study was performed under strictly controlled conditions to avoid the impact of chemical changes (*e.g.*, weathering) in the *DR*, allowing using all determined *DR* in the comparison of MCM and

S-t approaches. When weathering affects relevant oil components, a proper diagnosis of the signals affected by these processes must be performed.

2.2.6. A criterion for diagnostic ratios agreement

Since the DR is affected by random effects from sample preparation and GC-MS response variability, the comparison of DR observed in two samples must take the impact of those effects on DR comparison. The comparison criteria can be set using the replicate DR determination of one sample to define the minimum and maximum permissible values for the DR estimated for the second sample. The limits are defined for a confidence level, P , (e.g., 98%) whose complementary probability $(1 - P)$, (e.g., 2%), represents the risk of falsely assuming DR from samples with equivalent composition are different.

In this work, two methods of setting DR limits are compared: (1) S-t supported on the normality assumption of DR ; (2) MCM simulation of DR confidence limits by taking the estimated value, dispersion, degrees of freedom and correlation of input areas.

The limits set for a specific DR when comparing two samples, cannot be used for DR estimated in different batches or extrapolated to the comparison of the same DR from other samples pair, because DR is expected to vary with oil patterns and GC-MS performance.

2.2.6.1. Student's t based confidence limits

Equation 2.2 presents the expression used to define confidence limits for a specific DR from the replicate determination of DR from various injections of the same or different solvent extract of sample 1.

$$\overline{DR}_1 \pm t_1 \cdot s_{DR_1} \quad (2.2)$$

where $\overline{DR}_1$ and s_{DR_1} are the mean and standard deviation of estimated n DR values and t_1 the t -value of the Student's t distribution for $(n - 1)$ degrees of freedom and the selected confidence level, P , of the test (in this work $P = 95\%$ and 98%). These confidence limits are adequate to assess the agreement of $\overline{DR}_1$ with a single DR , DR_2 , estimated from the single injection of the extract of the sample 2. The comparison criteria can also be presented as checking the validity

of the following condition: $|\overline{DR}_1 - \overline{DR}_2| \leq t_1 \cdot s_{DR_1}$. If this condition is valid, it can be assumed the statistical equivalence of $\overline{DR}_1$ and $\overline{DR}_2$ for P confidence level.

In case sample 2 extract is injected m replicate times in the same precision conditions of the replicate analysis of sample 1, the comparison condition should be changed for:

$$|\overline{DR}_1 - \overline{DR}_2| \leq t \cdot \sqrt{\frac{s_{DR_1}^2}{n} + \frac{s_{DR_2}^2}{m}} \quad (2.3)$$

where $\overline{DR}_2$ and s_{DR_2} are the mean and standard deviation of DR estimated from the replicate analysis of sample 2, and t the t -value of the Student's t distribution for the selected confidence level and the number of degrees of freedom calculated from the nearest integer of the value, ξ , determined from **Equation 2.4** (Miller *et al.*, 2018).

$$\xi = \frac{\left(\frac{s_{DR_1}^2}{n} + \frac{s_{DR_2}^2}{m}\right)^2}{\left(\frac{s_{DR_1}^4}{n^2(n-1)} + \frac{s_{DR_2}^4}{m^2(m-1)}\right)} \quad (2.4)$$

If $n = m = N$ and $s_{DR_1} \cong s_{DR_2} = s_{DR}$, **Equation 2.3** is changed for:

$$|\overline{DR}_1 - \overline{DR}_2| \leq t_A \cdot \sqrt{2} \cdot s_{DR} / \sqrt{N} \quad (2.5)$$

where t_A is the t -value of the Student's t distribution for $(N - 1)$ degrees of freedom.

2.2.6.2. Monte Carlo simulation of confidence limits

The MCM is a very popular simulation method for solving complex deterministic or stochastic problems. For stochastic problems, typically, the distribution of an output variable, function of various inputs, is estimated by randomly simulating many values of the input variables used to determine the same number of the output values, for example, by a closed mathematical expression. From the simulated output variable values, it can be estimated the mode, dispersion and other characteristics of the output variable distribution. The MCM requirements are knowing the distribution and any relevant correlation between the inputs, and how inputs are used to determine the output, as well as having the computational resources for the simulation.

The MCM output can deviate from any well-known distribution type depending on inputs distribution and their impact on the output.

In this work, it is estimated the mean value, dispersion, degrees of freedom and correlation of both areas (A and B) combined in each DR from replicate extract injections. Afterwards, 10^4 to 2×10^5 pairs of these normally distributed and correlated areas are simulated producing simulated DR that can deviate from normality. The MS-Excel file used for this simulation is made available for download from the weblink presented in the **Annex A**.

The multivariate scaled and shifted t -distribution of the signals of all relevant oil components was simulated using a Student's t copula defined from the Cholesky decomposition of the estimated covariance matrix and degrees of freedom of the inputs. The copula is subsequently scaled and shifted using the standard deviation and mean values of the input variables (Possolo, 2010; JCGM, 2011).

The simulation of the distribution of a specific DR determined from n replicate values of A and B starts by simulating pairs of one-tailed t values of the Student's t distribution for the pertaining degrees of freedom producing matrix $\mathbf{T}$ ($10,000 \times 2$). The covariance matrix of peak areas A and B , $\mathbf{K}_{AB}$ (2×2), is obtained to attribute the dispersion and correlation to the simulated data. The $\mathbf{K}_{AB}$ is subsequently decomposed in matrix $\mathbf{L}$ (2×2) by Cholesky factorization using a VBA code available in the literature (Zaiontz, 2018; Bettencourt da Silva *et al.*, 2019; Morgado *et al.*, 2020). The matrices $\mathbf{T}$ and $\mathbf{L}$ are multiplied ($\mathbf{T} \cdot \mathbf{L}$), and the resulting matrix $\mathbf{M}$ ($10,000 \times 2$) summed with the matrix $\mathbf{O}$ ($10,000 \times 2$) where the first and second columns are repeated values of the mean of A and B , $\bar{A}$ and $\bar{B}$, respectively. The final matrix $\mathbf{F}$ ($\mathbf{F} = \mathbf{TL} + \mathbf{O}$) represents 10,000 pairs of simulated correlated A and B peak areas. Each pair of A and B simulate each DR by **Equation 2.1**. The simulated DR values can be used to build a histogram and to obtain several statistical parameters, such as mean, standard deviation and P confidence limits calculated as χ^{th} percentiles.

To evaluate the determination of composition agreement of two sample extracts by comparing 69 DR , it was simultaneously simulated 57 correlated areas. The same data processing procedure previously described from simulating a specific DR was applied where larger $\mathbf{T}$ ($10,000 \times 57$), $\mathbf{K}_{AB}$ (57×57), $\mathbf{L}$ (57×57) and $\mathbf{O}$ ($10,000 \times 2$) matrices were considered in the same operations, producing an $\mathbf{F}$ ($10,000 \times 57$) matrix with the simulation of the 57 peaks. Due to the covariance matrix's mathematic inconsistencies, the experimentally estimated correlation coefficients of different areas were reduced $10^{-140}\%$. This minor reduction produced a covariance

matrix that allows its Cholesky decomposition. The 57 simulated areas were combined in 69 simulated *DR*.

The developed spreadsheet was validated by comparing the MCM simulated percentiles of 69 *DR* (2.5th and 97.5th percentiles) with values estimated from the MCM simulation performed by the NIST Uncertainty Machine Version 1.5 based on 10⁶ realisations (Lafarge and Possolo, 2015; NIST, 2021). The NIST's software allows simulating the ratio of correlated variables with defined mean value, standard deviation, degrees of freedom and correlation. The **Annex A** presents the results from this comparison. The estimated percentiles from triplicate signals ($n = 3$) have relative differences with 2.5th and 97.5th percentiles (percentiles of the differences of percentiles) of -2.1% and 1.3%. The observed negligible differences are explained by the variability of MCM simulations and low number of significant figures reported by the NIST tool.

The developed spreadsheet allows the simultaneous MCM simulation of the percentiles of various *DR*, their comparison with S-t limits and the determination of total risks of falsely rejecting oil patterns equivalence.

2.2.6.3. Comparison of confidence limits

The confidence limits defined by assuming the normality of *DR* (**Equation 2.2**) were compared with the limits simulated by the MCM for 95% and 98% confidence level. Due to the possible deviation to normality of *DR* distribution, the MCM simulation describes the *DR* performance in a more accurate way. Therefore, it was quantified the fraction, φ , of the total area below the simulated probability density function by the MCM beyond the limits defined by the S-t model for a P confidence level. The φ represents the probability of S-t limits falsely concluding that compared *DR* are not statistically equivalent. Any deviation between φ and $(1 - P)$ is considered an inaccuracy of the S-t modelling.

Since the decision about the compositional equivalence of compared samples depends on the assessment of various, M , *DR* (in this work $M = 69$), it was also quantified the probability, θ , of two equivalent samples not producing M equivalent *DR* pairs. If the limits for *DR* confidence intervals were accurate for a P confidence level and all *DR* were independent or perfectly correlated (*i.e.*, all correlation between *DR* equal to 1), the θ would be $(1 - P^M)$ and $(1 - P)$, respectively. For instance, for 69 *DR* and 98% confidence level of *DR* comparisons, θ would

be $(1 - 0.98^{69} = 75.2\%)$ and 2%, respectively. Since DR correlation is below 1, the θ is greater than $(1 - P)$. Again, the MCM is used for the accurate estimation of θ and to assess how S-t limits impacts on θ .

The MS-Excel file available for download in the **Annex A** allows the determination of the M φ and of the θ from DR limits defined by the MCM and S-t methods. The φ and θ vary with the studied oil, selected DR , sample preparation and GC-MS analysis performance.

2.2.6.4. Distribution skewness

The skewness of a probability distribution can be positive or right-skewed if the longer tail of the distribution is located to the right of distribution mode. In that case, the mode is smaller than the mean and median, $P50$ (50th percentile). The opposite is found for the negative or left-skewed distribution, where the mean and the median are lower than the mode. In this work, the distribution asymmetry was quantified by the Pearson's second coefficient of skewness (Jambu, 1991; Fávero and Belfiore, 2017), A_{Pi} , described by **Equation 2.6**:

$$A_{Pi} = \frac{3 \cdot (\overline{DR}_i - P50_i)}{S_{DRi}} \quad (2.6)$$

where i is the i^{th} studied DR . A positive or negative A_{Pi} identify a positive or negative skewness, respectively. An absolute value of A_P , $|A_P|$, lower than 0.15, within 0.15 and 1.0 and greater than 1.0 indicates a weak, moderate and strong asymmetry (Fávero and Belfiore, 2017).

2.3. Results and discussion

2.3.1. Comparison of MCM and S-t methods

The comparison of MCM and S-t models of DR dispersion was based on results of the replicate injection of the MixCrude solution whose preparation is described in the **Subchapter 2.2**. The extracts were injected into the GC-MS in two consecutive days. **Tables A.1** and **A.2** of the **Annex A** lists the studied sample components and DR .

The first three, five or all eight injections were used to define DR dispersion models from a different number of injections ($n = 3, 5$ and 8). **Table 2.1** and **Table A.3** of the **Annex A** present the confidence limits defined for 95% and 98% confidence levels, P , by the S-t and

MCM for some and all 69 studied *DR*, respectively. The 95% and 98% confidence limits are defined by the 2.5th and 97.5th percentiles ($P_{2.5} - P_{97.5}$) and 1st and 99th percentiles ($P_1 - P_{99}$), respectively.

Table 2.1. Confidence interval limits of *DR* presented in Figure 2.1, defined by the MCM and S-t methods from different replicate injections of extracts ($n = 3, 5$ and 8) and 95% and 98% confidence levels. Quantification of *DR* skewness, A_p , interval range overlapping, η , and the probability of observing *DR* values beyond S-t limits, φ .

<i>DR</i> Code	n	A_p	MCM confidence limits		S-t confidence limits		φ (%)		η (%)	
			95%	98%	95%	98%	95%	98%	95%	98%
<i>DR10</i>	3	0.012	0.469 - 0.569	0.446 - 0.622	0.463 - 0.554	0.435 - 0.582	6.40	2.98	110	120
	5	0.114	0.483 - 0.565	0.475 - 0.584	0.477 - 0.556	0.463 - 0.569	6.35	2.93	104	103
	8	0.239	0.478 - 0.556	0.471 - 0.574	0.474 - 0.546	0.465 - 0.556	7.02	3.58	108	113
<i>DR28</i>	3	-0.017	0.134 - 0.193	0.110 - 0.211	0.136 - 0.193	0.118 - 0.210	5.52	2.24	104	110
	5	-0.007	0.149 - 0.182	0.143 - 0.188	0.150 - 0.182	0.145 - 0.188	5.48	2.29	103	105
	8	0.014	0.152 - 0.181	0.149 - 0.187	0.151 - 0.178	0.147 - 0.181	4.26	1.67	107	112
<i>DR30</i>	3	0.005	0.251 - 0.311	0.208 - 0.321	0.265 - 0.317	0.249 - 0.333	4.49	2.30	115	135
	5	-0.003	0.239 - 0.313	0.218 - 0.321	0.248 - 0.316	0.236 - 0.328	4.63	1.98	109	112
	8	-0.022	0.256 - 0.305	0.249 - 0.312	0.258 - 0.304	0.251 - 0.310	5.41	2.49	107	107
<i>DR40</i>	3	-0.013	0.137 - 0.191	0.112 - 0.211	0.146 - 0.190	0.133 - 0.203	6.73	3.28	123	141
	5	-0.173	0.153 - 0.179	0.147 - 0.182	0.157 - 0.180	0.153 - 0.184	7.01	3.51	113	113
	8	-0.097	0.154 - 0.176	0.150 - 0.178	0.157 - 0.177	0.154 - 0.180	6.38	3.28	110	108
<i>DR57</i>	3	-0.011	0.581 - 0.667	0.551 - 0.704	0.584 - 0.663	0.560 - 0.687	5.29	2.45	109	120
	5	-0.009	0.604 - 0.644	0.595 - 0.651	0.606 - 0.642	0.600 - 0.648	5.72	2.67	111	117
	8	0.030	0.597 - 0.647	0.591 - 0.659	0.596 - 0.640	0.590 - 0.646	7.23	3.74	114	121

These tables also include the quantification of *DR* distribution skewness, A_p , from MCM modelling, the overlapping of confidence intervals defined by MCM and S-t, η , and the probability of S-t limits falsely concluding that compared *DR* are not statistically equivalent, φ . The η is calculated by the ratio between the range of MCM and S-t intervals. A $\eta > 100\%$ indicate that MCM intervals are wider than the S-t ones. However, the φ is more informative about model differences since takes the probability density into account.

Figure 2.1 presents the simulated and modelled *DR* distribution by the MCM and S-t method of some *DR*. Distributions for three *DR* (*DR10*, *DR40* and *DR57*) estimated from three, five or eight replicate injections are presented. The selected ratios have negative, positive or negligible skewness quantified by A_p (Table 2.1).

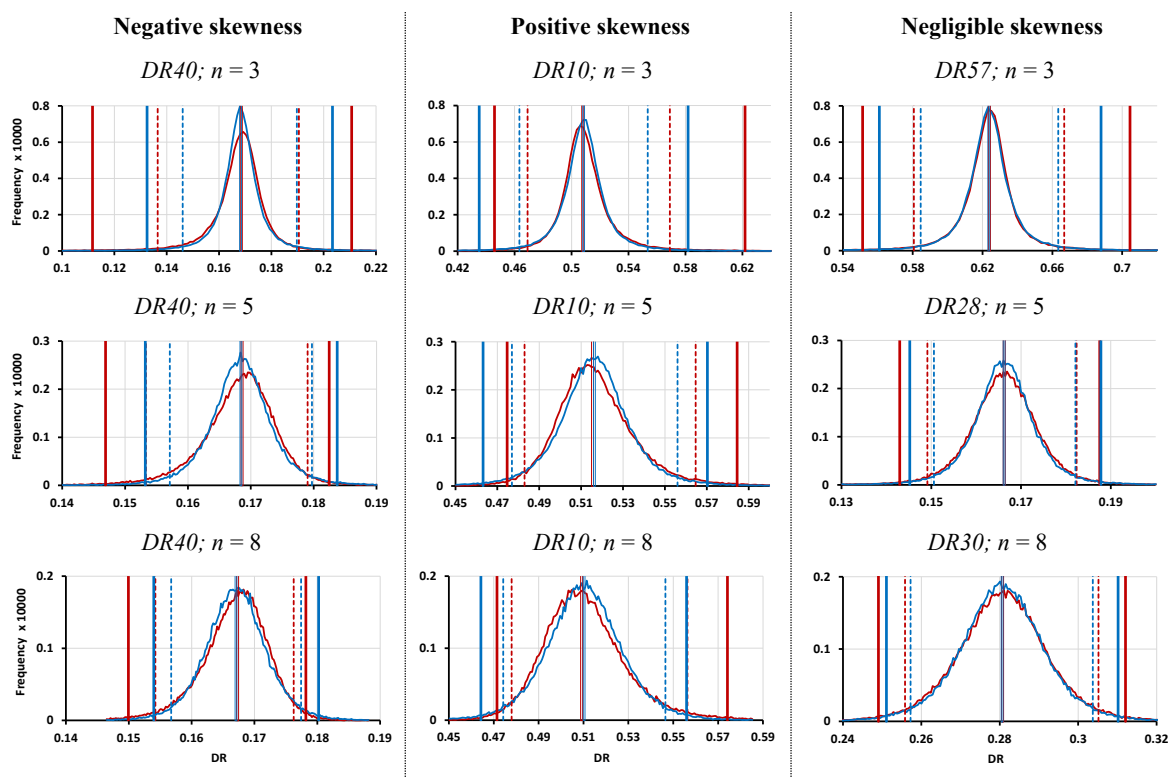


Figure 2.1. Examples of simulated and modelled probability distributions of some DR by the MCM ($\wedge$) and S-t methods ($\wedge$), determined from $n = 3, 5$ or 8 injections: — $P50$ – MCM; — $P50$ – S-t; --- $P2.5$ and $P97.5$ – MCM; --- $P2.5$ and $P97.5$ – S-t; --- $P1$ and $P99$ – MCM; --- $P1$ and $P99$ – S-t.

Figure 2.1 and **Table 2.1** show that all types of skewness are observed in DR and the A_p varies with the number of replicate injections. The percentiles presented in **Figure 2.1**, **Table 2.1** and **Table A.3** of the **Annex A** allow visualizing the asymmetry. The confidence intervals are narrower and DR distribution skewness more evident as the number of considered replicate injections increases. The low number of degrees of freedom of the input data masks the asymmetry. The A_p varies between -0.221 and 0.239 being prevalent weak asymmetries (*i.e.*, $|A_p| < 0.15$). Therefore, **Figure 2.1**, **Table 2.1** and **Table A.3** of the **Annex A** prove that DR can have different types of distribution skewness depending on the mean value, dispersion and correlation of A and B .

Figure 2.2 and **Figures A.1** and **A.2** of the **Annex A** present radar charts of the 1st, 2.5th, 50th, 97.5th and 99th percentiles ($P1, P2.5, P50, P97.5$ and $P99$) normalised for the $P50$ estimated by the MCM to allow the visualisation of the overlapping of all confidence intervals defined by the MCM and S-t.

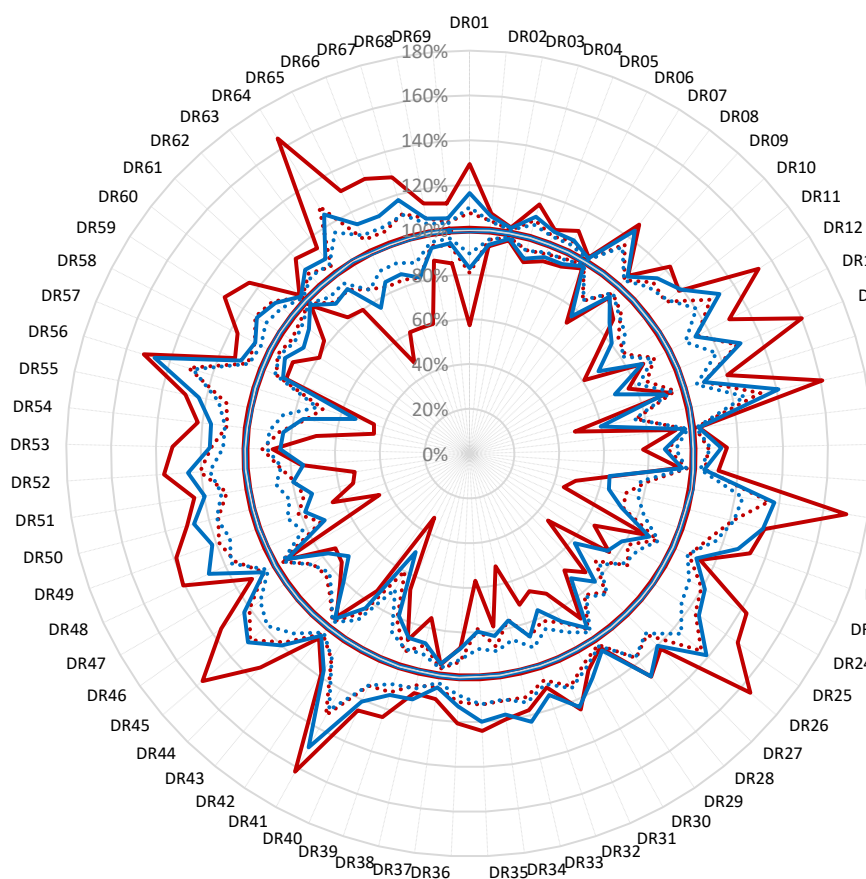


Figure 2.2. Percentiles required to define 95% and 98% confidence limits, by the MCM and S-t methods of all 69 DR studied, normalised to the 50th percentile simulated by MCM, for $n = 3$ injections: = P_{50} – MCM; = P_{50} – S-t; ... $P_{2.5}$ and $P_{97.5}$ – MCM; ... $P_{2.5}$ and $P_{97.5}$ – S-t; — P_1 and P_{99} – MCM; — P_1 and P_{99} – S-t.

These figures confirm the findings reported previously: confidence intervals are narrower when built from more replicate injections and DR distribution can have different types of asymmetry. Limits estimated by the MCM are frequently wider as observed by ϕ values greater than $(1 - P)$ (Table 2.1 and Table A.3 of the Annex A). For the 207 estimated DR intervals for 98% confidence level from 69 DR and different number of injections ($n = 3, 5$ and 8), in only 6 cases (*i.e.*, 2.9%) S-t limits are wider.

For the studied DR, confidence limits probability (*i.e.*, $P = 95\%$ and 98%) and n equal to three, five and eight, $(\phi - (1 - P))$ ranges from $(-0.8\%$ to $3.3\%)$, $(-1.7\%$ to $4.2\%)$ and $(-1.5\%$ to $4.3\%)$, respectively. A positive $(\phi - (1 - P))$ indicates that the MCM intervals are wider than the S-t intervals. Occasionally, negative $(\phi - (1 - P))$ are observed indicating that S-t overestimates DR dispersion.

Table 2.2 presents the simulated probability, θ , of at least one of the 69 compared *DR* in two samples with equivalent composition being considered different (Simulation estimation method). The θ was estimated for both methods for defining *DR* limits were the more accurate MCM is considered a reference for S-t modelling.

Table 2.2. Probability of at least one of the assessed 69 *DR*, θ , or mean probability of each *DR* estimated from the single injection of one sample, $\bar{\varphi}$, not meeting limits set for *DR* from replicate injections of another sample with equivalent composition. θ and $\bar{\varphi}$ were estimated by simulation and experimentally, respectively, for MCM and S-t methods. *DR* limits defined from three, five or eight replicate injections, n , were studied.

Estimation method	n	Confidence level			
		95%		98%	
		θ for MCM (%)	θ for S-t (%)	θ for MCM (%)	θ for S-t (%)
Simulation (10^5 simulations of 69 <i>DR</i>)	3	11.0	14.8	5.2	8.3
	5	25.7	28.3	11.2	13.8
	8	43.5	49.2	21.9	27.3
	n	$\bar{\varphi}$ for MCM (%)	$\bar{\varphi}$ for S-t (%)	$\bar{\varphi}$ for MCM (%)	$\bar{\varphi}$ for S-t (%)
Experimental (5×69 controls)	3	5.2	5.5	2.0	2.3

From **Table 2.2** it is concluded that, for both methods, θ is greater than the $(1 - P)$ defined for each *DR* as expected. The $(\theta - (1 - P))$ is greater when the statistical robustness of the input data, expressed by their degrees of freedom, increases. Again, inputs with lower degrees of freedom mask *DR* distribution characteristics. This somehow justifies the preference of some reference document of estimating *DR* from a low number of replicas. The θ from MCM limits is, on average, 3.9% lower than the θ for S-t limits. This mean that the S-t limits will fail about one more time in 26 runs than MCM limits. This difference is equivalent to the $(\theta - (1 - P))$ for MCM limits set from triplicates and P equal to 98%.

However, perhaps the most relevant information extracted from θ is how likely it should be observed deviations from at least one *DR* even when samples composition is equivalent.

The rather high θ can be easily decreased by performing a second injection of the second sample. The agreement between samples composition is assumed if at least one estimated *DR* value of each 69 ratios is within limits defined from the replicate injections of the first sample. If this procedure is followed, the θ can become lower than $(1 - P)$ defined for each *DR*. For MCM limits set for 98% confidence level from $n = 3, 5$ and 8, the θ becomes 0.3%, 0.5% and 1.2%, respectively. If S-t limits for 98% confidence level are considered for $n = 3, 5$ and 8,

the θ is 0.7%, 1.1% and 2.6%, respectively. Therefore, the describe strategy of comparing DR values has a total success rate above 98% and 97% if MCM and S-t limits are used.

2.3.2. Experimental assessment of MCM and S-t methods

In order to complement the assessment of MCM and S-t limits with experimental evidence, the data from the eight MixCrude solution injections was processed differently. Three injections, obtained spaced in the time of the analysis period, were used to set DR limits by the MCM and S-t methods, and it was determined if the other five injections produce DR values within the defined limits.

Table A.4 of the **Annex A** presents the MCM and S-t limits, and **Table A.5** of the **Annex A** details the agreement between the DR determined in the five injections with the limits. **Table 2.2** reports the mean probability, $\bar{\varphi}$, of agreement between the defined limits and an independent injection of an extract of the same sample (experimental estimation method). If the agreement between the DR of the five injections using 98% confidence limits is assessed (**Table A.5** of the **Annex A**), it can be concluded that for $DR07$, $DR23$, $DR34$ and $DR43$, the MCM limits fail twice, zero, twice and three times, while the S-t limits fail twice, once, twice and three, respectively. Therefore, for 95% and 98% confidence levels, MCM limits present $\bar{\varphi}$ lower than $(1 - P)$, where for S-t limits, $\bar{\varphi}$ is greater than $(1 - P)$. Therefore, the success rate of MCM $(1 - \bar{\varphi})$ is greater than for S-t. However, the low number of experimental tests and the fact that the success rate of the five DR are correlated since based on the same limits, suggest that more experimental test are required to check the observed differences experimentally.

The quantified identification performance is specific for the studied oil extract mixture, DR and GC-MS performance. Tests on other scenarios will allow understanding how performance gain varies with type of spill, monitored DR and analytical conditions. The authors will test the developed tool with additional and more diverse experimental data to quantify the performance improvement of wider MCM limits.

2.4. Conclusions

The developed methodology for the Monte Carlo Method (MCM) simulation of the distributions of diagnostic ratios, DR , of unweathered components defines, in most of the cases, wider limits for the comparison of a mean and single DR from different samples than assuming

DR normality (S-t). The more accurate description of *DR* distribution reduces the risk of falsely rejecting oil pattern equivalence. The small performance gains observed in single *DR* comparisons become relevant in identifications based on the comparison of various *DR*. The developed *DR* comparison methodology was implemented in a validated user-friendly MS-Excel spreadsheet, made available for download from the weblink presented in the **Annex A**.

The *DR* comparison tool was successfully applied to assess the compositional equivalence of two oil samples from the comparison of 69 *DR* defined from 57 correlated peaks known not to be affected by weathering. The observed *DR* distribution can be right or left skewed, or symmetrical depending on the *DR* and number of replicate analyses.

The reliability of the S-t method was quantified by comparing it with the more accurate MCM method. The difference between the confidence level, P , of S-t limits and the actual probability of limits enclosing a *DR* from a sample with equivalent composition, varied between -0.8% and 4.3%.

Considering the probability of 69 *DR* estimated from two samples of the same oil being statistically equivalent ($1 - \theta$), on average, the S-t limits fail 3.9% times more than the MCM limits. However, even for the MCM limits, the $(1 - \theta)$ is lower than the P since the *DR* correlation is not perfect. The $(1 - \theta)$ can be increased by injecting the second sample twice and assuming the compositional equivalence if each *DR* agrees in at least one injection. For MCM limits defined from three, five and eight replicate injections, the $(1 - \theta)$ becomes greater than P .

The results obtained by simulation were checked experimentally by assessing the disagreement of five determinations of each *DR* from a second sample with limits set from triplicate injections of the first sample with similar composition. The success rate of the *DR* limits defined by the MCM is slightly better than the ones described by the S-t. However, the number and type of obtained experimental data do not allow determining the success rate of the *DR* with reliability equivalent to the one from computational simulation.

The observed identification performance is specific for the studied mixture of crude extracts, selected *DR*, sample preparation and GC-MS performance. The developed methodology will be applied to additional oil spill scenarios to quantify the performance gains in those situations.

This work is the first statistically sound assessment of the probability of correctly concluding about the compositional equivalence of two oil samples from the comparison of multiple *DR* of

unweathered components. The detailed understating of the success rate of these tests allowed defining a methodology for increasing analysis reliability.

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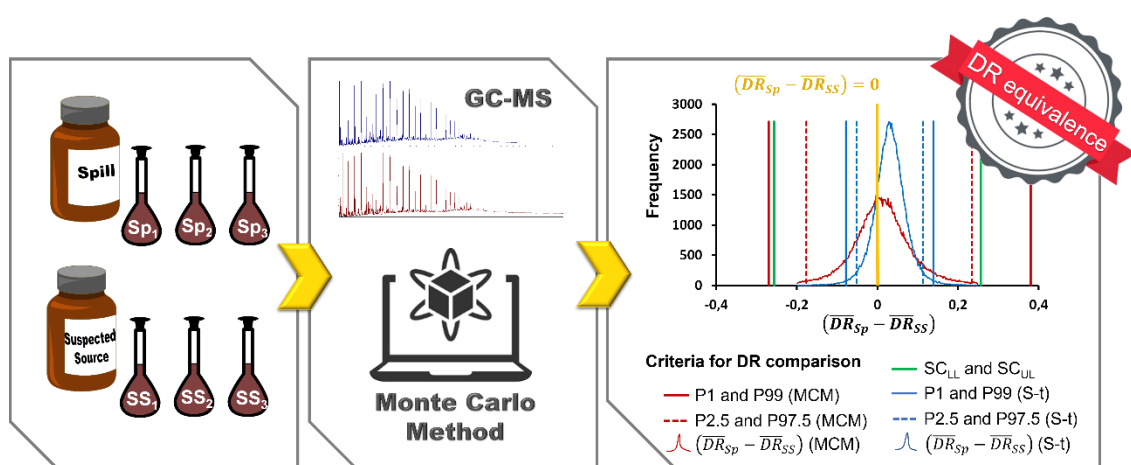
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3. Optimisation of the uncertainty of oil spill identification from replicate comparative analyses: comparison of standardised and novel identification methods



Abstract

Oil spill identifications involve the comparison of oil fingerprints between the oil spill and suspected oil sources, defined by ratios between the abundances of oil-discriminating compounds, Diagnostic Ratios (*DR*). The normalised Nordtest and EN 15522-2 methodologies use Student's *t* statistic (S-t) or a maximum relative difference (SC) to compare mean *DR* from replicate sample analysis. While the S-t method assumes the normality of *DR* distribution, the SC method is based on controlled *DR* dispersion. However, when false, the assumptions and approximations adopted can lead to low true identification rates. This work presents a novel computational tool for the statistically sound oil spill identification that allows following requirements defined by EN 15522-2, the comparison of replicate *DR* determinations, and the use of different *DR* sets and formats. The tool uses the Monte Carlo Method (MCM) to describe the probability distribution of the difference of mean *DR*, allowing estimating the probability of the true acceptance of fingerprints equivalence. The studied methods were applied to the comparison of signals from the same oil and to a real scenario reproduced in an International Round Robin Test. The methods were compared considering the probabilities of true acceptance of oil patterns equivalence based on a single, γ , or various, δ , *DR*. The MCM method performs identifications with γ equivalent to the defined confidence level for the comparison, *P*. Since the various *DR* studied are not perfectly correlated, the δ is below *P*. The number of replicate analyses performed, and the *DR* considered in the comparison affect identification performance. The S-t produces comparison criteria with a γ lower than *P*. The SC criteria for duplicate analysis is associated with a δ lower than the obtained by the MCM. A user-friendly MS-Excel spreadsheet is available to perform oil pattern comparisons using various methods and conditions.

Keywords: Oil fingerprinting; Oil spills; Monte Carlo Method; True result rate; Validation

3.1. Introduction

The spills of oil and refined products are a widespread problem that leads to high costs for society in economic and environmental terms. The identification of the offender and his punishment by the law is essential but requires objective and reliable evidence. The chemical analyses performed on samples collected in the contaminated area and in suspected spill sources have proved to be a valuable support to the forensic investigation.

Crude oils from different provenances and their derivatives have distinct compositions conferred by the different petroleum formation conditions and refining processes, known as fingerprints (Wang *et al.*, 1999; Douglas *et al.*, 2016). Oil spill identification is based on the comparison of oil fingerprints of the oil spill and suspected source samples. These analyses require a comprehensive characterisation of the samples achieved by gas chromatography coupled to a flame ionisation detector (GC-FID) and/or by gas chromatography hyphenated with mass spectrometry (GC-MS) (Wang *et al.*, 1999; Wang and Fingas, 2003). Conventional statistical methods have been used to infer the similarity between fingerprints of sample pairs. In the last decades, two methodologies have been developed and optimised: Nordtest (Daling *et al.*, 2002; Faksness *et al.*, 2002) and CEN/TR 15522-2 (CEN, 2006; CEN, 2012). The CEN/TR 15522-2 approach has been recently improved and should be published in the near future as the reference method EN 15522-2 (CEN, 2020). In these methodologies, ratios between chromatographic peak sizes of oil-discriminating compounds, *i.e.*, diagnostic ratios (*DR*), are used to assess fingerprints affected by weathering phenomena (*e.g.*, evaporation, dissolution, biodegradation, photo-oxidation) and to compare sample's oil patterns. Although all mentioned methodologies are closely related, they differ in the chemical components used in oil pattern identification, in the statistical method for the *DR* comparison and in the number of replicated analyses performed for each sample. Additionally, the Nordtest and CEN/TR 15522-2 methodologies suggest different algorithms for *DR*: $A/(A+B)$ and A/B , respectively, with A and B being the chromatographic signals of the components that define each ratio. To compare *DR* observed in two samples analysed in triplicate, the Nordtest method uses the Student's t test (S-t), assuming the normality of the *DR* probability distributions. However, the probability distribution of the ratio of correlated variables, such as the *DR*, can show deviations from normality. Therefore, if *DR* normality is assumed, the criteria for ratio equivalence assessment can become inadequate (Rocha *et al.*, 2022). The CEN/TR 15522-2 methodology applies a maximum relative difference between estimated *DR* (SC) (SC stands for single criterion) to compare *DR* observed in two samples analysed in duplicate. The SC is based on

the empirical knowledge experts have acquired over the years that, after excluding cases where signals or ratios have a large dispersion, the relative standard deviation, RSD, of *DR* is not larger than 5%. However, both *DR* comparison methods, S-t and SC, rely on assumptions and approximations that are not always valid, which can lead to wrong assessments of the *DR* equivalence. *DR* comparison criteria fragilities are particularly problematic given that oil spill identification is based on the comparison of many *DR* pairs, reducing the probability of true equivalence determinations (*i.e.*, total risk). The ratios compared cannot be determined using compounds affected by weathering because these processes affect the ratio value, requiring an appropriate identification of these compounds.

The development of new approaches for results interpretation, based on adequate statistical assumptions and methods, is essential to guarantee the quality of the identifications. Rocha *et al.* (2022) recently developed a computational tool capable of comparing *DR* by accurately modelling its probability distribution, allowing estimating the total risk of true acceptance and false rejection of compositional equivalence between samples. The approach developed involved the numerical simulation of the *DR* by the Monte Carlo Method (MCM), commonly used to solve complex deterministic or stochastic problems. The MCM simulation of the *DR* is based on the estimated dispersion and correlation of GC-MS chromatographic signals of the chemical components that define each ratio to be compared. In the study, the authors compared the alternative MCM approach for *DR* comparison with the conventional S-t approach by comparing *DR* comparison criteria and estimating the total risk of false rejection of the compositional equivalence of two samples. The confidence intervals were estimated for 69 *DR* considering 3, 5 and 8 analyses of the first sample. The MCM approach developed identified fragilities of the conventional S-t approach due to observed deviations to the normality of the *DR*. However, the developed tool only allows replicate analysis of one sample, making it not fit to assess cases where both samples are analysed several times to improve comparison quality.

The present work aims to present a significant evolution of the existing computational tool, allowing the *DR* simulation using two alternative calculation formats proposed by the Nordtest method and EN 15522-2 standard, and the comparison of *DR* mean values estimated from the replicate analysis of both samples. This development required modelling the mean of *DR* differences instead of the modelling of *DR* values. The impact of the different *DR* comparison conditions (*e.g.*, replicates number and *DR* format) on *DR* comparison by the alternative MCM, S-t suggested by the Nordtest methodology, and SC proposed by the EN 15522-2 was evaluated.

The quality of the identifications based on the *DR* simulations by the MCM was compared with those obtained by the S-t and SC methods, considering a set of *DR* suitable for crude oil characterisation proposed by EN 15522-2.

The identification methodologies were applied to the confirmation of the equivalence of oil patterns observed from replicate and independent analysis of the same oil mixture and to a real oil spill identification scenario reproduced in an International Round Robin Test (RR) promoted by the Oil Spill Identification Network of Experts within the Bonn-Agreement (Bonn-OSINet) in 2018.

3.2. Material and methods

3.2.1. Equipment

For crude oil extractions were used a Mettler PE1600 balance (Mettler, Greifensee, Switzerland) to weigh the crude oil portion, a Heidolph Reax Top vortex mixer (Heidolph, Schwabach, Germany) to stir the crude oil with the extractant solvent and a Thermo Heraeus Megafuge 1.0 centrifuge (Thermo Fisher Scientific Inc., Langenselbold, Germany) to separate the undissolved solid phase from the liquid extract. A micropipette Transferpetter® with adjustable volume between 20 µL and 100 µL (Brand, Wertheim, Germany) was used to dilute the RR extracts.

The instrumental analysis was performed using an Agilent Technologies Gas Chromatograph (6890 N series) coupled with an Agilent Technologies Mass Spectrometer (5975 B series), both controlled with Mass Selective Detector Productivity ChemStation D.03.00 software (Agilent Technologies). The GC-MS was equipped with an Agilent Technologies auto-sampler (7683 B series) and an EPC cool on-column injection port connected to the MS using, approximately, 1 m of deactivated fused silica capillary pre-column with 0.53 mm internal diameter (Agilent Technologies, Santa Clara, USA), followed by a DB-5ms coated capillary column (non-polar phenyl arylene polymer capillary column virtually equivalent to (5%-phenyl)-methylpolysiloxane; 60 m length × 0.25 mm ID × 0.25 µm film thickness) (Agilent Technologies, Santa Clara, USA).

3.2.2. Chemicals

n-Hexane and dichloromethane for gas chromatography (SupraSolv®), obtained from Merck (Darmstadt, Germany), were used as solvent to extract the crude oils, and prepare the MixCrude solution and the diluted extracts of RR samples, respectively. The crude oils extracted, namely Miri Light (Malaysia), Bonny Light (Nigeria), Cabinda (Angola) and Ural (Russia), belong to the petroleum products database of *Instituto Hidrográfico*. The crude oils and the RR sample extracts have been preserved protected from light and between 2 °C and 8 °C, in closed glass bottles, keeping the original physio-chemical properties.

3.2.3. Analytical data collection

3.2.3.1. Confirmation of oil pattern equivalence

A mixture of crude oil extracts (MixCrude) at a ratio of 4:1:1:1 of the Ural, Miri Light, Bonny Light and Cabinda oil extracts was prepared to determine as many *DR* as possible that characterise the oils since some components with analytical interest may be at low concentrations or even absent in different crude oils. The study of an unweathered MixCrude solution aims to finely assess the impact of GC-MS performance in *DR* comparison.

0.20 g of each oil was mixed with 5 mL of *n*-hexane into a glass centrifuge tube using a vortex stirrer. The oil extract was separated from the solid phase by centrifugation (3000 rpm for 15 min) and transferred to a 25 mL volumetric flask. The solid phase that remained inside the centrifuge tube was subjected to four more consecutive extractions. The solution volume was adjusted to 25 mL with *n*-hexane and homogenised. The MixCrude solution was prepared by diluting 2 mL of Ural and 0.5 mL of Miri Light, Bonny Light and Cabinda oil extracts in a final volume of 15 mL using dichloromethane. The MixCrude has extracted compound from 1.1 mg of Ural oil and 0.27 mg of each of the other oils per mL of solvent.

Ten replicate and consecutive injections of the MixCrude in the GC-MS were performed according to instrumental conditions presented in the **Experimental details** and **Table B.1** of the **Annex B**.

3.2.3.2. Round robin test

One spill sample (Sp) and two suspected source samples, 1 (SS1) and 2 (SS2), of the RR were received as sample extracts, in dichloromethane, at 10 mg/mL. The Sp, SS1 and SS2 extracts were diluted to a final concentration of 0.8 mg/mL using dichloromethane. This injection concentration was defined considering the recommendations of EN 15522–2 for the sample oil type, *i.e.*, diesel with biodiesel (light fuel oil as classified by EN 15522–2), and adjusted by a previous evaluation of the chromatograms to avoid peak fronting and to provide closer peaks' abundances among the samples.

3.2.4. Peak analysis and quality control assessment

The GC-MS performance was checked, according to EN 15522-2 criteria, by the analysis of the MixCrude solution before, during and at the end of the sequence to assess retention time drift, changes in mass discrimination and column resolution.

Sixty-nine compounds or compound groups, listed in **Table B.2** of the **Annex B**, were identified and quantified in order to determine the normative *DR* considered relevant for crude oils and light fuels identification by the EN 15522-2 standard. For the RR samples, an additional *DR* set of informative *DR* suggested by EN 15522-2 was also determined to increase the robustness of the oil pattern comparison. According to the literature, all compounds were identified by the retention time, abundance pattern and confirmation ions (Faksness *et al.*, 2002; CEN, 2006; CEN, 2012; CEN, 2020). The peak size quantification was based on manual peak limits determination of the ion chromatograms considering the *m/z* listed in **Table B.1** of the **Annex B**. Single compounds and compound groups were quantified by height and by area, respectively. Chromatographic peaks with a signal-to-noise ratio (*S/N*) below five were not considered as defined by the standard EN 15522-2. Additionally, in order to exclude low precision signals or compounds affected by weathering from oil spill identification, the ratio between the compound *A* and a normaliser compound *H*, *e.g.*, phytane (Phy), present in oils (*A/H*) was determined for oil spill (OS), (*A/H*)_{OS}, and suspected oil source (SS), (*A/H*)_{SS}, samples. The *DR* determined with compounds *A* and *B* is considered adequate for oil pattern comparison if the rates between (*A/H*) and (*B/H*) of both samples, [(*A/H*)_{OS}/*(A/H)*_{SS}] and [(*B/H*)_{OS}/*(B/H)*_{SS}], are between 85% and 118%. This data filtration criterion is usually presented as Percentage Weathering (PW)-plots ((*A/H*)_{OS}/*(A/H)*_{SS} and (*B/H*)_{OS}/*(B/H)*_{SS} vs.

retention time of *A* and *B*, respectively), defined by EN 15522-2, that favours the reporting of oil pattern equivalence. The MCM method is applicable regardless of signal precision.

3.2.5. Diagnostic ratio determination

The comparison of 23 and 24 normative *DR* for crude and light fuel oil, respectively, is mandatory (CEN, 2020) unless the compounds that define the ratio are not present in the oil. These ratios were selected based on several criteria, *e.g.*, the presence of the compounds in oils, the discriminative power of several oils and the robustness to weathering effects. **Table B.2** of the **Annex B** shows the 22 and the 32 *DR* studied for the MixCrude solution and the RR samples comprising different classes of compounds, namely *n*-alkanes, isoprenoids, branched alkanes, decalins, sesquiterpanes, adamantanes, alkyl toluenes, polycyclic aromatic hydrocarbons (PAH), alkyl-PAH, sulphur-PAH, hopanes, steranes and triaromatic steranes.

There are two standardised ways of determining *DR*. EN 15522-2 standard applies the format *A/B* considering the chromatographic signals of compounds *A* and *B* in the numerator and denominator, respectively. According to this document, and after excluding the more dispersed signals, the ratios determined this way have an RSD not larger than 5%. In that case, a single maximum admissible relative range of 14% for a pair of *DR* from different samples can be applied. Alternatively, the *DR* is determined using the format $A/(A+B)$, with the chromatographic signal of compound *A* as the numerator and the sum of chromatographic signals of compounds *A* and *B* as the denominator. This way of assessing the proportion of *A* and *B* avoids the division by zero and a large diversity of ratio values from comparatively very low or high denominators of the *A/B* ratio (Daling *et al.*, 2002, Faksness *et al.*, 2002). In the current work, the *DR* was calculated using the two mentioned formats (*i.e.*, *A/B* or $A/(A+B)$), allowing to compare both ways for ratio determination.

Some oil components are affected by weathering processes producing a drift in the *DR* values, making them unsuitable for oil spill identification. When it becomes evident that a *DR* is affected by weathering, the ratio should be removed from fingerprint comparison. The weathering processes and compounds affected by these are well documented in diverse literature (Wang *et al.*, 1999; Wang *et al.*, 2005; CEN, 2006; CEN, 2012; Malmborg, 2017; CEN, 2020). Its identification and the impact assessment on the abundance of oil components of samples can be easily performed using previously described PW-plots and bar charts with

normalised abundances of compounds, A/H (Faksness *et al.*, 2002; CEN, 2006; CEN, 2012; CEN, 2020).

The assessment of oil pattern equivalence from independent and replicate analysis of MixCrude extracts allows a fine comparison of MCM, S-t and SC methods to define criteria for the agreement of mean DR values from compared samples.

The application of the identification tools to a real scenario simulated in a RR is used to check if performance observed in the analysis of MixCrude extracts can guide the management of such scenarios.

3.2.6. Assessment of diagnostic ratio agreement

Replicate sample preparation and/or instrumental analysis of at least one of the samples is needed to assess whether there is a significant difference between a DR observed in two samples (Faksness *et al.*, 2002; CEN, 2006; CEN, 2012; CEN, 2020). According to oil spill identification methodologies, the criterion for DR comparison can be established for each DR based on the standard deviation of the ratio itself (Daling *et al.*, 2002; Faksness *et al.*, 2002), or can be used a single criterion if the RSD is proved to be independent of the DR value (CEN, 2006; CEN, 2012; CEN, 2020). For the first case, S-t statistics can be easily applied to define confidence limits using replicates of a sample x and a certain confidence level (P), *e.g.*, 95% or 98%. The DR value of a sample y is assumed to be statistically equivalent to the DR value of the sample x if it is within the confidence limits defined from the data of sample x . In the second case, the relative difference between the DR values observed for both samples, x and y , need to be lower than 14% to be assumed DR equivalence.

Rocha *et al.* (2022) proposed an alternative method for DR comparison in an earlier work that uses the MCM to simulate the confidence limits of DR to assess the equivalence of DR values observed in two samples. However, the developed tool assumes only one DR is determined from replicate analysis and has the $A/(A+B)$ format. In this study, the three approaches for establishing the DR limits are compared: (1) S-t, which assumes the normality of the DR probability distributions and defines confidence limits for each DR , (2) SC which uses a single criterion for comparing DR determined assuming a default DR precision, and (3) MCM that simulates the DR confidence limits based on the observed mean value, precision and correlation

of abundances combined in the DR . Both S-t and MCM allow the replicate determination of compared DR .

The equivalence of a DR determined in a single analysis of sample y (DR_y) and a mean DR determined from replicate analysis of sample x ($\overline{DR}_x$) is assigned if DR_y falls within the confidence interval defined for $\overline{DR}_x$. For the S-t method, the confidence interval is defined by **Equation 3.1**.

$$\overline{DR}_x \pm s_{DR_x} \cdot t_x \quad (3.1)$$

where s_{DR_x} is the standard deviation of n_x DR values observed for sample x and t_x is the t -value of the Student's t distribution for a selected confidence level (95% and 98% in this work) and $(n_x - 1)$ degrees of freedom. However, the comparison between the mean DR estimated for both samples, x and y , should be based on the following condition:

$$|\overline{DR}_x - \overline{DR}_y| \leq t \cdot s_d \quad (3.2)$$

where $\overline{DR}_y$ and s_{DR_y} are the mean and the standard deviation of the DR estimated from n_y replicate analysis of sample y , s_d is the standard deviation of the DR difference (*i.e.*, $\overline{DR}_x - \overline{DR}_y$) specified in **Equation 3.3**, and t is the t -value of the Student's t distribution for a selected confidence level and ξ degrees of freedom determined from the nearest integer of the value obtained by **Equation 3.4** (Miller *et al.*, 2018).

$$s_d = \sqrt{\frac{s_{DRx}^2}{n_x} + \frac{s_{DRy}^2}{n_y}} \quad (3.3)$$

$$\xi = \frac{\left(\frac{s_{DRx}^2}{n_x} + \frac{s_{DRy}^2}{n_y}\right)^2}{\left(\frac{s_{DRx}^4}{n_x^2 \cdot (n_x - 1)} + \frac{s_{DRy}^4}{n_y^2 \cdot (n_y - 1)}\right)} \quad (3.4)$$

The comparison of two mean DR by the SC method assuming a maximum relative DR difference of 14% is performed following the condition of **Equation 3.5**.

$$|\overline{DR}_x - \overline{DR}_y| \leq 0.14 \cdot \overline{DR}_d \quad (3.5)$$

where $\overline{DR_d}$ is the mean of $\overline{DR_x}$ and $\overline{DR_y}$ values. If a mean DR , $\overline{DR_x}$, is compared with a single DR_y and the same maximum relative difference is considered, **Equation 3.5** can be used by changing $\overline{DR_y}$ for DR_y . This condition can be tested equivalently by using the **Equation 3.6**, which expresses confidence limits for DR_y .

$$\frac{0.93}{1.07} \cdot \overline{DR_x} \leq DR_y \leq \frac{1.07}{0.93} \cdot \overline{DR_x} \quad (3.6)$$

Equation 3.5 and **Equation 3.6** give rise to two limits estimated for the SC method identified as lower limit (SC_{LL}) and upper limit (SC_{UL}).

The MCM method simulates DR_x or $(\overline{DR_x} - \overline{DR_y})$ values to characterise their probability distributions. The confidence limits for DR comparison are determined by this method as χ^{th} percentiles ($P\chi^{\text{th}}$) of the simulated DR_x or $(\overline{DR_x} - \overline{DR_y})$ values, *e.g.*, $P2.5$ and $P97.5$, and $P1$ and $P99$, for 95% and 98% of confidence level, respectively.

3.2.6.1. Monte Carlo simulation

The MCM is a computational method used to solve stochastic problems by simulation. The simulation of an output variable starts with the generation of random values of the relevant input variables that define the output, according to known probability density functions, to which are conferred known characteristics such as expectation, dispersion and correlation. The input variables are used to determine the output variable, typically through a mathematical expression, simulating as many values of the output variable as the values of the input variables. With the simulated values of the output variable, its probability distribution can be described using parameters such as the mean, mode, dispersion, and percentiles.

The novel and flexible tool developed in this work was implemented in an MS-Excel spreadsheet to simulate two different output variables: DR_x when sample x is analysed in replicate and a single analysis of sample y is performed, and $(\overline{DR_x} - \overline{DR_y})$ when both samples to compare are analysed in replicate. Additionally, the computational tool is composed by two modules allowing the simulation of a selected DR (“Single DR Simulator”) or multiple DR (“Multi DR Simulator”). The main difference between both modules is the size of the generated matrices that depend on the number of chromatographic signals (m) needed to define the DR to

be simulated, *i.e.*, two signals to simulate a selected DR , or 145 signals to simulate up to 78 DR together.

The MCM simulation process of DR involves the simulation of the correlated chromatographic signals that define each ratio and have a normal distribution. Depending on the number of analyses performed for sample y , it is determined for sample x or for both samples, from GC-MS data, the mean value, standard deviation, degrees of freedom and correlation of chromatographic signals, A and B , that define each DR . Subsequently, a matrix T ($10,000 \times m$) of random and independent one-tailed t -values of Student's t distribution, with cumulative probabilities ranging 0 to 1 and $(n - 1)$ degrees of freedom (n as n_x or n_y) is generated. A correlation matrix C_{AB} ($m \times m$) between A and B signals was created to design a covariance matrix, K_{AB} ($m \times m$), which also expresses chromatographic signals' dispersion. The matrix K_{AB} ($m \times m$) is subjected to a Cholesky decomposition, generating the matrix L ($m \times m$), using a VBA code available in the literature (Zaiontz, 2018; Bettencourt da Silva *et al.*, 2019; Rocha *et al.*, 2022). However, even small mathematical inconsistencies of the K_{AB} matrix (145×145) do not allow its decomposition in the case of multiple DR simulations. Thus, a pseudo-correlation matrix C_{AB}' (145×145) is designed, composed of Pearson correlation coefficients reduced as low as possible (10^{-14} % in this study), allowing the covariance Cholesky factorisation. The T ($10,000 \times m$) and L ($m \times m$) matrices are multiplied ($T \cdot L$), producing the matrix M ($10,000 \times m$), with zero mean and experimentally observed correlation and dispersion. A matrix O ($10,000 \times m$), consisting of rows with repeated values of the mean of each signal observed experimentally, is added to the matrix M ($10,000 \times m$) to adjust the central value properly. The resulting matrix F ($10,000 \times m$) represents 10,000 simulated values of m correlated chromatographic signals, subsequently combined by the expressions $A/(A+B)$ or A/B , giving 10,000 simulated values of a selected DR or up to 78 DR , depending on the simulation module of the computational tool used. This simulation process is performed only with data of sample x to describe the DR_x probability distribution and define the confidence limits for DR_y . The simulations are made independently for sample x and sample y , when replicates of both samples are considered. Each simulated value of $\overline{DR}_x$ and $\overline{DR}_y$ are subtracted to obtain 10,000 simulated values of $(\overline{DR}_x - \overline{DR}_y)$, used to describe the probability distribution of $(\overline{DR}_x - \overline{DR}_y)$ and to determine the respective confidence limits.

More accurate determinations of confidence limits are obtained by increasing the number of simulated values. In the “Single DR Simulator”, 2×10^5 simulations of a selected DR can be

obtained, but a macro is available to replicate 20 times the above-mentioned simulation process. A similar procedure is applied to the “Multi DR Simulator” to obtain 10^4 simulated values of each *DR*.

The developed MS-Excel spreadsheet, made available for download from the weblink presented in the **Annex B**, simultaneously estimates the confidence limits by MCM, S-t and SC methods allowing their comparison and the determination of total risks of the correct acceptance of the equivalence of fingerprints from two oil samples. The spreadsheet includes a folder with detailed instructions on their use, making the developed tool's applications straightforward.

3.2.6.2. Estimation of specific risk and total risk

Two types of risk are studied in the present research: the specific risk and the total risk. The specific risk (γ) is the probability of the confidence limits defined by the MCM, S-t or SC method for a specific *DR* correctly supporting the claim that the *DR* observed in two samples are equivalent. In contrast, the total risk is a measure of the quality of the oil spill identification based on data from several *DR*. In the present study, the total risk assessed corresponds to the probability of true acceptance (δ) of the compositional equivalence between two samples with or of the same oil. The compositional equivalence of oil fingerprints is only assigned when all compared *DR* are equivalent. If at least the values of one compared *DR* are different, it can be assumed the compositional difference.

The specific and total risks are estimated using the MCM simulation ("Multi DR Simulator") of a set of M *DR* selected for oil fingerprints. For each *DR* are obtained 11×10^4 simulated values of DR_x or $(\overline{DR}_x - \overline{DR}_y)$ depending if the extract of the sample y is analysed one or more times, respectively. The equivalence between *DR* is assessed by comparing 10,000 simulated values of each *DR* with the confidence intervals defined by the MCM, S-t and SC methods. The remaining 10^4 simulated values are used to estimate the confidence limits by the MCM method, *i.e.*, $P_{2.5}$ and $P_{97.5}$, and P_1 and P_{99} , for 95% and 98% confidence levels, respectively. For S-t and SC methods, the confidence intervals are estimated based on **Equations 3.1, 3.2, 3.5 and 3.6**, considering the experimental data from the GC-MS analysis. For each *DR*, γ is calculated as the percentage of simulated values within the confidence limits defined for MCM, S-t and SC methods. The δ is estimated by the percentage of *DR* sets with statistical equivalence for all *DR*. Assuming that the confidence limits for *DR* comparison are

estimated accurately for the P confidence level, the δ should be equal to P^M or equal to P if all ratios of the DR set are independent or perfectly correlated, respectively. However, the 22 DR studied in the MixCrude solution are correlated with a Pearson correlation coefficient less than one being expected δ lower than P (95% or 98%) and greater than P^M (32.3% or 64.1%).

As the MCM simulation better describes the real DR performance taking into account possible deviations to the normality of the DR probability distributions, the MCM method is used as a reference for evaluating the other S-t and SC methods.

3.3. Results and discussion

Results and discussion is divided into the use of described tools for the confirmation of the equivalence of oil patterns observed in independent and replicated analysis of MixCrude solution and the determination of an oil spill source from a real spill scenario reproduced in a RR. The first assessment aims to accurately quantify the risk of true identifications, and the RR example illustrates how the developed tool is applied to a real case.

3.3.1. Confirmation of oil patter equivalence

The assessment and comparison of the performance of the MCM, S-t and SC methods were based on confidence intervals amplitude, and specific and total risks of true acceptance of the equivalence between DR and oil fingerprints, respectively, of two samples with traces or of the same oil. The methods were applied to instrumental signals collected from 10 injections, obtained in a single run, of the MixCrude solution prepared as described in the **Subchapter 3.2**. **Table B.2** of the **Annex B** presents the studied components and how these are combined in the various DR . The confidence limits and the specific and total risks estimated by the studied methods were obtained using three, five and eight replicated analyses of sample x ($n_x = 3; 5; 8$) and one, two and three replicated analyses of sample y ($n_y = 1; 2; 3$). In particular, duplicate analysis for both samples ($n_x = n_y = 2$) allowed to compare the MCM, S-t and SC methods with the conditions specified by the EN 15522 standard. Two confidence levels were considered for MCM and S-t methods, 95% and 98%, corresponding to the confidence levels established by the Nordtest methodology for oil spill identification (Daling *et al.*, 2002; Faksness *et al.*, 2002). These confidence intervals have limits defined by the $P_{2.5}$ and $P_{97.5}$,

and by the $P1$ and $P99$, for 95% and 98% of confidence levels, respectively. Two ratio calculation formats were evaluated: $A/(A+B)$ and A/B .

3.3.1.1. Comparison of confidence limits

Tables B.3 to B.6 and **Tables B.7 to B.10** of the **Annex B** present the confidence intervals of DR_x and $(\overline{DR}_x - \overline{DR}_y)$ and their amplitudes (amplitude, Δ , and normalised amplitude to $P50$ estimated by the MCM method, Δ^N), respectively, determined for the 22 DR by MCM, S-t and SC methods considering different numbers of replicated analyses of samples x and y and for the two ratio calculation formats. **Figures 3.1** and **3.2** represent radar charts of the confidence limits for the various scenarios and methods studied, allowing the visualisation of the interval's amplitude and the deviations from normality of the intervals defined by the MCM method.

The confidence limits defined for DR_x (**Table B.7** of the **Annex B** and **Figure 3.1**), are normalised to $P50$ estimated by the MCM method. Visualising the results obtained when sample x is analysed in replicate and sample y is analysed only once ($n_x = 3; 5; 8$ and $n_y = 1$) (**Tables B.3** and **B.7** of the **Annex B**, and **Figure 3.1**), it is evident that the amplitude of the DR_x confidence intervals for MCM and S-t methods decrease as more replicate analyses are considered. The confidence intervals established by the MCM simulation reveal to be slightly wider than those modelled by the S-t, but the difference between methods is reduced with the increase in the number of degrees of freedom. In contrast, the confidence intervals defined by the SC method using $\overline{DR}_x$ do not differ significantly with the increase of the number of the injection showing, in general, a greater amplitude compared with the other two methods. These trends are observed for both ratio formats and are consistent with the authors' previous study (Rocha *et al.*, 2022). However, the deviations to the normality of the MCM simulated probability distributions are less pronounced in the present study than in the previous one for the same conditions, *i.e.*, considered DR , number of replicates, and ratio format. This fact is explained by the lower dispersion of chromatographic signals due to their quantification by height, in the present study, instead of area, in the previous one.

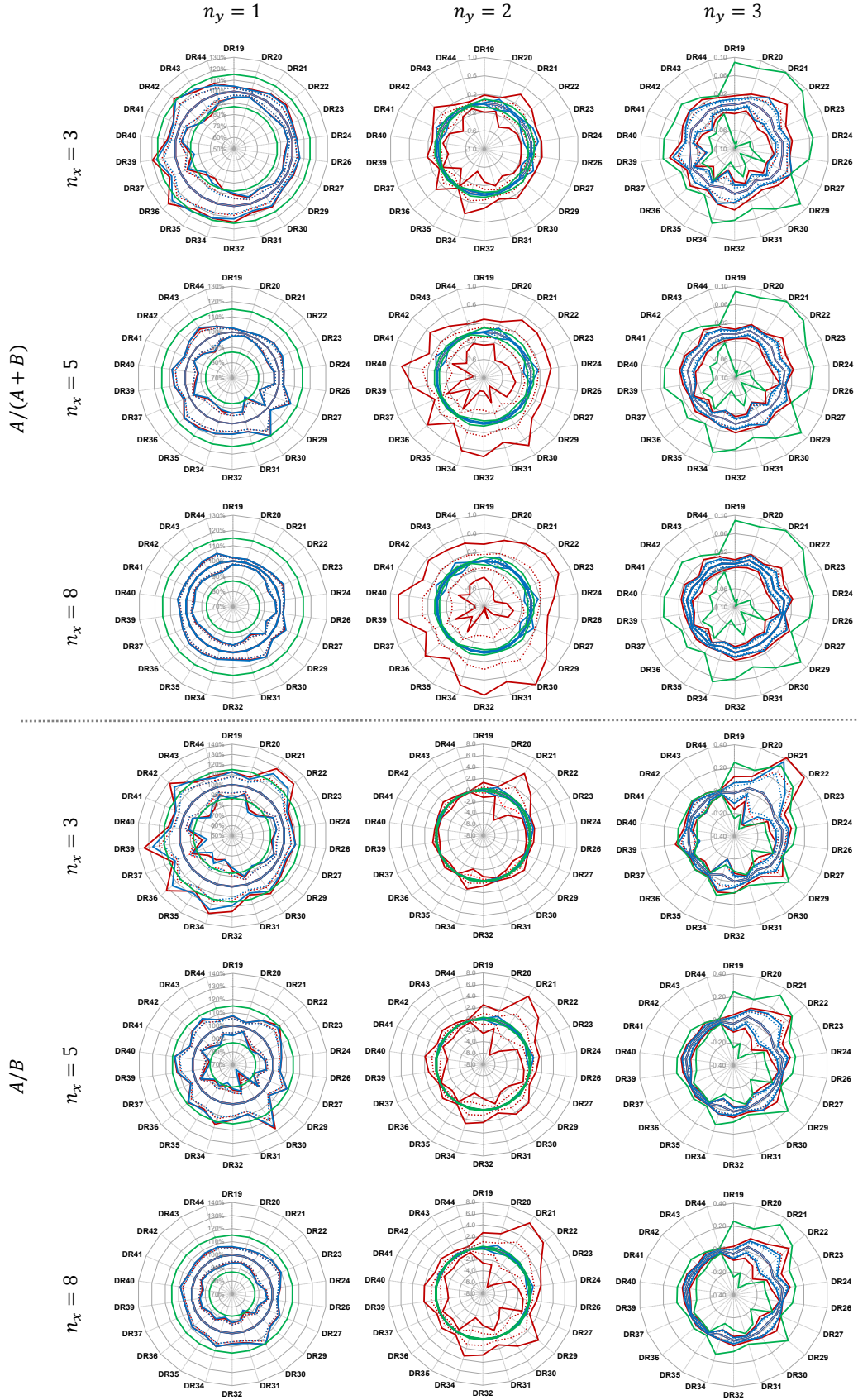


Figure 3.1. Confidence limits of DR_x or $(\overline{DR}_x - \overline{DR}_y)$ for all 22 DR studied, determined by the MCM (red), S-t (blue) and SC (green) methods, for three, five and eight injections n_x , of sample x and one, two and three injections, n_y , of sample y , and for ratio formats $A/(A+B)$ and A/B . Confidence limits of DR_x were normalised to the 50th percentile simulated by MCM. = $P50$; $\cdots$ $P2.5$ and $P97.5$; — $P1$ and $P99$.

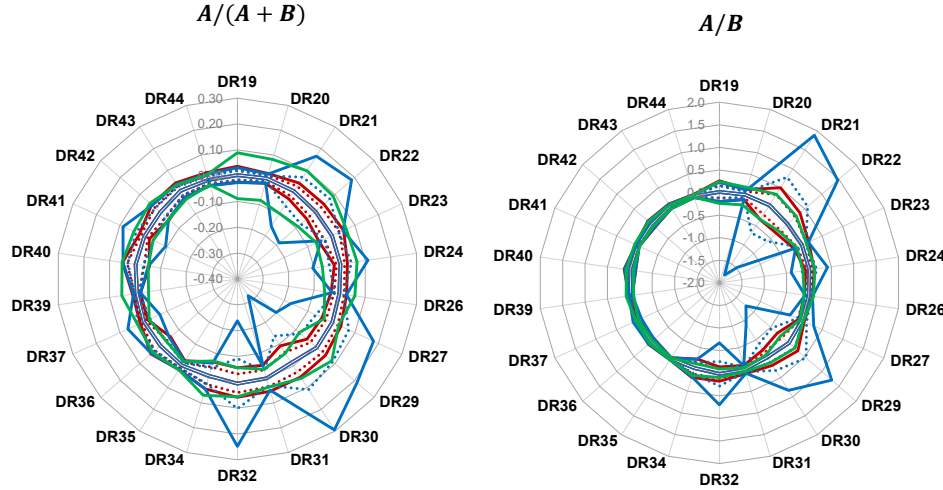


Figure 3.2. Confidence limits of $(\overline{DR}_x - \overline{DR}_y)$ for all 22 DR studied, determined by the MCM (red), S-t (blue) and SC (green) methods, for duplicate injections of samples x and y , and ratio formats $A/(A+B)$ and A/B . $= P50$; $\cdots P2.5$ and $P97.5$; $— P1$ and $P99$.

Similar conclusions are obtained when triplicate analysis for sample y ($n_x = 3; 5; 8$ and $n_y = 3$) and both ratio formats are considered. **Tables B.5** and **B.9** of the **Annex B**, and **Figure 3.1** show a decrease in the amplitude of the confidence intervals of $(\overline{DR}_x - \overline{DR}_y)$, simulated by MCM and modelled by S-t, as a result of the statistical robustness expressed by the degrees of freedom. In contrast, the confidence intervals estimated by SC are dependent on $\overline{DR}_x$ and $\overline{DR}_y$ and show no variation with the increase of replicate analyses of sample x . Deviations from the normality of the $(\overline{DR}_x - \overline{DR}_y)$ probability distributions are also noted.

The use of duplicates of sample y ($n_x = 3; 5; 8$ and $n_y = 2$) in the MCM simulation of $(\overline{DR}_x - \overline{DR}_y)$ confidence limits proved to be a particular case. As observed in the previous scenarios and for both ratio formats, the S-t confidence intervals tend to get narrower, while the confidence intervals defined by the SC method do not fluctuate with the increase in the number of replicated analyses of sample x (**Tables B.4** and **B.8** of the **Annex B**, and **Figure 3.1**). On the contrary, the confidence intervals obtained by MCM simulation become wider, explained by the flatter shape of the probability distributions of the simulated $(\overline{DR}_x - \overline{DR}_y)$ compared to the sharper shape of the S-t distributions. **Figure 3.3** reveals that the degree of the flattening is more intense when the number of replicates of samples x and y increases, leading to broader confidence limits due to lower data density near the centre of the distribution. The discrepancies in the $(\overline{DR}_x - \overline{DR}_y)$ probability distributions can be explained by the complex impact that

different input data have on the simulation, *i.e.*, degrees of freedom, dispersion and correlation of chromatographic signals.

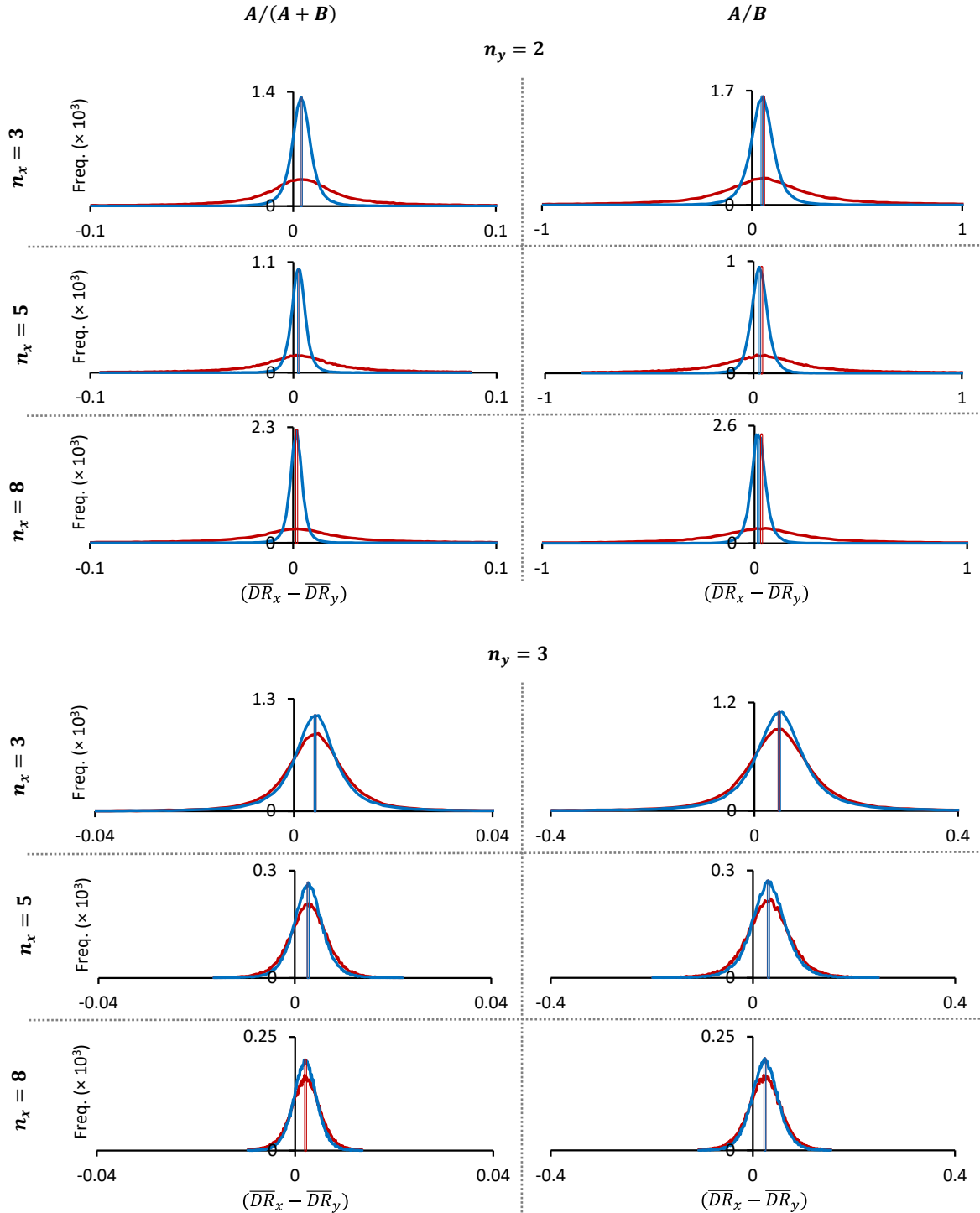


Figure 3.3. Simulated and modelled probability distributions of $(\overline{DR}_{21_x} - \overline{DR}_{21_y})$ by the MCM (red) and S-t methods (blue), determined from $n_x = 3, 5$ and 8 , and $n_y = 2$ and 3 injections of samples x and y , and for ratio formats $A/(A+B)$ and A/B . $n = P50$.

The EN 15522-2 standard suggests determining DR using duplicate analysis of both samples ($n_x = n_y = 2$). For this scenario, the results are presented in **Tables B.6** and **B.10** of the **Annex B** and **Figure 3.2**. It is observed that the intervals estimated by the SC method are wider than those obtained by MCM simulation for the 95% confidence level but tend to be narrower than those estimated for 98%, in particular for the A/B ratio format. Thus, the SC method proves to be stricter than the MCM method implemented for a 98% confidence level in conditions defined by EN 15522-2 standard. **Figure 3.2** shows some confidence intervals defined by the S-t method considerably wider than those established by the other methods (e.g., $DR21$, $DR30$ and $DR32$). These situations result from a smaller number of degrees of freedom and/or a higher standard deviation, according to **Equation 3.2**. The impact of degrees of freedom (ξ) and difference standard deviation (s_d) on S-t confidence interval amplitudes ($P = 98\%$) can be illustrated by the example of the ratios $DR21$, $DR31$ and $DR37$ in A/B format. The comparison of $DR21$ (Δ : 3.67; ξ : 1; s_d : 0.0578) and $DR37$ (Δ : 0.199; ξ : 1; s_d : 0.000314) intervals illustrate that Δ increases with s_d increase. In addition, the comparison of $DR31$ (Δ : 0.172; ξ : 2; s_d : 0.0124) with $DR21$ (Δ : 3.67; ξ : 1; s_d : 0.0578) illustrates that Δ increases with ξ decrease.

3.3.1.2. Specific and total risks assessment

The γ assessed in the present study is defined as the probability of correctly concluding equivalence between DR , observed in two samples with the same fingerprint, considering the estimated confidence intervals for DR_x ($n_x > 1$ and $n_y = 1$) or $(\overline{DR}_x - \overline{DR}_y)$ ($n_x > 1$ and $n_y > 1$). **Tables B.11** to **B.14** of the **Annex B** present the γ estimated for the 22 DR studied, in $A/(A+B)$ and A/B ratio formats by the MCM, S-t and SC methods. **Table 3.1** shows the minimum and maximum γ presented in **Tables B.11** to **B.14** of the **Annex B**. For the MCM method, the γ is equivalent to P , 95% and 98%, ranging from 94.5% to 96.2% and 97.6% to 98.7%, respectively, regardless of the ratio format and the number of replicates of samples x and y . These results are expected since the MCM simulation is used to define the DR comparison criteria and control the limits. When sample y is analysed only once, the γ estimated for the S-t method is also equivalent to P since confidence limits defined by the MCM and S-t methods are very close. In contrast, when replicate analyses of sample y are considered, the estimated γ for the S-t method decreases considerably, i.e., less than P , in particular for $n_x \geq 3$ and $n_y = 2$ where γ ranges from 13.4% to 93.2% and 16.9% to 97.4% for both ratio

formats. However, when duplicate analysis for both samples and the S-t method is used, it is observed γ greater than P for the exceptional situations of wider confidence intervals (*e.g.*, *DR21*; *DR30* and *DR32*). For the SC method, the γ are, in general, higher than those estimated for 95% confidence by the MCM and S-t methods, except for the scenario that considers $n_x \geq 3$ and $n_y = 2$. In this case, the γ are clearly lower than P , varying between 49.1% and 97.0%. In addition, the ratio format shows to affect γ determined by SC method, driving to lower γ when the ratio format A/B is used. As expected, the γ are greater than P since the established confidence intervals are wider than those estimated by the MCM method for most of the scenarios studied.

Table 3.1 presents the δ estimated for the MCM, S-t and SC methods considering all the scenarios studied. As expected, δ are generally less than P (95% and 98%) but greater than P^{22} (32.3% and 64.1%, for 95% and 98% of confidence levels limits, respectively). However, exceptions are noted for the SC method and the $A/(A+B)$ ratio format, as well as for the SC and S-t methods when $n_x \geq 3$ and $n_y = 2$ are considered. As observed for the γ , the δ are in line with the size of the confidence intervals observed for the MCM, S-t and SC methods.

Table 3.1. Minimum and maximum specific risks of true acceptance of *DR* equivalence (γ) and total risks of true acceptance of compositional equivalence between samples (δ) estimated by MCM, S-t and SC methods from different replicate injections of sample x ($n_x = 2, 3, 5, 8$) and sample y ($n_y = 1, 2, 3$), ratio formats $A/(A+B)$ and A/B , and 95% and 98% confidence levels for MCM and S-t methods.

n_x	n_y	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{sc}	γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{sc}
3	1	94.8 – 95.4	98.0 – 98.1	94.2 – 94.9	97.8 – 98.0	96.4 – 99.8	94.8 – 95.1	97.9 – 98.0	94.1 – 94.7	97.5 – 97.8	92.9 – 99.4
5		94.9 – 95.2	97.7 – 98.3	94.6 – 95.4	97.9 – 98.5	97.7 – 100	94.7 – 95.2	97.8 – 98.2	94.5 – 95.3	98.0 – 98.4	89.0 – 100
8		94.9 – 95.3	97.8 – 98.3	94.8 – 95.6	98.3 – 98.6	99.9 – 100	94.8 – 95.5	97.8 – 98.1	94.5 – 95.7	98.1 – 98.7	97.5 – 100
3	2	94.5 – 96.2	97.8 – 98.7	46.2 – 93.2	58.2 – 97.4	76.6 – 97.0	94.3 – 95.6	97.6 – 98.3	46.9 – 93.2	58.8 – 97.2	69.9 – 96.3
5		94.4 – 96.0	97.6 – 98.4	22.9 – 88.7	29.8 – 95.5	66.1 – 93.5	94.3 – 96.2	97.6 – 98.5	21.2 – 88.6	28.3 – 95.3	53.5 – 86.0
8		94.8 – 95.7	97.8 – 98.3	13.4 – 87.3	16.9 – 94.9	64.1 – 92.7	94.2 – 95.7	97.7 – 98.3	14.2 – 86.7	17.8 – 94.9	49.1 – 78.7
3	3	94.5 – 95.4	97.7 – 98.2	84.6 – 94.6	91.2 – 97.9	97.8 – 99.9	94.9 – 95.8	97.9 – 98.6	85.0 – 95.4	91.5 – 98.4	95.8 – 99.6
5		94.4 – 95.8	97.6 – 98.3	85.8 – 94.7	91.9 – 98.0	98.0 – 100	94.7 – 95.7	97.9 – 98.2	85.9 – 94.9	92.1 – 98.1	97.1 – 100
8		94.9 – 95.5	97.8 – 98.4	87.1 – 93.6	92.5 – 97.5	98.4 – 100	94.7 – 95.5	97.8 – 98.3	86.9 – 93.7	92.6 – 97.5	97.1 – 99.9
2	2	94.7 – 95.3	97.8 – 98.2	93.3 – 99.3	97.4 – 99.9	95.3 – 99.9	94.8 – 95.2	97.9 – 98.3	93.5 – 99.4	97.6 – 99.9	86.2 – 99.6
n_x	n_y	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		δ_{95}	δ_{98}	δ_{95}	δ_{98}	δ_{sc}	δ_{95}	δ_{98}	δ_{95}	δ_{98}	δ_{sc}
3	1	90.4	96.1	88.8	95.4	94.8	90.1	95.8	88.5	94.9	88.3
5		77.1	89.9	76.6	90.9	97.1	76.9	89.7	76.2	90.5	86.9
8		63.6	82.4	64.8	85.5	99.9	63.8	82.3	64.6	85.3	96.8
3	2	89.3	94.8	29.9	45.2	71.9	89.1	94.5	30.3	45.1	53.0
5		88.3	92.8	2.3	5.9	52.8	86.7	91.5	2.3	5.7	31.3
8		85.8	90.8	0.14	0.39	35.7	84.1	89.7	0.070	0.43	18.0
3	3	83.1	93.4	64.6	80.3	95.7	83.5	93.0	64.6	80.7	90.6
5		76.6	91.0	56.8	76.8	97.8	75.7	90.7	56.0	75.7	95.7
8		74.7	90.4	51.4	72.5	98.3	74.5	90.7	51.3	72.3	96.7
2	2	83.1	93.2	82.4	93.6	90.1	83.2	93.2	82.4	93.3	75.9

From **Table 3.1**, it can be seen that higher δ is achieved for the MCM and S-t methods when a smaller number of replicates for both samples are considered, concluding that a reduced number of degrees of freedom masks the characteristics of the probability distributions of DR_x and of $(\overline{DR}_x - \overline{DR}_y)$. This scenario was also observed in a previous study carried out by the authors (Rocha *et al.*, 2022). The opposite is concluded for the SC method, obtaining higher δ when a greater number of replicates of both samples are used, except for the scenario that considers $n_x \geq 3$ and $n_y = 2$. This trend results probably from the option of not somehow adapting the SC method to the number of replicates since it is defined for $n_x = n_y = 2$. Regardless of the ratio format, for SC and S-t methods and $n_x \geq 3$ and $n_y = 2$, low δ are observed, ranging from 18.0% to 71.9% for the SC method, and from 0.070% to 30.3% and 0.39% to 45.2% for 95% and 98% of confidence levels for the S-t method, respectively. Higher δ are estimated for the $A/(A+B)$ ratio format by the SC method compared to the A/B format. Nevertheless, there are no noticeable differences between the δ estimated by the MCM and S-t methods for the two ratio formats studied. The estimated δ (*i.e.*, 75.9%) for the SC method under the conditions defined by the EN 15522-2 standard, namely $n_x = n_y = 2$ and ratio format A/B , are lower than those estimated by the MCM method for $P = 95\%$ (83.2%). Thus, in the specific studied case, identifications based on the SC method under the conditions of EN 15522-2 standard have a lower quality than analysis performed using the developed MCM method. The low δ for the SC method resulted from the low γ observed in a few DR , namely $DR30$ (86.2%), $DR36$ (91.0%) and $DR31$ (92.5%) (**Table B.14** of the **Annex B**), which reduced the chance of the agreement between all DR compared in the equivalent samples x and y .

3.3.2. Round robin test

The developed tool was applied to assess the equivalence between oil patterns of one oil spill sample (Sp) and two suspected source samples (SS1 and SS2), one known to be the origin of the spill (SS1). The confidence limits obtained by the MCM, S-t and SC methods were estimated using the conditions suggested by EN 15522-2, *i.e.*, two replicate analyses of each sample, A/B DR format and comparison of specific normative DR and informative DR . Prior to oil patterns comparison, and as described in the **Subchapter 3.2**, the dispersion of the chromatographic peaks and the weathering of compounds were checked, and all the DR affected were removed from the DR set to compare. **Tables B.2** and **B.15** of the **Annex B** show the DR

determined for the Sp, SS1 and SS2 samples and the assessment of the *DR* equivalence between the sample pairs by determining difference confidence limits ($\overline{DR}_{Sp} - \overline{DR}_{SS}$). The *DR* equivalence between the two samples is indicated by the inclusion of the zero value in the confidence interval of the difference. For the samples pair Sp vs. SS2 was observed that 44%, 22%, and 38% of the *DR* assessed by MCM ($P = 98\%$), S-t ($P = 98\%$) and SC approaches, respectively, are different indicating compositional divergence. In contrast, the SS1 was identified as the origin of the spill due to the similarity of the oil patterns observed for the Sp and SS1 samples pair, which shows the equivalence of all the *DR* by S-t ($P = 98\%$) and SC approaches and statistical difference for only one *DR* by the MCM approach ($P = 98\%$). The *DR* differences observed for $P = 95\%$ and 98% between the Sp and SS1 can be attributed to statistical reasons since for equivalent samples, on average, 1 in each 20 or 50 *DR* comparisons will differ, respectively. The follow-up of *DR* differences for $P = 98\%$ involved performing an additional *DR* comparison to assess if the divergent *DR* is confirmed in a second comparison trial (**Tables B.16** of the **Annex B**). This follow-up procedure was already proposed by Rocha *et al.* (2022) in order to increase the risk of true acceptance of equivalences to above 98%.

3.4. Conclusions

Three methods for assessing the equivalence of oil patterns of oil or oil contaminated environmental samples, by comparing the ratio of abundances of characteristic oil components, *DR*, determined by GC-MS and useful for oil spill source identification, were compared. These methods were applied to the determination of *DR* as the ratio between the abundance of two components (A/B) or the ratio between the abundance of the first component and the sum of the abundances of both components considered in the *DR* ($A/(A+B)$).

Two normalised methods developed by Nordtest and CEN were compared with a novel methodology based on the computational simulation of comparison criteria. The Nordtest method assumes the normal distribution of the *DR*, determined as $A/(A+B)$, and uses Student's t statistics (S-t) to define the comparison criteria of *DR*. The EN 15522-2 standard defines a maximum relative difference of 14% (SC) to compare duplicate determinations of *DR*, defined as A/B , after excluding low precision *DR* from the comparison. The novel method experimentally determines the mean values, dispersion and correlation of abundances combined in the *DR* (A/B or $A/(A+B)$ format), and through the Monte Carlo Method simulation (MCM)

of correlated abundances accurately estimates the complex distribution of *DR* and criteria for the comparison of a pair of *DR*.

When the replicate determination of *DR* of one sample is compared with the single determination of the *DR* for the second sample, the S-t and MCM determine the limits of the confidence interval characterising the dispersion of the *DR* of the first sample. If the *DR* of the second sample is within the confidence limits of the *DR* of the first sample, the equivalence of *DR* is assumed. If the mean *DR* of both samples is estimated from their replicate determination, the S-t and MCM determine the distribution of the difference between *DR* means. The *DR* means are considered equivalent if the zero is within the confidence limits of the difference.

The oil pattern equivalence is assumed if various *DR* (normative *DR*), considered relevant for the characterisation of the oil type present in samples, are equivalent in compared samples. Normative *DR* supported on low abundance values and with low precision are excluded from the comparison. Additionally, the developed methodologies can only be used for non-weathered oil components where the weathering affected compounds can be identified using the PW-plots suggested in the EN 15522-2 standard.

The described three methods for setting *DR* comparison criteria, and two types of *DR* formats (six combinations of method/ *DR* format) were applied to specific scenarios of oil pattern comparison to understand the advantages and limitations of the various approaches. The tools were applied to a different number of replicate determinations of the *DR* to define the optimal conditions for oil spill identification.

A mixture of various crude oils, that allows the determination of all normative *DR* for crude oil spill identification with adequate precision, was used to assess the probability of correctly concluding the equivalence of oil patterns from injections of extracts of the same crude oil. This assessment concluded that the MCM allows a more accurate definition of *DR* comparison criteria, increasing the total risk of true acceptance of oil pattern equivalence, δ , observed with the S-t and SC methods. Identification quality improves with the number of replicate determinations of the *DR* because *DR* comparison criteria become stricter, although associated with a lower δ of the first *DR* comparison trial.

Since studied *DR* are not perfectly correlated, the δ is much lower than the confidence level of the comparison of specific *DR*. This low probability can be overcome if the decision on the equivalence of a *DR* set is based on two independent comparisons of the *DR* set were only if

the difference of the *DR* is confirmed in the second comparison, it is assumed oil pattern difference.

The δ of oil pattern comparison varies with the oil compared, the *DR* set considered, and the performance of the GC-MS.

The evaluated oil pattern comparison tools were applied to a real oil spill scenario reproduced in an International Round Robin Test. The S-t, SC and MCM methods confirmed the equivalence of all relevant *DR* estimated from an oil sample collected in the contaminated water and an oil sample known to be the source of the spill. For the MCM, a second *DR* comparison trial was necessary, as expected, due to the low total risk of true acceptance of oil pattern equivalent from a large number of *DR*. The MCM proved to be more adequate than S-t and SC in distinguishing the spilt oil sample from a second oil sample known not to be the source of the spill. The ability to distinguish different *DR* is particularly relevant when only a few *DR* are available for oil pattern comparison.

This work makes available for download, in the **Annex B**, the user-friendly MS-Excel file used to determine *DR* comparison criteria by the MCM, S-t and SC methods using any of the studied *DR* formats, A/B or $A/(A+B)$, and single or replicate determinations of *DR*. The file allows determining the risk of correctly concluding about oil pattern equivalence for the studied specific *DR* set.

3.5. References

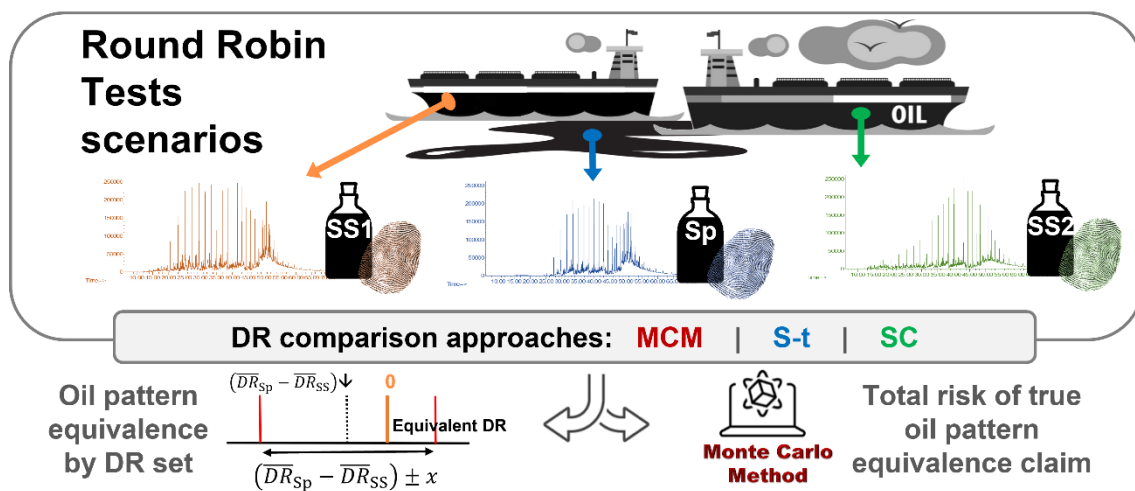
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4. Statistically sound comparison of standardised and simulation methods for oil spill source identification in real spill scenarios



Abstract

The comparison of oil patterns of a spill (Sp) and suspected spill source (SS) samples is based on ratios between correlated GC-MS signals of oil-discriminating compounds, *i.e.*, diagnostic ratios (*DR*). The Student's *t* statistics (S-t) and a maximum relative difference (SC), proposed in standard methods, have been used for *DR* comparison due to their simplicity. An alternative methodology based on Monte Carlo Method (MCM) simulations of correlated signals, capable of accurately defining *DR* comparison criteria, proved that S-t and SC assumptions regarding *DR* normality and precision are frequently not valid, affecting comparison reliability. The performance of the approaches was accurately compared from independent signals of the same oil sample from a perfect match between Sp and SS. The present study describes the comparison of the approaches in real oil spill scenarios reproduced in International Round Robin Tests. As the number of compared *DR* increases, also rises the probability of not all equivalent *DR* being actually considered equivalent, the decision of oil pattern equivalence was based on two comparisons of independent sets of Sp and SS signals. The risk of true oil standard equivalency claims is compared for the three oil spill scenarios studied, which are different considering oil types, *DR* sets and spill weathering. The ability of the approaches to distinguish the Sp from an oil sample known not to be the source of the spill was also assessed. The MCM based on two independent *DR* comparison trials was the only one consistently producing fingerprint comparison risks of correct equivalence claims larger than 98%. MCM also performed better in distinguishing different oil patterns. It was concluded that comparing > 22 *DR* does not change the risk of correct oil pattern equivalence assessment significantly. The complexity of the MCM approach is overcome by using user-friendly and validated software.

Keywords: Oil fingerprinting; Oil spills; Round Robin Tests; True results rate; Validation

4.1. Introduction

Chemical analyses performed on spill (Sp) and suspected sources (SS) samples have been used to identify the pollution origin and support the legal liability as evidence. Over the last two decades, the analytical methodology used in many European countries has been substantially improved (Kienhuis *et al.*, 2016), resulting in different approaches: Nordtest method (Daling *et al.*, 2002; Faksness *et al.*, 2002) and CEN/TR 15522-2 (CEN, 2006; CEN, 2012), recently improved and adapted to become the EN 15522-2 standard (CEN, 2023). The identification of the spill source based on the correlation of oil pattern components involves the chromatographic analysis (*e.g.*, gas chromatography-mass spectrometry (GC-MS)) of the Sp and SS extracts and the comparison of oil patterns based on objective criteria. The analytical data are processed to determine the commonly designated oil fingerprint of the sample, *i.e.*, a set of ratios between the abundances of oil-discriminating compounds, namely diagnostic ratios (*DR*). The Nordtest method and EN 15522-2 standard have suggested two different approaches to compare *DR* observed in two samples: the Student's *t*-test (S-t), that assumes the normality of the *DR* probability distributions, and a maximum relative difference between *DR* of 14% (single criterion, SC) for *DR* with a relative standard deviation (RSD) not larger than 5%, respectively. More recently, Rocha *et al.* (2022a,b) presented a novel approach that uses the simulation of the *DR* by the Monte Carlo Method (MCM) to estimate the criteria for *DR* comparison. The MCM approach, implemented in a user-friendly MS-Excel spreadsheet (Rocha *et al.*, 2022b), simulates *DR* based on precision and correlation data of the compounds' chromatographic signals that define the ratio. The simulated results obtained allow (a) to estimate the non-normal probability distribution of the *DR* or of the difference of a pair of *DR* means from two samples, (b) to determine the confidence limits of the *DR* or of the difference of *DR* means to assess their equivalence and (c) to estimate the probability or risk of true and false claims of oil pattern equivalence based on the comparisons of many correlated *DR* from two samples. In addition, the developed MS-Excel spreadsheet also applies the *DR* comparison criteria from S-t and SC, allowing determining the risk of true and false oil pattern equivalence claims from these approaches. A mixture of volumes of four crude oils extracts was used to test the spreadsheet and to determine the performance of the MCM, S-t and SC approaches in different scenarios of oil pattern comparison, *i.e.*, number of replicates of each sample, *DR* calculation format, and *DR* set, in particular those suggested by the Nordtest method and EN 15522-2 standard. The mixed extracts were selected in order to maximise the number of studied *DR*, in a single run, that require signal intensities larger than five times instrumental signal noise.

The authors demonstrated that deviations from the normality of the *DR* probability distributions and the diversity of *DR* precision affect the performance of S-t and SC approaches. These studies are the first to perform a statistically sound assessment of the probability of correctly concluding about compositional equivalence between samples by comparing a selected *DR* set. However, the studies were carried out under controlled weathering conditions to more finely evaluate the advantages and limitations of the various *DR* comparison approaches tested.

In this work, it is used the risk term defined in the ISO Guide 73 (ISO, 2009) as the “effect of uncertainty on objectives” that can have a positive or negative impact on the relevant interest. Since it is discussed the risk of true or false decisions on oil pattern equivalence between specific spill and suspected spill source samples, is quantified a “specific risk” as defined in an IUPAC recommendation (Kuselman *et al.*, 2021) followed in various research (Oliveira and Lourenço, 2021; Separovic *et al.*, 2021). The adjective “specific” for the risk is omitted throughout the text for simplicity.

The present work reports the performance of MCM, S-t and SC approaches on the identification of spill sources in real scenarios reproduced in International Round Robin Tests (RR) where weathered Sp and various SS are compared. RR promoted by the Oil Spill Identification Network of Experts within Bonn-Agreement (Bonn-OSINet) in 2018, 2019 and 2020 were studied. The different petroleum products in the Sp and SS, and the fact that it is known the spill source, allowed to evaluate the influence of selected *DR* sets, *DR* format, number of replicate *DR* determinations and *DR* comparison criteria on the quality of oil pattern equivalence determination. As recommended by the EN 15522-2 standard, the *DR* affected by weathering, identified using the criteria defined in this standard, are excluded from *DR* comparison between Sp and SS. The quality of the spill source identification, quantified as the total risk of true and false equivalence claims between samples estimated by MCM, S-t and SC approaches was compared for each scenario tested, *i.e.*, comparison conditions (*DR* calculation format and number of replicate analysis of each sample). The variation of the total risk with the number of *DR* considered is also evaluated. The oil pattern comparison between the Sp and SS known not to be the origin of the spill allows assessing the risk of a false equivalence claim, function of the similarity of Sp and SS oil fingerprints.

4.2. Material and methods

4.2.1. Equipment

A micropipette Transferpetter® with an adjustable volume between 20 µL and 100 µL (Brand, Wertheim, Germany) was used to dilute the extracts of RR2018 and RR2020 samples, and a Mettler PE1600 balance (Mettler, Greifensee, Switzerland) was employed to weigh each sample of the RR2019.

The GC-MS analysis was performed using a Gas Chromatograph (6890N series) attached to an auto-sampler (7683B series) and coupled with a Mass Spectrometer (5975B series), all from Agilent Technologies. The instrument operated with an EPC cool on-column injection port connected to the detector by a deactivated fused silica capillary pre-column with 0.53 mm internal diameter and 0.5 m length (Agilent Technologies, Santa Clara, USA) followed by a DB-5ms coated capillary column (non-polar phenyl arylene polymer capillary column virtually equivalent to (5%-phenyl)-methylpolysiloxane; 60 m length × 0.25 mm ID × 0.25 µm film thickness) (Agilent Technologies, Santa Clara, USA). The Mass Selective Detector Productivity ChemStation D.03.00 software (Agilent Technologies) was used to control the system.

4.2.2. Chemicals

Dichloromethane for gas chromatography (SupraSolv®), obtained from Merck (Darmstadt, Germany), was used to extract oil samples and dilute extracts. The Sp and SS, known to be and not to be the source of the spill (SS1 and SS2, respectively), of the RR2018, RR2019, and RR2020 consisted of diesel with the addition of biodiesel, lubricating oil and heavy fuel oil, respectively. The RR2019 samples were received as oil products, while the RR2018 and RR2020 samples were dichloromethane extracts. The crude oils used to prepare the MixCrude solution, *i.e.*, Miri Light (Malaysia), Bonny Light (Nigeria), Cabinda (Angola) and Ural (Russia), belong to the petroleum products database of *Instituto Hidrográfico*.

4.2.3. Sample preparation and GC-MS analysis

The sample extracts from RR2018, RR2019 and RR2020 were diluted as recommended by EN 15522-2 standard to produce chromatograms of Sp and SS extracts with close peak

abundances. The lack of linearity of GC-MS response can affect the ratio of the abundance of pairs of peaks with significantly different abundances values. The Sp, SS1 and SS2 extracts of RR2018 and RR2020 received by the laboratory, with concentrations of 10 mg/mL and 50 mg/mL of oil per extract volume, respectively, were diluted in dichloromethane to obtain Sp, SS1 and SS2 extracts of RR2018 at 0.8 mg/mL, and Sp, SS1 and SS2 extracts of RR2020 at 8.5 mg/mL, 8.0 mg/mL and 5.0 mg/mL, respectively. Since the Sp, SS1 and SS2 of RR2019 received by the laboratory were lubricating oils, the extracts for analysis were obtained as suggested in EN 15522-2 standard. The Sp, SS1 and SS2 extracts of RR2019, at 2.9 mg/mL, 3.5 mg/mL and 3.7 mg/mL of oil, respectively, were diluted by weighing a mass to a 10 mL volumetric flask adjusted with dichloromethane. All the sample extracts from the RR2018, RR2019 and RR2020 prepared were analysed by GC-MS, in replicate and sequentially (six injections of Sp and three injections of SS1 and SS2), with the instrumental conditions suggested by EN 15522-2. One microliter of each sample extract was injected by an ALS syringe of 10 μ L tapered, fixed needle, 23-26s/42/cone (Agilent Technologies, Santa Clara, USA) with a fast plunger and no pre- and post-injection dwell, in the on-column injection port operated 3 °C above oven temperature, and transferred to the chromatography column using helium (purity $\geq 99.999\%$) at a constant flow of 1.1 mL/min. The GC oven program employed was isothermal at 42 °C for 1.3 min, 320 °C at a rate of 5.5 °C/min and isothermal at 320 °C for 25 min. The MS operated with 70 eV electron impact, ion source at 230 °C, quadrupole at 150 °C and transfer line at 320 °C. The analytical data were collected with spectrum recording in selected ion monitoring mode (SIM) according to the fragments (m/z) presented in **Table C.1** of the **Annex C**.

A MixCrude solution, composed by Ural, Miri Light, Bonny Light and Cabinda crude oil extracts, at a volumetric formulation of 4+1+1+1, respectively, was prepared according to Rocha *et al.* (2022b). This solution allowed, in a single run, to evaluate the GC-MS performance and to set retention time windows in the processing method for the identification of all compounds and compounds' sets specified in EN 15522-2. The retention time drift, the changes in mass discrimination and the column resolution were checked, according to EN 15522-2, through the analysis of the MixCrude solution before and after the batch of each RR extracts.

4.2.4. Peak identification and quantification

Between one hundred and forty-five compounds or sets of compounds were analysed in the chromatograms of the Sp and SS (**Figure C.1** of the **Annex C**). Different compounds were identified and quantified in the various RR samples due to the compositional differences of the petroleum products. The compounds/sets of compounds' abbreviations and those quantified in each RR sample were listed in **Tables C.2** and **C.3** of the **Annex C**, respectively. The peak identification was performed by retention time, confirmation fragments and chromatographic patterns given by the literature (Faksness *et al.*, 2002; CEN, 2012; CEN, 2023). All chromatographic peaks in the ion chromatograms were manually revised (quantification fragments listed in **Table C.1** of the **Annex C**) with single peaks quantified by height and peaks' groups by area. The chromatographic peaks with a signal-to-noise ratio (S/N) below five were not considered (CEN, 2023).

4.2.5. Assessment of signal dispersion and weathering occurrence

The identification of a spill source becomes more reliable the greater the precision in the determination of the chromatographic signals and of the DR . Thus, an assessment of chromatographic signals and/or DR precision is required by the Nordtest and EN 15522-2 methodologies. Although the MCM approach for DR comparison is applicable regardless of the precision of the chromatographic signals, signals dispersion was evaluated to allow comparing the studied S-t, SC and MCM approaches.

Compounds partition or degradation (*e.g.*, evaporation, dissolution, biodegradation, and photo-oxidation) by exposure to environmental conditions affect the DR values and can lead to significant differences between the ratios observed in the Sp and SS composed of the same oil product. Weathering-affected ratios are inadequate for oil pattern comparison and, therefore, should not be considered in oil fingerprinting. Even though the identification of the weathering occurrence is challenging, the susceptibility of oil components to the different degradation processes is well documented (Wang *et al.*, 1999; Díez *et al.*, 2005; Wang *et al.*, 2005; DeMello *et al.*, 2007; CEN, 2012; Wang *et al.*, 2013a; Wang *et al.*, 2013b; Radović *et al.*, 2014; Zhang *et al.*, 2015; Malmborg, 2017; CEN, 2023) and can be applied to identify the most relevant weathering processes using tools described in Nordtest and EN 15522-2 methods. In the present study, both precision and weathering were assessed using Percentage Weathering (PW)-plots. Ratios, (A/H) , between the signal, A , of each studied oil compound and the signal, H , of a

normalizer oil compound known not to be significantly weathered, are determined in triplicate for Sp and SS (*i.e.*, $(A/H)_{Sp}$ or $(A/H)_{SS}$). Afterwards, the maximum (subscript “[MAX]”) and minimum (subscript “[MIN]”) of the triplicate determinations of $(A/H)_{Sp}$ and $(A/H)_{SS}$ are combined in ratios $(A/H)_{Sp|MIN}/(A/H)_{Sp|MAX}$ and $(A/H)_{SS|MIN}/(A/H)_{SS|MAX}$ and plotted, for instance, function of studied compound retention time, to control signals precision. If $(A/H)_{Sp|MIN}/(A/H)_{Sp|MAX}$ and $(A/H)_{SS|MIN}/(A/H)_{SS|MAX}$ is between 85% and 118%, the A signal precision is adequate to determine DR values. The ratio between mean A/H for Sp and SS ($(\overline{A/H})_{Sp}/(\overline{A/H})_{SS}$) are also plotted function of studied compound retention time to monitor their weathering. If $(\overline{A/H})_{Sp}/(\overline{A/H})_{SS}$ is outside 85% to 118% interval it can be concluded that the signal A is affected with weathering and should not be used in spill fingerprinting. In this work, DR formats A/B or $A/(A+B)$, where signals from two compounds, A and B , meeting previously specified requirements are studied (CEN, 2023). **Figures C.2 and C.3** of the **Annex C** shows the weathering assessment, by PW-plots, of $(\overline{A/H})_{Sp}/(\overline{A/H})_{SS}$ from RR2018, RR2019 and RR2020.

4.2.6. Diagnostic ratio determination

The EN 15522-2 standard specifies sets of diagnostic ratios, designated normative ratios (NR), specific for each oil type that, if respective signals are detected, have adequate precision and are not weathered, should be considered in oil fingerprinting. These ratios were selected from their discriminative power and robustness to weathering (CEN, 2023). Other diagnostic ratios, designated informative ratios (IR), can be considered to increase the robustness of the compositional comparison between samples and/or to provide additional information about the particularities of the sample’s composition. The NR and IR cover a wide range of compound classes (**Tables C.1 and C.2** of the **Annex C**), leading to a proper characterization of each oil product. In the present study, both the NR and IR were considered to define the fingerprint of each sample. **Table C.4** of the **Annex C** presents all the DR determined for oil pattern comparison between the Sp and the SS1 and SS2 of RR2018, RR2019 and RR2020 and lists the reason why some ratios were not considered. The exclusion of a DR is justified if at least one of the compounds that define the ratio is absent, affected by weathering, has a S/N lower than five or does not pass in the defined precision requirements. Out of 78 DR , 32 DR (19 NR and 13 IR), nine DR (seven NR and two IR) and nine DR (eight NR and one IR) indicated by the EN 15522-2 standard were considered in the RR2018, RR2019 and RR2020 samples,

respectively. Two ratio formats were tested, namely $A/(A+B)$ and A/B , to compare the developed MCM approach with the standardised Nordtest and EN15522-2 approaches, respectively. The $A/(A+B)$ format, being the numerator the chromatographic signal of a compound and the denominator the sum of the chromatographic signals of the same and another compound, avoids the division by a very low value and a wide range of DR values (Daling *et al.*, 2002, Faksness *et al.*, 2002). In contrast, the A/B format, with chromatographic signals of both compounds as numerator and denominator, is suggested by EN 15522-2 standard since if the RSD of both signals is smaller than 5%, the range of the difference of a pair of A/B should not be larger than 14% for 95% confidence level. This inference is based on the standard deviation propagation law and expansion to a 95% confidence level using a two factor ($14\% = 2 \cdot (0.05^2 + 0.05^2)^{1/2}$).

4.2.7. Diagnostic ratio agreement

The MCM approach was compared with the S-t and SC approaches using the DR management suggested by the Nordtest method and EN 15522-2 standard. The Nordtest and EN 15522-2 methodologies use different DR formats ($A/(A+B)$ and A/B) and indicate different replicate analyses of the Sp and SS (triplicate and duplicate determinations).

The comparison between two mean DR observed in the Sp ($\overline{DR}_{Sp}$) and in the SS ($\overline{DR}_{SS}$) by the S-t approach is based on the validity of the condition from **Equation 4.1**.

$$|\overline{DR}_{Sp} - \overline{DR}_{SS}| \leq t \cdot s_d \quad (4.1)$$

where s_d is the standard deviation of the difference of DR means determined by applying **Equation 4.2** and t is the t -value of the Student's t distribution for a certain confidence level (P), *i.e.*, 95% or 98% suggested by the Nordtest method, and $[\xi]$ degrees of freedom determined as the nearest integer of ξ calculated from **Equation 4.3** (Miller *et al.*, 2018).

$$s_d = \sqrt{\frac{s_{DRSp}^2}{n_{Sp}} + \frac{s_{DRSS}^2}{n_{SS}}} \quad (4.2)$$

$$\xi = \frac{\left(\frac{s_{DRSp}^2}{n_{Sp}} + \frac{s_{DRSS}^2}{n_{SS}}\right)^2}{\left(\frac{s_{DRSp}^4}{n_{Sp}^2 \cdot (n_{Sp} - 1)} + \frac{s_{DRSS}^4}{n_{SS}^2 \cdot (n_{SS} - 1)}\right)} \quad (4.3)$$

with n_{Sp} and n_{SS} as the number of replicates, and $s_{DR_{Sp}}$ and $s_{DR_{SS}}$ as the standard deviations of DR determined for the Sp and SS, respectively.

For the SC approach, the comparison between mean DR was based on the mean, $\overline{DR}_d$, of both means $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$ ($\overline{DR}_d = (\overline{DR}_{Sp} + \overline{DR}_{SS})/2$) using the condition of **Equation 4.4**.

$$|\overline{DR}_{Sp} - \overline{DR}_{SS}| \leq 0.14 \cdot \overline{DR}_d \quad (4.4)$$

If the conditions from **Equation 4.1** and **Equation 4.4** are valid, it is concluded that $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$ are equivalent by the S-t and SC approaches, respectively.

The alternative MCM approach resorts to the numerical simulation of a large number of values of each DR , for both Sp and SS, and consequently for the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$). This substantial number of ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) values allow to describe its exact probability distribution, as well as to estimate required distribution descriptors. Various percentiles ($P\chi^{th}$) of the DR differences were determined (namely the $P2.5$ and $P97.5$ and $P1$ and $P99$ that defined 95% and 98% confidence limits) to conclude about $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$ equivalence. If $P2.5 < 0 < P97.5$ and $P1 < 0 < P99$ it can be concluded that mean values are equivalent for 95% and 98% confidence level, respectively.

4.2.8. Confidence intervals of diagnostic ratio and total risk estimation

In the present work, a user-friendly MS-Excel spreadsheet, developed and made available by Rocha *et al.* (2022b), was used to obtain all the data for the comparison of the MCM, S-t and SC approaches. The MS-Excel spreadsheet is described in detail in Rocha *et al.* (2022b). This tool automatically implements the S-t, SC and MCM approaches for oil fingerprint comparison and estimates the total risk of true and false fingerprint equivalence claims. The tool allows an easy selection of the DR format and DR set used, and can process different numbers of replicate DR determinations (up to eight and three for each sample, *e.g.*, Sp and SS). The MCM approach is the reference for the evaluation of the other approaches since the MCM better describes the probabilistic reality of the variables under study. Two possible scenarios for DR comparison, according to the Nordtest method and EN 15522-2 standard requirements, were tested: triplicate or duplicate analysis for both Sp and SS associated with DR formats $A/(A+B)$ or A/B , respectively.

When samples with the same oil fingerprints are compared, the MS-Excel spreadsheet can calculate the total risks of true compositional equivalence claims (δ) by determining the number of simulated $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ sets meeting equivalence criteria. The δ are expected to vary between P^M (as M being the number of DR in the DR set, *i.e.*, 19.4% or 52.4% for samples RR2018 and 63.0% or 83.4% for samples RR2019 and RR2020) and P (95% or 98%) since all DR are not independent or perfectly correlated.

To guarantee a higher risk of true compositional claims, ω , the DR observed in Sp and SS1 were compared from two comparison trails (Rocha *et al.*, 2022b): in the first and second trials, the DR from Sp was estimated from different sets of replicate injections while the same replicate injections of SS1 were considered in both trials.

For the studied DR comparison scenarios, were run three separate simulations of δ and ω by the MCM, S-t and SC approaches of each Sp and SS1 pairs of the RR2018, RR2019 and RR2020 to assess the significance of the difference between δ and ω values. The t -test, after checking the equivalence of δ or ω variance, was performed for a 95% confidence level (Miller *et al.*, 2018). Additionally, the variation of δ with the number of DR of the DR set (*i.e.*, seven, 12, 22 and 27 DR) was evaluated using data from the Sp and SS1 pair of the RR2018 since it is the case with the highest number of DR used. The DR excluded from the reduced sets were randomly selected.

4.3. Results and discussion

The results and discussion are divided into the assessment of oil pattern equivalence by the studied three approaches in specified conditions, including the determination of total risks, the statistical comparison of total risks and the assessment of risk variation with the number of considered DR .

4.3.1. Comparison of criteria ranges

The DR comparison criteria defined by the S-t and SC approaches can be presented as **Equation 4.1** and **Equation 4.4** or by reporting the confidence limits for the DR difference $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ as $(0 \pm t \cdot s_d)$ or $(0 \pm 0.14 \cdot \overline{DR}_d)$, respectively. For the MCM approach, the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence limits were simulated by the MCM. Confidence intervals for 95%

and 98% confidence levels were estimated for both S-t and MCM. **Tables C.5 to C.11** of the **Annex C** present the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals estimated by the compared approaches for the pair Sp and SS1 (**Tables C.5 to C.9** of the **Annex C**) and Sp and SS2 (**Tables C.10 and C.11** of the **Annex C**) for the various RR. The confidence intervals of the S-t approach obtained for the three RR and the Nordtest scenario ($P = 95\%$ and 98%) are generally narrower than those obtained by the other approaches. However, for the same comparison scenario and the three RR, the SC confidence intervals are sometimes wider or narrower than the MCM ones. The SC confidence intervals obtained for the 32 *DR* determined in Sp vs. SS1 of the RR2018 (**Table C.5** of the **Annex C**) proved to be wider than the MCM for P of 98% , but those acquired for the nine calculated *DR* in Sp vs. SS1 of RR2019 and RR2020 (**Tables C.9 and C.10** of the **Annex C**, respectively) are wider than MCM for P of 95% and tend to be narrower than MCM for P of 98% . Additionally, it is noted distinct trends in the comparison of the MCM ($P = 98\%$) and SC confidence intervals amplitudes for the same *DR* determined both in RR2019 and RR2020 samples (*e.g.*, *DR33*, *DR34* and *DR37*) pointing to the specificity of each *DR* determined in different oil samples due to differences in abundances mean, dispersion and correlation of the chromatographic signals.

Considering the EN 15522-2 scenario, the same observation could be made verifying that most of the SC confidence intervals are wider than the MCM ($P = 95\%$), but for many *DR*, the SC confidence intervals are narrower than the MCM ($P = 98\%$). The opposite is observed for the RR2019 and RR2020 samples, with few exceptions. In most cases, the confidence intervals estimated by MCM ($P = 95\%$ and 98%) tend to be wider than S-t ($P = 95\%$ and 98%). The difference in confidence limits estimated by the S-t and MCM approaches is justified by the fact that the S-t takes the observed dispersion of the *DR* assuming their normal distribution, while the MCM takes the dispersion of abundance values and their correlation that can simulate not normally distributed *DR*. In brief, the observations discussed are in line with the conclusions made by the authors in a previous study applied to a mixture of different crude oil extracts prepared in the laboratory (Rocha *et al.*, 2022b).

4.3.2. Comparison of oil pattern equivalence claims

For each RR, the SS1 and SS2 were compared with the respective Sp by using the S-t, SC, and MCM approaches to check their ability to confirm the equivalence or difference between oil patterns. The oil pattern equivalence is assumed when a relevant set of *DR* means observed in

the Sp vs. SS are considered equivalent, *i.e.*, when there is an indication that the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals include zero. Even when the mode of the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ is not zero due to distribution heterogeneity, the target zero difference represents no difference case.

It is noted that for accurately defined $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ limits for 95% or 98% confidence level, on average, one in 20 or 50 comparisons should indicate *DR* mean differences. In order to avoid affecting oil pattern equivalence claims with such likely occurrences, a second mean *DR* comparison trial is performed that should involve the comparison of mean *DR* estimated from independent GC-MS injections both for Sp and SS. In the two trials of this work, the *DR* from Sp were estimated from different replicate injections, while the same replicate injection from SS1 was considered, reducing the total risk of true equivalent claims based on Sp and SS1 independent injections. It was assessed the adequacy of this simplification.

The oil pattern equivalence is assumed when, in the two mean *DR* comparison trials of the selected *DR* set, for each and all *DR*, the SS and Sp *DR* means are equivalent in at least one comparison trial. **Tables C.5 to C.11** of the **Annex C** present, for the various RR, the confidence intervals of $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ estimated by the MCM, S-t and SC approaches for the first and second trials of the pair Sp and SS1 (**Tables C.5 to C.9** of the **Annex C**) and only for a single trial of the pair Sp and SS2 (**Tables C.10 and C.11** of the **Annex C**). These tables also identify the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals that do not include zero indicating *DR* difference, as well as the percentage of non-equivalent *DR* (τ). As expected, the results show that the range of the estimated $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals impacts the *DR* comparisons with narrower confidence intervals producing less equivalent *DR*. For Sp vs. SS1 of the RR2019 (**Table C.7** of the **Annex C**), the first trial was enough to prove the equivalence of oil patterns by all comparison approaches. In this case, a second trial from independent replicate injections is not required to claim compositional equivalence between the compared samples. For the *DR* comparison of Sp vs. SS1 of RR2018 and RR2020 (**Tables C.5 and C.8** of the **Annex C**) a second trial is required. With the exception of Sp vs. SS1 of RR2018 in the EN 15522-2 scenario, which identifies one non-equivalent *DR*, the SC assigns compositional equivalence between Sp and SS1 for both scenarios, even from a single comparison trial (**Tables C.5, C.6, C.8 and C.9** of the **Annex C**), suggesting *DR* comparison criteria is too permissible. As for the MCM and S-t, some different *DR*, for 98% confidence level and particularly for the Nordtest scenario, are observed in the first Sp vs. SS1 comparison trial of RR2018 (**Table C.5** of the **Annex C**), with the S-t approach identifying more unequal *DR* than

the MCM approach. The non-equivalent *DR* identified in the first trial were not confirmed in the second trial, where the mismatched *DR* varied with the comparison scenario and number of ratios in the *DR* set, proving the oil pattern equivalence by the MCM and S-t, with the exception of RR2018 in the Nordtest scenario where S-t does not declare compositional equivalence between Sp and SS1. Although in the comparison of the nine *DR* determined in Sp vs. SS1 of the RR2020, MCM, S-t and SC assert the equivalence between oil patterns when the EN 15522-2 scenario is employed even in the first comparison trial (τ of 0%) (**Table C.8** of the **Annex C**), the second comparison trial is required to assign compositional equivalence by S-t ($P = 98\%$) in the Nordtest scenario (**Table C.9** of the **Annex C**). Unsurprisingly, the statement of compositional equivalence between samples is more easily recognised when the sample fingerprint is characterised by a lower number of *DR*. In addition, the Nordtest scenario tends to produce stricter criteria than the EN 15522-2 scenario in MCM and S-t compositional equivalence assessments due to the larger number of degrees of freedom of data used in the Nordtest scenario.

The ability of the assessed oil pattern comparison criteria to correctly conclude about the non-equivalence of different oil patterns was also evaluated, based on the number of mismatched *DR*, by comparing the *DR* observed for the Sp and SS2 of RR2018 and RR2020 (**Tables C.10** and **C.11** of the **Annex C**). This evaluation was not performed for the Sp vs. SS2 of RR2019 since were quantified only four chromatographic signals (**Table C.3** of the **Annex C**) not relevant to Sp pattern comparison. As expected, all *DR* comparison approaches identified more non-equivalent *DR* for Sp vs. SS2 (**Tables C.10** and **C.11** of the **Annex C**) than for Sp vs. SS1 (**Tables C.5**, **C.6**, **C.8** and **C.9** of the **Annex C**). The S-t and MCM distinguished more differences between *DR* in the Nordtest scenario than in the EN 15522-2 scenario, observing the opposite for the SC approach. The MCM ($P = 98\%$) showed to distinguish differences between *DR* (τ of 50.0% and 43.8% in RR2018, and 62.5% and 50.0% in RR2020 for Nordtest and EN 15522-2 scenarios, respectively) in percentages similar or higher to those by S-t ($P = 98\%$) (τ of 31.3% in RR2018 and 50.0% in RR2020) in the EN 15522-2 scenario and by SC in both scenarios (τ of 15.6% and 40.6% in RR2018, and 50.0% and 62.5% in RR2020, for Nordtest and EN 15522-2 scenarios, respectively). Although S-t recognises a greater number of different *DR* in the compared Sp and SS2, the same is observed in Sp vs. SS1, questioning the robustness of compositional equivalence claims by this approach. This performance of the S-t approach can be explained not only by the narrower *DR* comparison criteria observed and discussed in this study but also by the deviations from the normality of the *DR* and

$(\overline{DR}_{Sp} - \overline{DR}_{SS})$ probability distributions, previously identified by the authors (Rocha *et al.*, 2022a,b). The wider SC comparison criteria already proved to lead to a non-equivalence claim supported in fewer *DR* mismatches than for the other approaches, *e.g.*, τ of 15.6% for the SC approach in comparison to τ of 50.0% and 68.8% for MCM and S-t approaches ($P = 98\%$ and Nordtest scenario of RR2018).

It can be concluded that, in most of the cases, the approaches asserted that the oil patterns of the pair Sp and SS2 are not equivalent from a single trial because the number of observed *DR* mean mismatches is much higher than compatible with oil pattern equivalence. Assuming mean *DR* are independent and accurately compared for a 98% confidence level, using parameters with one or two degrees of freedom, in 98% of comparisons (*i.e.*, 98th percentile) of nine and 32 *DR*, the number of mean *DR* considered different is not larger than one or three, respectively. Therefore, if more than one and three mismatches are observed for nine and 32 *DR*, the second trial does not need to be performed.

In future work, authors will quantify the risk of true oil pattern divergence claims.

4.3.3. Statistical comparison of total risks

Since the estimated risks, δ and ω , for the studied *DR* comparison approaches and oil pattern comparison scenarios vary with the simulation run, it was estimated the δ and ω precision to be subsequently used to assess the statistical relevance of differences in estimated δ and ω values. The risks vary for the S-t and SC approaches because the MCM simulated distribution is the reference for risk estimates.

Three simulations of δ and ω for each comparison condition were performed to estimate the mean δ ($\bar{\delta}$) and the mean ω ($\bar{\omega}$), as well as the respective variances. The δ and ω estimated for the Sp vs. SS1 of the RR express the variability of both risks with the number and characteristics of the different *DR* considered dependent on the type of oil and spill scenario. Additionally, the impact of *DR* number on δ was assessed using data from the same spill scenario of RR2018 considering sets of 32, 27, 22, 17, 12, and seven *DR* with the exclusion of five *DR* sequentially and randomly in each set.

4.3.3.1. Oil pattern comparison methods

Table 4.1 shows the comparison of the estimated δ by MCM with those found by S-t and SC for the first Sp vs. SS1 comparison trial of the RR2018 (32 *DR*), RR2019 (nine *DR*) and RR2020 (nine *DR*) considering the Nordtest and EN 15522-2 scenarios.

The δ obtained in different simulations showed a very low dispersion, with RSD varying between 0.05% and 1.8% and the highest RSD being found for the SC when the EN 15522-2 scenario is applied. For the Nordtest scenario, the δ estimated for S-t and SC are statistically lower than those obtained by MCM ($P = 98\%$). For the EN 15522-2 scenario, the δ obtained for MCM is significantly higher than that estimated for SC, but equivalent than the achieved by S-t. All estimated $\bar{\delta}$ for S-t and MCM are, as expected, between P^M and P (with M being the number of ratios in the *DR* set), *i.e.*, 19.3% to 95.0% or 52.4% to 98.0% for RR2018, and 63.0% to 95.0% or 83.4% to 98.0% for RR2019 and RR2020, respectively, except δ estimated by S-t for RR2019 and RR2020 using the Nordtest scenario and 98% confidence level. This exception indicates that the confidence level of the *DR* comparison criteria estimated by S-t for some *DR* is overestimated, most likely due to deviations from the normality of the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ probability distributions. For the SC approach, the δ estimated could not be compared with these probability limits, *i.e.*, P^M and P , because this *DR* comparison criterion is not set for a specific confidence level. However, it should be noted that for the RR2018, the SC method produces a δ lower than the most pessimistic one for S-t and MCM for independent *DR* compared for a 95% confidence level (*e.g.*, 18.3%). This low δ is the result of frequent mismatches (between 30% and 50%) of specific *DR* of the studied set (*e.g.*, *DR03*, *DR09*, *DR12* and *DR21*).

In order to increase the risk of a true compositional equivalence claim, it was considered that compositional equivalence should be supported on two comparison trials, as described previously. This risk should be at least 98% to be considered adequate.

Table 4.1. Comparison between the mean of three total risks estimates of true compositional equivalence claim based on one comparison trial ($\bar{\delta}$), by the SC approach, and by the MCM and S-t approaches for 95% and 98% of confidence levels, using the Nordtest and EN 15522-2 scenarios, for the Round Robin Tests (RR) 2018, 2019 and 2020.

RR	Number of <i>DR</i>	Parameter	MCM		S-t		SC	t_{exp}	t_{cr}
			95%	98%	95%	98%			
Nordtest scenario									
2018	32	$\bar{\delta}$ (%)	83.3	93.4	62.3	78.7	91.5	-	-
		RSD (%)	0.11	0.37	0.49	0.19	0.35	-	-
		$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (95%)	-	-	-	-	-	115 (>)	2.78
		$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (98%)	-	-	-	-	-	68.2 (>)	2.78
		$\bar{\delta}_{\text{MCM}}$ (95%) vs. $\bar{\delta}_{\text{SC}}$	-	-	-	-	-	42.0 (<)	2.78
		$\bar{\delta}_{\text{MCM}}$ (98%) vs. $\bar{\delta}_{\text{SC}}$	-	-	-	-	-	6.98 (>)	2.78
2019	9	$\bar{\delta}$ (%)	86.1	94.4	67.8	81.5	85.5	-	-
		RSD (%)	0.16	0.13	0.43	0.28	0.33	-	-
		$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (95%)	-	-	-	-	-	97.6 (>)	2.78
		$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (98%)	-	-	-	-	-	87.4 (>)	2.78
		$\bar{\delta}_{\text{MCM}}$ (95%) vs. $\bar{\delta}_{\text{SC}}$	-	-	-	-	-	3.17 (>)	2.78
		$\bar{\delta}_{\text{MCM}}$ (98%) vs. $\bar{\delta}_{\text{SC}}$	-	-	-	-	-	50.3 (>)	2.78
2020	9	$\bar{\delta}$ (%)	87.2	94.99	66.8	81.1	89.7	-	-
		RSD (%)	0.19	0.058	0.38	0.37	0.22	-	-
		$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (95%)	-	-	-	-	-	118 (>)	2.78
		$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (98%)	-	-	-	-	-	78.8 (>)	2.78
		$\bar{\delta}_{\text{MCM}}$ (95%) vs. $\bar{\delta}_{\text{SC}}$	-	-	-	-	-	17.0 (<)	2.78
		$\bar{\delta}_{\text{MCM}}$ (98%) vs. $\bar{\delta}_{\text{SC}}$	-	-	-	-	-	45.2 (>)	2.78
EN 15522-2 scenario									
2018	32	$\bar{\delta}$ (%)	82.9	93.2	81.8	93.3	18.3	-	-
		RSD (%)	0.35	0.18	0.51	0.22	1.8	-	-
		$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (95%)	-	-	-	-	-	4.02 (>)	2.78
		$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (98%)	-	-	-	-	-	1.03 ($\approx$)	2.78
		$\bar{\delta}_{\text{MCM}}$ (95%) vs. $\bar{\delta}_{\text{SC}}$	-	-	-	-	-	257 (>)	2.78
		$\bar{\delta}_{\text{MCM}}$ (98%) vs. $\bar{\delta}_{\text{SC}}$	-	-	-	-	-	357 (>)	2.78
2019	9	$\bar{\delta}$ (%)	85.7	94.36	86.3	94.8	54.6	-	-
		RSD (%)	0.20	0.049	0.49	0.32	1.2	-	-
		$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (95%)	-	-	-	-	-	2.16 ($\approx$)	2.78
		$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (98%)	-	-	-	-	-	2.30 ^(*) ($\approx$)	4.30 ^(*)
		$\bar{\delta}_{\text{MCM}}$ (95%) vs. $\bar{\delta}_{\text{SC}}$	-	-	-	-	-	77.3 (>)	2.78
		$\bar{\delta}_{\text{MCM}}$ (98%) vs. $\bar{\delta}_{\text{SC}}$	-	-	-	-	-	102 ^(*) (>)	4.30 ^(*)
2020	9	$\bar{\delta}$ (%)	87.2	94.9	83.9	93.7	72.2	-	-
		RSD (%)	0.89	0.36	0.73	0.38	1.1	-	-
		$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (95%)	-	-	-	-	-	5.84 (>)	2.78
		$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (98%)	-	-	-	-	-	4.11 (>)	2.78
		$\bar{\delta}_{\text{MCM}}$ (95%) vs. $\bar{\delta}_{\text{SC}}$	-	-	-	-	-	23.9 (>)	2.78
		$\bar{\delta}_{\text{MCM}}$ (98%) vs. $\bar{\delta}_{\text{SC}}$	-	-	-	-	-	47.0 (>)	2.78

RSD – Relative standard deviation.

 t_{exp} – estimated t value as the ratio between the absolute difference of $\bar{\delta}$ and the standard deviation of the difference estimated from statistically equivalent or different (*) standard deviations of compared $\bar{\delta}$. t_{cr} – critical value of the Student's t for 95% confidence level. Compared $\bar{\delta}$ are statistically different ($\bar{\delta}_{\text{MCM}}$ less than $\bar{\delta}_{\text{S-t}}$ or $\bar{\delta}_{\text{SC}}$, <, or $\bar{\delta}_{\text{MCM}}$ greater than $\bar{\delta}_{\text{S-t}}$ or $\bar{\delta}_{\text{SC}}$, >) for 95% confidence level ($t_{\text{exp}} > t_{\text{cr}}$), otherwise are statistically equivalent ($\approx$).(*) $t_{\text{cr}} = 4.30$ used for $\bar{\delta}$ comparisons with different standard deviations.

Table 4.2 presents the $\bar{\omega}$ and their comparison estimated for the studied spills, and comparison approaches and scenarios. **Table 4.3** presents the comparison of $\bar{\omega}$ with a minimum admissible value of 98%. The ω found for S-t and SC tend to be lower than those estimated for MCM. This risk is, for all approaches and the two scenarios and RR, $> 98\%$, with the exception of the ω achieved by S-t in both RR and in the Nordtest scenario, and the ω obtained by SC in the RR2018 for the EN 15522-2 scenario. These exceptions show that the S-t and SC approaches lead to lower quality identifications compared to MCM, even when under the comparison conditions for which they were designed, *i.e.*, Nordtest and EN 15522-2, respectively.

Table 4.2. Comparison between the mean of three total risks estimates of true compositional equivalence claim based on two comparison trials ($\bar{\omega}$), by the SC approach, and by the MCM and S-t approaches for 98% of confidence level, using the Nordtest and EN 15522-2 scenarios, for the Round Robin Tests (RR) 2018 and 2020.

RR	Number of <i>DR</i>	Parameter	MCM	S-t	SC	t_{exp}	t_{cr}
			98%	98%			
Nordtest scenario							
2018	32	$\bar{\omega}$ (%)	100	97.02	99.96	-	-
		RSD (%)	0.010 ^(‡)	0.052	0.015	-	-
		$\bar{\omega}_{\text{MCM}}$ vs. $\bar{\omega}_{\text{S-t}}$	-	-	-	101 (>)	2.78
		$\bar{\omega}_{\text{MCM}}$ vs. $\bar{\omega}_{\text{SC}}$	-	-	-	3.48 (>)	2.78
2020	9	$\bar{\omega}$ (%)	100	97.9	99.86	-	-
		RSD (%)	0.010 ^(‡)	0.32	0.061	-	-
		$\bar{\omega}_{\text{MCM}}$ vs. $\bar{\omega}_{\text{S-t}}$	-	-	-	11.5 ^(*) (>)	4.30 ^(*)
		$\bar{\omega}_{\text{MCM}}$ vs. $\bar{\omega}_{\text{SC}}$	-	-	-	3.82 (>)	2.78
EN 15522-2 scenario							
2018	32	$\bar{\omega}$ (%)	100	99.8	91.5	-	-
		RSD (%)	0.010 ^(‡)	0.11	0.10	-	-
		$\bar{\omega}_{\text{MCM}}$ vs. $\bar{\omega}_{\text{S-t}}$	-	-	-	3.76 ^(*) ($\approx$)	4.30 ^(*)
		$\bar{\omega}_{\text{MCM}}$ vs. $\bar{\omega}_{\text{SC}}$	-	-	-	157 ^(*) (>)	4.30 ^(*)
2020	9	$\bar{\omega}$ (%)	100	99.76	98.5	-	-
		RSD (%)	0.010 ^(‡)	0.038	0.15	-	-
		$\bar{\omega}_{\text{MCM}}$ vs. $\bar{\omega}_{\text{S-t}}$	-	-	-	10.5 (>)	2.78
		$\bar{\omega}_{\text{MCM}}$ vs. $\bar{\omega}_{\text{SC}}$	-	-	-	17.3 ^(*) (>)	4.30 ^(*)

RSD – Relative standard deviation.

t_{exp} – estimated t value as the ratio between the absolute difference of $\bar{\omega}$ and the standard deviation of the difference estimated from statistically equivalent or different (*) standard deviations of compared $\bar{\omega}$.

t_{cr} – critical value of the Student's t for 95% confidence level. Compared $\bar{\omega}$ are statistically different ($\bar{\omega}_{\text{MCM}}$ greater than $\bar{\omega}_{\text{S-t}}$ or $\bar{\omega}_{\text{SC}}$, >) for 95% confidence level ($t_{\text{exp}} > t_{\text{cr}}$) otherwise are statistically equivalent ($\approx$).

(*) $t_{\text{cr}} = 4.30$ used for $\bar{\omega}$ comparisons with different standard deviations.

([‡]) A RSD of 0.010% was assumed for the statistical comparison purpose since the estimated ω in the three simulations was the same (100%).

Table 4.3. Comparison of the mean of three total risks estimates of true compositional equivalence claim based on two comparison trials ($\bar{\omega}$), by the SC approach, and by the MCM and S-t approaches for 98% of confidence levels, using the Nordtest and EN 15522-2 scenarios, for the Round Robin Tests (RR) 2018 and 2020, with a minimum risk estimate of 98%.

RR	Number of <i>DR</i>	Parameter	MCM	S-t	SC
			98%	98%	
Nordtest scenario					
2018	32	$\bar{\omega}$ (%)	100	97.02	99.96
		RSD (%)	0.010 ($\S$)	0.052	0.015
		t_{exp}	346 (>)	33.9 (<)	222 (>)
		t_{cr}	4.30	4.30	4.30
2020	9	$\bar{\omega}$ (%)	100	97.9	99.86
		RSD (%)	0.010 ($\S$)	0.32	0.061
		t_{exp}	346 (>)	0.461 ($\approx$)	52.8 (>)
		t_{cr}	4.30	4.30	4.30
EN 15522-2 scenario					
2018	32	$\bar{\omega}$ (%)	100	99.8	91.5
		RSD (%)	0.010 ($\S$)	0.11	0.10
		t_{exp}	346 (>)	28.6 (>)	120 (<)
		t_{cr}	4.30	4.30	4.30
2020	9	$\bar{\omega}$ (%)	100	99.76	98.5
		RSD (%)	0.010 ($\S$)	0.038	0.15
		t_{exp}	346 (>)	80.7 (>)	5.49 (>)
		t_{cr}	4.30	4.30	4.30

RSD – Relative standard deviation.

 t_{exp} – estimated t value as the ratio between the absolute difference of $\bar{\omega}$ and 98%, and the standard deviation of $\bar{\omega}$. t_{cr} – critical value of the Student's t for 95% confidence level. Compared $\bar{\omega}$ are statistically different (> 98%, >, or < 98%, <) for 95% confidence level ($t_{\text{exp}} > t_{\text{cr}}$) otherwise are statistically equivalent to 98% ($\approx$).(*) A RSD of 0.010% was assumed for the statistical comparison purpose since the estimated ω in the three simulations was the same (100%).

4.3.3.2. Variation with diagnostic ratio number

The results presented in **Table 4.1** for the comparisons between Sp and SS1 of RR2018, RR2019 and RR2020, already demonstrate a reduction of δ with the increase of the number of ratios in the *DR* set. **Figure 4.1** shows the variation of δ with the number of ratios in the *DR* set for the RR2018, estimated by MCM and S-t, and by MCM and SC under Nordtest and EN 15522-2 scenarios, respectively.

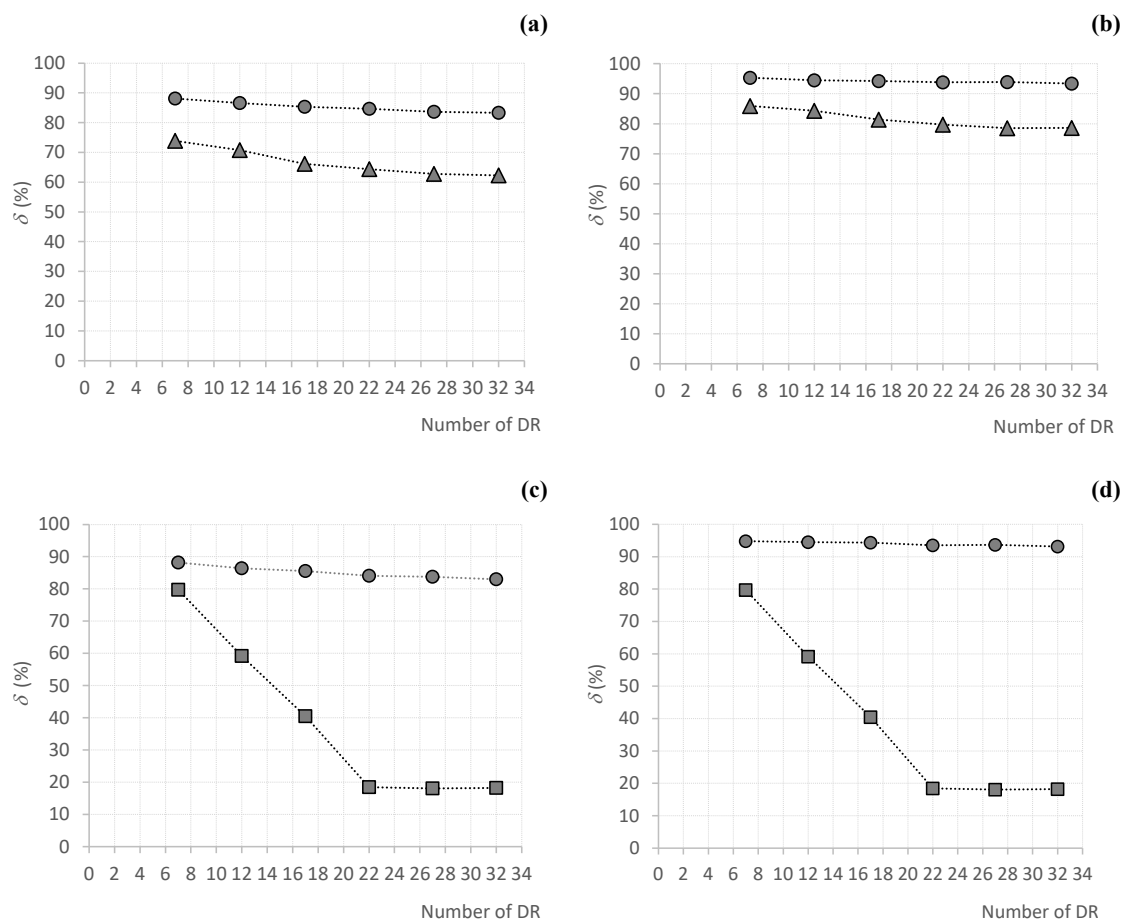


Figure 4.1. Variation of the total risk of true compositional equivalence claim between samples based on one comparison trial (δ) with the number of diagnostic ratios for the RR2018: (a) MCM vs. S-t ($P = 95\%$) and (b) MCM vs. S-t ($P = 98\%$), using ratio format $A/(A+B)$ and triplicate injections for both spill sample and suspected source sample 1 (Nordtest scenario), and (c) MCM ($P = 95\%$) vs. SC and (d) MCM ($P = 98\%$) vs. SC using ratio format A/B and duplicate of injections for both spill sample and suspected source sample 1 (EN 15522-2 scenario). ● MCM, ▲ S-t and ■ SC.

Visualising **Figure 4.1**, it is observed that δ estimated by MCM are higher than those estimated by S-t and SC, regardless of the scenario and the number of ratios in the *DR* set. In addition, δ shows a reduction with the increase of the number of ratios even though δ varies for MCM only 5% and 2%, for P of 95% and 98%, respectively. The same is observed for S-t applied to the Nordtest scenario, with a slightly more pronounced variation of 12% and 7% ($P = 95\%$ and 98%, respectively), and for SC applied to the EN 15522-2 scenario, with an abrupt variation of 62%. However, certain stability of δ is notorious, especially for SC and S-t, for *DR* sets with 22 or more ratios, with δ changing only 0.2% for SC and 2% and 1% for S-t and P of 95% and 98%, respectively. This may indicate that *DR* sets with a large number of ratios may not increase the δ , suggesting that there is no relevant benefit in assessing > 22 *DR*.

4.4. Conclusions

The performance advantages of the MCM approach over the other approaches for comparing oil fingerprints are notorious even when the S-t and SC methods are used considering the comparison conditions regarding the *DR* algorithm and the number of replicate *DR* determinations defined for these approaches. Only the MCM approach guarantees oil fingerprints comparison with probabilities of true equivalent composition claims above 98%. Although the S-t and SC approaches do not specify the need for performing two independent *DR* comparison trials, this is necessary, at least for the S-t approach and the MCM approach, which achieves a statistically sound control of mean *DR* comparisons. The studied application of the developed MCM method to real oil spill cases proves that spill and source differences do not affect comparison performance substantially if weathered compounds are excluded from the comparison. This research also suggests that identification quality does not significantly improve when supported on > 22 *DR*, although this threshold must be further tested. The only disadvantages of the MCM approach attributed to simulation complexity can be easily overcome by using user-friendly software such as the one developed by Rocha *et al.* (2022b).

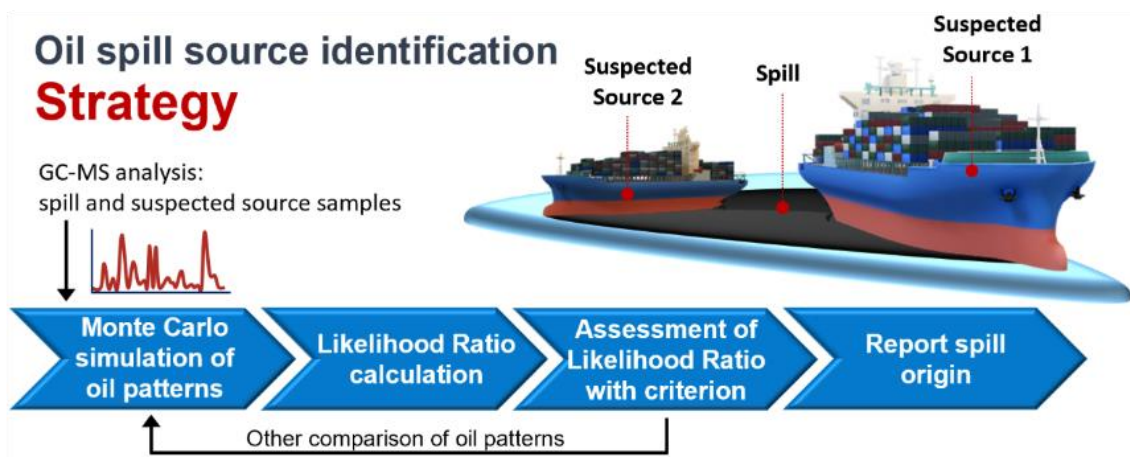
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5. Sound uncertainty-based strategy for oil spill source identification



Abstract

Oil spills are frequent and a major environmental threat, whether they are massive or small. Therefore, authorities and experts have developed analytical chemistry tools to identify spill sources and address these illegal acts by comparing oil patterns obtained by Gas Chromatography-Mass Spectrometry analysis of the spill (Sp) and suspected sources (SS) samples. Several methodologies have proposed different balances between data processing complexity and reliability. Supported by the accessibility and validity of Microsoft Excel spreadsheets, an alternative, accurate, and user-friendly tool was developed for spill source identification based on Monte Carlo Method (MCM) simulation of correlated oil components expressed by abundance ratio (*DR*). However, the statistical control of various *DR* and the degree of similarity of samples' compositions, at defined confidence levels, impact the probability of true and false compositional equivalence claim of Sp and SS becoming a challenge to recognise the offender. This work not only compares the MCM and the conventional approaches allowing to highlight the limitations that result in evidence with greater uncertainty, but also offers a statistically sound strategy that manages the probabilities of a compositional equivalence claim assessing the ability to distinguish competing spill sources and reporting the most likely polluting source with reduced uncertainty. A decision chart proposed, based on objective and statistically sound criteria, indicates the performance of consecutive *DR* comparison trials if necessary. The target values established for the probability of compositional equivalence claim of the Sp and the first and second most likely SS ($\geq 95.0\%$ and $\leq 0.50\%$, respectively) provide to forensic experts' sound evidence to be presented in court (likelihood ratio ≥ 190). This work represents a significant breakthrough in comparing complex chemical oil patterns.

Keywords: Evidence interpretation; Likelihood ratio; Oil fingerprinting; Oil spills; True and false results rate

5.1. Introduction

Forensic science frequently compares items to check if they are of the same origin. Subsequently, the findings of the experts are used in court as evidence to support criminal responsibility for the illegal act. In oil spill source identification, the evidence is presented as the degree of compositional similarity, established through chemical analysis of samples collected in the spill and in suspected sources of its origin. The Nordtest (Daling *et al.*, 2002; Faksness *et al.*, 2002) and the EN 15522-2 methods (CEN, 2023) are two analytical approaches that have been used to compare oil patterns from relevant samples. Both use a set of ratios between abundances of oil-discriminating compounds (A and B), designated diagnostic ratios (DR), to determine the oil pattern. However, these methods compare the oil patterns employing different DR comparison conditions and criteria: (1) Nordtest: triplicate analysis, DR format $A/(A+B)$ and Student's t statistics (S-t) assuming normally distributed DR , and (2) EN 15522-2: duplicate analysis, DR format A/B and a maximum relative difference of 14% (single criterion, SC). The Monte Carlo Method (MCM) has been used in different situations to solve analytical issues, *e.g.*, to improve the identification of compounds by chromatographic techniques (Bettencourt da Silva, 2016; Salgueiro and Bettencourt da Silva, 2025), to evaluate meaningful variations, trends and correlation among contaminants levels and physical-chemical parameters in environmental systems (Borges *et al.*, 2023; Morgado *et al.*, 2023), and to assess a medicine quality (Martins and Lourenço, 2024), the total risk of false conformity decisions (Oliveira and Lourenço, 2021a) and the conformity analysis by data reconciliation (Oliveira and Lourenço, 2021b). Thus, more recently, Rocha *et al.* (2022a,b, 2023) proved that identification reliability in oil spill source identification can be improved by MCM simulation of correlated ion abundances and their ratios that can significantly deviate from normality. Since each M assessed DR from samples is compared for P confidence level, the probability of true compositional equivalence claim based on the equivalence of all DR varies between P^M and P for independent or perfectly correlated DR . The probability of true oil patterns equivalence claim is increased by performing two DR comparison trials based on additional sample injections when equivalence between each DR is considered if indicated in at least one trial.

After overcoming the difficulty of the comparison of oil patterns, it is necessary to embrace the reporting of finding in court in an intelligible manner. Difficulties can arise when presenting evidence due to the complexity and quantity of compositional data from the spill and various suspected sources. In general, and at last, a sample from a potential source (SS) is compared with the spill sample (Sp), aiming to assess if it is possible to gather additional independent

evidence of the suspicion. Spill source identification is hampered by the similarity of competing spill sources and the weathering of the spilt oil.

Bayesian inference can be used in court to determine the probability of guilt or innocence based on the findings presented by forensic scientists. Thus, the evidence (E) has a value (*i.e.*, probative value) that modifies the prior probability to a posterior probability of guilt or innocence (Lucy, 2012; Thompson *et al.*, 2018). Presenting the probative value is the responsibility of the forensic scientist, who does it by reporting probabilities that express the uncertainty associated with claiming a specific spill source (Vergeer *et al.*, 2014; ENFSI, 2015). These probabilities are based on data quality, training and experience of forensic scientists that sets the identification criteria, the case-specific information and the propositions (ENFSI, 2015). Objective identification criteria should be set to avoid analyst's subjectivity and arbitrariness in results interpretation.

The determination of likelihood ratios (LR) is a way of presenting some information on the strength of the evidence obtained by forensic laboratories (ENFSI, 2015; Thompson *et al.*, 2018) and is already recommended by the EN 15522-2 standard. The LR is the ratio between the probabilities of observing evidence of prosecutor's claim given that the prosecutor (H_p) and the defence (H_d) hypothesis are true (**Equation 5.1**):

$$LR = \frac{P(E|H_p)}{P(E|H_d)} \quad (5.1)$$

In oil spill origin assessment, E are obtained from DR comparison, and H_p and H_d represent the cases where the oils present in the assessed SS and Sp are or are not the same, respectively. Typically, the H_p is supported on the most likely spill source (SS_α) and H_d represent an alternative spill source (SS_γ) that compete with the former for spill origin attribution. The greater the LR value, greater is the ability to distinguish SS_α from SS_γ . However, a large LR can be observed from relevant match difference between Sp vs. SS_α and Sp vs. SS_γ , when the match Sp vs. SS_α is rather low. Therefore, the characterisation of the strongness of spill origin claim to be SS_α , requires the determination of the match Sp vs. SS_α and the LR of competing spill sources.

If the prior probability of a reliable detection of the oil spill origin ($P(H_p)$) is known from the success rate of previous oil spill forensics (*e.g.*, in 70% of previous investigations, it was possible to identify the oil spill correctly, $P(H_p) = 0.70$), the LR can be converted in the

probability of the claimed oil spill origin being correct given the E presented by the forensic scientist. The probability of prosecutor's claim being correct given collected GC-MS evidences ($P(H_p|E)$) (**Equation 5.2**), known as the posterior probability in a Bayesian framework (Bettencourt da Silva and Ellison, 2021), is the pursued information instead of the probability of observing a specific experimental evidence given an hypothesis ($P(E|H_p)$ or $P(E|H_d)$). Therefore, the determination of $P(H_p|E)$ requires anticipating the probability of being identified the spill origin even before the analysis.

$$P(H_p|E) = \frac{\left(\frac{P(H_p)}{1 - P(H_p)}\right) \cdot LR}{\left(\frac{P(H_p)}{1 - P(H_p)}\right) \cdot LR + 1} \quad (5.2)$$

The difficulty of determining $P(H_p)$ makes the use of LR and their “verbal equivalent” more common in a forensic context (Nordgaard *et al.*, 2012).

This work describes a statistically sound and optimised strategy to identify the origin of an oil spill by quantifying the match between the oil patterns in the spill and most the likely spill source, as well as for distinguishing the various competing possible spill sources. Target criteria for the agreement between oil patterns observed in the Sp and SS and for the difference between competing SS are defined for reporting conclusive oil spill origin. The developed strategy involves using one or additional oil pattern comparison trials to improve identification quality if needed. It is compared the identification performance when the identification strategy is feed with duplicate or triplicate GC-MS signals, two DR formats are employed (Nordtest method and EN 15522-2 standard), and three DR comparison algorithms are considered (S-t, SC and MCM). Results from the participation in an international Round Robin Test (RR) promoted by the Oil Spill Identification Network of Experts within the Bonn Agreement (Bonn-OSINet) were used for the assessment of the identification strategies in a diversity of identification challenges.

5.2. Material and methods

5.2.1. Equipment

An eVol XR hand-held automated analytical syringe of 1000 μL (SGE Analytical Science, Victoria, Australia), calibrated annually and internally verified every six months, was used to

dilute the extracts of the Sp and SS. The crude oil extracts were obtained by weighing an oil portion using a Mettler PE1600 balance (Mettler, Greifensee, Switzerland) calibrated every two years and internally inspected every two weeks, a Heidolph Reax Top vortex mixer (Heidolph, Schwabach, Germany) to stir the oil with the extractant, and a Thermo Heraeus Megafuge 1.0 centrifuge (Thermo Fisher Scientific Inc, Langenselbold, Germany) to separate the undissolved solid phase from the liquid extract.

The instrumental analysis was carried out by a Gas Chromatograph (6890N series) paired with a Mass Spectrometer detector (5975B series) (GC-MS) with an automated injection performed by an auto-sampler (7683B series), all provided by Agilent Technologies. The equipment operated with a deactivated fused silica capillary pre-column, with a 0.53 mm internal diameter and 0.5 m length (Agilent Technologies, Santa Clara, USA), connected to the instrument's EPC cool on-column injection port, followed by a DB-5ms coated capillary column (non-polar phenyl arylene polymer capillary column virtually equivalent to (5%-phenyl)-methylpolysiloxane; 60 m length $\times$ 0.25 mm ID $\times$ 0.25 μ m film thickness) (Agilent Technologies, Santa Clara, USA) coupled to the Mass Spectrometer detector. All the GC-MS system was controlled by Agilent Technologie's Mass Selective Detector Productivity ChemStation D.03.00 software.

5.2.2. Chemicals

Dichloromethane and *n*-hexane, both for gas chromatography (SupraSolv®) obtained from Merck (Darmstadt, Germany), were used to prepare the MixCrude solution and dilute the sample extracts. The crude oils employed in the preparation of the MixCrude solution, namely Miri Light (Malaysia), Bonny Light (Nigeria), Cabinda (Angola), and Ural (Russia), belong to the petroleum products database of *Instituto Hidrográfico*. The RR samples were received from Bonn-OSINet as dichloromethane extracts at 20 mg/mL of oil per volume of extractant. Two Sp were received: Sp1 was collected in the spill and suffered some environmental degradation, and Sp2 was collected after the *in situ* burning of the spill area. Each Sp was compared with three SS: SS1 is known as being the origin of the spill, and SS2 and SS3 are known as not being the spill source. Therefore, the Sp1, Sp2 and SS1 were extracts of weathered oil, residue of combusted fresh oil and fresh oil, respectively, all from Ultra Low Sulphur Fuel Oil (< 1000 ppm of sulphur). SS2 and SS3 consisted in extracts from Kyrtael and Norne fresh crude oils.

5.2.3. Sample preparation

Prior to GC-MS analysis and in accordance with EN 15522-2 standard, the concentration of the extracts was adjusted to equivalent injection concentrations because the *DR* is affected by the lack of linearity of the instrumental signal due to overload of the GC column (CEN, 2023). Thus, all Sp and SS extracts received as 20 mg/mL of oil per volume of extractant, were diluted in dichloromethane to 5 mg/mL. Additionally, a MixCrude solution was prepared combining Ural, Miri Light, Bonny Light, and Cabinda crude oil extracts, at a proportion of 4:1:1:1, as described in a previous study of the authors (Rocha *et al.*, 2022b). The MixCrude solution was used to evaluate the GC-MS performance and stability during the analysis, as well as, to establish, in a single run, the retention time frames for the peaks identification of all compounds suggested to be determined by the EN 15522-2 standard.

5.2.4. GC-MS data acquisition and processing

The Sp and SS extracts were analysed by GC-MS, nine times each alternately so that they could be grouped into three *DR* comparison trials (1stT, 2ndT and 3rdT) composed by three different injections of each sample. Therefore, the analysis sequence comprised three sets of triplicate analyses of each sample. The instrumental analysis was performed according to EN 15522-2 acquisition conditions, as described in detail by Rocha *et al.* (2023), and its quality control was carried out throughout the entire sequence, injecting the MixCrude solution before and after each set of triplicate injections of all samples (*i.e.*, *DR* comparison trials). The GC-MS performance was assessed as required by EN 15522-2, checking the retention time drift, mass discrimination changes and column resolution. Additionally, the retention time deviation was evaluated for each sample injection.

As recommended by the EN 15522-2 standard, one hundred and forty-five compounds and compound sets were analysed. **Table D.1** of the **Annex D** their descriptions and labels. The peaks identification and quantification were carried out as detailed in previous studies (Rocha *et al.*, 2022b; Rocha *et al.*, 2023), by comparing retention times and oil patterns, as well as assessing the presence of confirmation ions. Due to the complexity of the oil matrix, all chromatographic peak integrations were visually inspected. The chromatographic peaks with a signal-to-noise ratio (*S/N*) less than five were not used to calculate *DR*. **Figure D.1** of the **Annex D** presents the total ion chromatograms of all Sp and SS used to determine the relevant

compounds. **Table D.2** of the **Annex D** shows the quantified and unquantified compounds in the Sp and SS samples analysed.

5.2.5. Diagnostic ratio determination

The assessment of compositional equivalence or difference between Sp and SS is based on the comparison of a previously selected set of *DR*. The *DR* from this set should be obtained from chromatographic signals of unweathered compounds with adequate precision, such that differences in the *DR* could be recognised as attributed to sample compositional discrepancies affected by controlled signal precision. This is relevant when using the Nordtest (Daling *et al.*, 2022, Faksness *et al.*, 2002) and EN 15522-2 methodologies (CEN, 2023), *i.e.*, S-t and SC approaches, since they require a minimum of chromatographic signals' precision used to calculate *DR*. The MCM approach can be used despite the precision of the chromatographic signal. Therefore, the signal precision was verified, leading to a fair comparison of the data provided by the S-t and SC approaches with the data obtained by the MCM approach. The assessment of chromatographic signals precision and the occurrence of weathering events were performed, using percentage of weathering plots (PW-plots), as indicated by EN 15522-2 standard and detailed by Rocha *et al.* (2023).

The EN 15522-2 standard lists 78 *DR* used to characterise the chemical composition of an oil sample: 44 are considered normative ratios (NR) and different NR sets are established depending on the oil type in the samples, while 34 are informative ratios (IR) that can optionally be used to improve oil pattern definition. In the studied samples, all the determined NR and IR were considered for the *DR* set, with exception to those not determined due to the absence of detectable signals of at least one component used to calculate the *DR*. For each pair of compared samples, **Table D.3** of the **Annex D** summarises the selected and not considered *DR*, including the explanation for exclusions. Thus, comparisons between Sp1 and SS1, SS2 and SS3 were conducted with sets of 28, 27, and 23 *DR*, respectively, while comparisons between Sp2 and SS1, SS2 and SS3 were all performed with sets of 8 *DR*.

5.2.6. Diagnostic ratio agreement

Equations 5.3 to **5.5** present the algorithms used by the MCM, S-t and SC approaches, respectively, for *DR* comparison from Sp and SS samples through the definition of confidence

limits or intervals for the difference of mean DR , $(\overline{DR}_{Sp} - \overline{DR}_{SS})$, observed in both samples. Mean DR are considered equivalent if the zero value is enclosed in the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence limits.

$$P_{\chi}[\overline{DR}_{Sp} - \overline{DR}_{SS}] \& P_{1-\chi}[\overline{DR}_{Sp} - \overline{DR}_{SS}] \quad (5.3)$$

$$(\overline{DR}_{Sp} - \overline{DR}_{SS}) \pm t((1 - P); \lfloor \xi \rfloor) \cdot s_d \quad (5.4)$$

$$(\overline{DR}_{Sp} - \overline{DR}_{SS}) \pm 0.14 \cdot \overline{DR}_d \quad (5.5)$$

where $P_{\chi}[\overline{DR}_{Sp} - \overline{DR}_{SS}]$ and $P_{1-\chi}[\overline{DR}_{Sp} - \overline{DR}_{SS}]$ are the χ^{th} and $1 - \chi^{th}$ percentiles of simulated $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ by MCM defined for the selected confidence level (P), $t((1 - P); \lfloor \xi \rfloor)$ is the t -value of the t distribution considering the P and $\lfloor \xi \rfloor$ degrees of freedom determined as the nearest integer of ξ , s_d is the standard deviation of the difference of DR means, and $\overline{DR}_d$ is the mean value of DR means observed for Sp and SS (*i.e.*, $\overline{DR}_d = (\overline{DR}_{Sp} + \overline{DR}_{SS})/2$). The ξ and s_d are determined as described by Rocha *et al.* (2022b) and Rocha *et al.* (2023).

The comparison of DR from Sp1 and Sp2 with the DR from SS1, SS2 and SS3 was carried out by determining the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence limits of MCM, S-t and SC approaches (**Equations 5.3, 5.4 and 5.5**), using, separately, input data of the 1stT, 2ndT and 3rdT, and applying the DR comparison scenarios indicated by the Nordtest ($\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$ from triplicates and $A/(A+B)$ of DR format) and EN 15522-2 standard ($\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$ from duplicates and A/B of DR format). Furthermore, to compare the MCM and S-t approaches at same conditions, the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence limits were calculated for the P recommended by the Nordtest methodology for the DR comparison (*i.e.*, 95% and 98%). For this purpose, the computational simulation tool, previously developed and made available by the authors was used (Rocha *et al.*, 2022b).

5.2.7. Assessment of the evidence's strength

As the spill origin was known in this study, the LR (**Equation 5.1**) can be determined by the quotient between the probabilities of a true (δ) and a false (ε) compositional equivalence claims. The δ and ε were estimated by MCM, S-t and SC approaches, applying the the Nordtest and

EN 15522-2 scenarios, and for 1stT, 2ndT and 3rdT separately, as well as for the combination of assessments from two and three *DR* comparison trials.

5.2.7.1. Probabilities of true and false compositional equivalence claim

The δ were estimated from the comparison of replicated *DR* of Sp1 and Sp2 with SS1, with equivalent oil patterns, using the previously developed computational simulation tool. Rocha *et al.* (2022b) provide a detailed description of the δ estimation for each *DR* comparison trial.

The ε were estimated using newly developed MS-Excel spreadsheets made available for download from the weblink presented in the **Annex D.4**. To determine ε by the MCM and SC approaches, it was simulated $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ and $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$ pairs, respectively, whereas ε estimated for S-t used simulated DR_{Sp} and DR_{SS} values (*i.e.*, considering a single simulation for each Sp and SS sample). The required simulated data were obtained considering experimental data from replicate Sp and SS analyses, for the pairs Sp1 or Sp2 vs. SS2 or SS3 (Sp and SS with different oil patterns).

The tools to determine ε by the MCM, S-t and SC approaches simulate 50,000 confidence intervals, for each *DR* of the *DR* set, using 50,002 $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ for the MCM approach, 50,002 DR_{Sp} and 50,002 DR_{SS} for the S-t approach, and 50,002 $\overline{DR}_{Sp}$ and 50,002 $\overline{DR}_{SS}$ for the SC approach. Each of the 50,000 simulated confidence intervals obtained by MCM and SC approaches was determined considering three consecutives simulated $(\overline{DR}_{Sp} - \overline{DR}_{SS})$, and $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$ pairs, respectively, where mean *DR* from duplicate or triplicate values were considered. In contrast, the confidence intervals determined by the S-t approach were obtained considering two or three consecutive values of DR_{Sp} and DR_{SS} to correspond the *DR* comparison conditions defined by EN 15522-2 and Nordtest scenarios, respectively.

The simulated confidence limits for the MCM, S-t and SC approaches were defined as shown by **Equation 5.6**, **Equations 5.7 to 5.9** and **Equations 5.10 and 5.11**, respectively.

$$(\overline{DR}_{Sp} - \overline{DR}_{SS}) \pm t((1 - P); 2) \cdot s \quad (5.6)$$

$$(\overline{DR}_{Sp} - \overline{DR}_{SS}) \pm t((1 - P); [\xi]) \cdot s_d \quad (5.7)$$

$$s_d = \sqrt{\frac{s_{DR_{Sp}}^2}{n_{Sp}} + \frac{s_{DR_{SS}}^2}{n_{SS}}} \quad (5.8)$$

$$\xi = \frac{\left(\frac{s_{DR_{Sp}}^2}{n_{Sp}} + \frac{s_{DR_{SS}}^2}{n_{SS}} \right)^2}{\left(\frac{s_{DR_{Sp}}^4}{n_{Sp}^2 \cdot (n_{Sp} - 1)} + \frac{s_{DR_{SS}}^4}{n_{SS}^2 \cdot (n_{SS} - 1)} \right)} \quad (5.9)$$

$$(\overline{DR}_{Sp} - \overline{DR}_{SS}) \pm 0.14 \cdot \overline{DR}_d \quad (5.10)$$

$$\overline{DR}_d = \frac{(\overline{DR}_{Sp} + \overline{DR}_{SS})}{2} \quad (5.11)$$

where $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ and s are the mean value and the standard deviation of three consecutive simulated $(\overline{DR}_{Sp} - \overline{DR}_{SS})$, and $t((1 - P); 2)$ is the t -value of the t distribution considering P of 95% or 98% and two degrees of freedom, $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ are the difference between the mean values of two or three consecutive simulated DR_{Sp} and DR_{SS} , s_d are the standard deviation of the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$, $t((1 - P); \lfloor \xi \rfloor)$ is the t -value of the t distribution considering P of 95% or 98% and $\lfloor \xi \rfloor$ degrees of freedom (ξ is obtained by **Equation 5.9** and adjusted to the nearest integer), $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ are the difference between the mean values of three consecutive simulated $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$, and $\overline{DR}_d$ is the mean value of the $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$ calculated by **Equation 5.11**. To simulate confidence intervals for the MCM approach it was assumed the normality of the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$. This simplification is adequate given the expected low probability of false compositional equivalence claim and the fact that mean values tend to be normally distributed as proved by the central limit theorem.

The inclusion of the zero value in each simulated confidence interval was checked to evaluate equivalence between $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$. Based on these outcomes, the compositional equivalence of Sp and SS was verified for each of the 50,000 DR sets, allowing to estimate ε by determining the percentage of the 50,000 DR sets that claim compositional equivalence (*i.e.*, all $\overline{DR}_{Sp}$ equivalent to respective $\overline{DR}_{SS}$).

5.2.7.2. Combined effect of diagnostic ratio comparison trials

The combination of DR equivalence assessments obtained from different DR comparison trials, not only allows us to verify the occurrence of a false difference between $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$, but also estimates higher δ (Rocha *et al.*, 2023). The δ and ε were estimated by combining equivalence assessments between $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$ using two (δ^{2T} and ε^{2T}) and three (δ^{3T} and

ε^{3T}) DR comparison trials. The 50,000 outcomes of the equivalence assessments between $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$ found during the δ and ε estimations for each DR comparison trial were used. These outcomes were combined to declare compositional equivalence between Sp and SS compared, with the compositional equivalence assumed if all DR are indicated as equivalent in one of the two or two of the three trials. The δ^{2T} , δ^{3T} , ε^{2T} and ε^{3T} were determined as the percentage of comparisons that indicated compositional equivalence considering two or three trials.

5.2.7.3. Likelihood ratio and posterior probability

Since the spill source is known, the LR can be described by the ratio of δ , estimated comparing $Sp1$ or $Sp2$ with $SS1$, and ε , estimated comparing $Sp1$ or $Sp2$ with $SS2$ or $SS3$. In this way, for each DR comparison trial, the LR and the $P(H_p|E)$ (**Equation 5.2**) were calculated considering the sample combinations $Sp1$ vs. $SS1$ and $SS2$, $Sp1$ vs. $SS1$ and $SS3$, $Sp2$ vs. $SS1$ and $SS2$ and $Sp2$ vs. $SS1$ and $SS3$. The $P(H_p|E)$ were determined assuming equal probability that Sp and SS have or not have the same origin (*i.e.*, $P(H_p) = P(H_d) = 50.0\%$). Furthermore, the LR and the $P(H_p|E)$ were determined for the same sample combinations using the data obtained from the combined effect of two ($2T$) and three ($3T$) DR comparison trials.

5.3. Results and discussion

The results and discussion address the investigation of the occurrence of equivalence between the oil patterns of two Sp and three SS , allowing (a) the identification of the polluting source, (b) the estimation of the probabilities of true and false compositional equivalence claims used in the determination of the LR , and (c) the interpretation of the determined LR . In addition, the impact of conducting more than one DR comparison trial on Sp and SS compositional equivalence claims and on LR calculated for different pairs of Sp and SS are assessed, enabling the establishment of a strategy that improves the ability to distinguish potential pollution sources and identify the spill source with adequately low uncertainty.

5.3.1. Assessment of oil pattern equivalence

The spill source is identified comparing DR using the MCM, S-t and SC approaches in the Nordtest and EN 15522-2 scenarios. The Sp weathering was assessed using the methodology

proposed in the EN 15522-2 as described in detail in **Annex D. Figure D.1** of the **Annex D** shows the total ion chromatograms of all samples analysed and **Figures D.2, D.3 and D.4** of the **Annex D** present the PW-plots for the comparisons of Sp1 and Sp2 with SS1, Sp1 and Sp2 with SS2 and Sp1 and Sp2 with SS3, respectively. **Table D.3** of the **Annex D** shows the *DR* set employed to compare each pair of samples.

The comparison of *DR* with *P* of 98% has a 2% chance of indicating that a pair of truly equivalent *DR* is considered different. Therefore, as the number of *DR* considered in oil pattern comparison increases, the chance of at least one *DR* pair not matching also increases, wrongly suggesting pattern difference (false difference claim). This chance is a complex function of *DR* dispersion, correlation and comparison criteria. The false non-equivalence claims are reduced by performing additional *DR* comparison trials, employing distinct injections of Sp and SS. Thus, the assessment of compositional equivalence between Sp and SS was carried out considering the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals determined for three trials. The compositional equivalence is assumed if all *DR* of the set is indicated as equivalent in at least one or two of the two or three trials. Since the equivalence between $\dot{DR}_{Sp}$ and $\dot{DR}_{SS}$ values results in a null difference $((\dot{DR}_{Sp} - \dot{DR}_{SS}) = 0)$ (the dot in the top of *DR* identifies the “real” value), the equivalence between $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$ is confirmed by incorporating the zero value in the estimated $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals. **Tables D.4 to D.21** of the **Annex D** and **Figures D.5 to D.10** of the **Annex D** present the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals determined for each of the three trials and for all Sp and SS sample pairs. These tables also identify the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals that do not include the zero value, as well as present the percentage of non-equivalent *DR* (τ).

All approaches, in both scenarios and *P*, claim compositional equivalence of Sp1 and SS1 (**Tables D.4 to D.6** and **Figure D.5** of the **Annex D**) in the 1stT, as no *DR* was identified as different. However, the S-t approach in the Nordtest scenario for *P* of 95% declares compositional difference because it finds the *DR*63 as non-equivalent in two trials for *P* of 95%, whereas for *P* of 98% performing only two trials is sufficient to state compositional equivalence. A similar behaviour is observed when comparing Sp2 with SS1 (**Tables D.13 to D.15** and **Figure D.8** of the **Annex D**) by all approaches in both scenarios and *P*, declaring compositional equivalence in the 1stT, except the S-t approach in the Nordtest scenario and for *P* of 95% that states disparity of oil patterns because *DR*37 non-match in the first two trials.

In summary, the S-t approach, which is stricter than the others when the Nordtest scenario is used, probably requires more than three trials to state compositional equivalence for a P of 95%, but using 98%, two trials appear to be appropriate. The broader $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals defined by the MCM and SC approaches in the Nordtest scenario, as well as those produced by all three approaches in the EN 15522-2 scenario, suggest that only one trial is needed to establish equivalence between Sp and SS oil patterns.

In comparisons of Sp1 and Sp2 with SS2 (Tables D.7 to D.9 and Figure D.6, and Tables D.16 to D.18 and Figure D.9 of the Annex D, respectively) and with SS3 (Tables D.10 to D.12 and Figure D.7, and Tables D.19 to D.21 and Figure D.10 of the Annex D, respectively), much more non-equivalent DR were identified, despite τ differs between applied DR comparison approaches and scenarios. The MCM and SC approaches seems to identify practically the same non-match DR in both scenarios. In contrast, the S-t approach finds more non-match DR in the Nordtest scenario, but less non-match DR in the EN 15522-2 scenario. This is the result of the tighter and more tolerant DR comparison criteria produced in Nordtest and EN 15522-2 scenarios, respectively, due to different degrees of freedom of the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$. All approaches, in both scenarios tested, declare that Sp1 has a different composition than SS2 and SS3 already in the 1stT, because at least 11 of the 27 (Sp1 vs. SS2) and 23 (Sp1 vs. SS3) DR compared are non-matched. Declaring that Sp2 has a different oil pattern than SS2 and SS3 based on a single trial seems to be risky, given that the oil patterns were only characterised by eight DR and only at least three of them did not match. In such cases, performing another DR comparison trial might be appropriate to ensure that the false match assessment is adequately unlikely.

5.3.2. Probabilities of true and false compositional equivalence claim

For the three DR comparison trials, the two scenarios and the three approaches under study, it was determined the δ and the ε for Sp and SS pairs with the same or different oil patterns, respectively (number of considered DR ; determined δ or ε): Sp1 vs. SS1 (28 DR ; δ), Sp1 vs. SS2 (27 DR ; ε), Sp1 vs. SS3 (23 DR ; ε), Sp2 vs. SS1 (8 DR ; δ), Sp2 vs. SS2 (8 DR ; ε) and Sp2 vs. SS3 (8 DR ; ε). Tables D.22 and D.23 of the Annex D present the δ and ε estimated in the three trials performed, as well as their mean values ($\bar{\delta}$ and $\bar{\varepsilon}$) and the relative standard deviations (RSD). Table 5.1 shows the comparison, using the Student's t test, of $\bar{\delta}$ and $\bar{\varepsilon}$ estimated by the MCM approach with those estimated by the S-t and SC approaches.

Table 5.1. Statistical assessment of significance differences between the mean values, obtained from three *DR* comparison trials, of the probabilities of true ($\bar{\delta}$) or false ($\bar{\varepsilon}$) composition equivalence claims estimated by the SC approach and by the MCM and S-t approaches for 95% and 98% confidence levels, considering the comparison of spill samples 1 and 2 (Sp1 and Sp2) with suspected source samples 1, 2 and 3 (SS1, SS2 and SS3), applying the Nordtest and EN 15522-2 comparison scenarios.

		$\bar{\delta}$ or $\bar{\varepsilon}$ RSD (%)				SC	Comparison	t_{exp} t_{cr} <; $\approx$; >
		MCM		S-t				
		95%	98%	95%	98%			
Nordtest scenario	Sp1 vs. SS1	83.0 0.45	93.6 0.49	62.0 1.5	70.7 0.79	86.5 3.0	$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (95%)	35.6 2.78 >
							$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (98%)	36.1 2.78 >
							$\bar{\delta}_{\text{MCM}}$ (95%) vs. $\bar{\delta}_{\text{SC}}$	2.28 4.30 ^(a) $\approx$
							$\bar{\delta}_{\text{MCM}}$ (98%) vs. $\bar{\delta}_{\text{SC}}$	4.59 2.78 >
	Sp2 vs. SS1	87.3 0.72	95.3 0.19	70.9 7.4	83.4 3.4	85.4 4.7	$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (95%)	5.35 4.30 ^(a) >
							$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (98%)	7.22 4.30 ^(a) >
							$\bar{\delta}_{\text{MCM}}$ (95%) vs. $\bar{\delta}_{\text{SC}}$	0.784 4.30 ^(a) $\approx$
							$\bar{\delta}_{\text{MCM}}$ (98%) vs. $\bar{\delta}_{\text{SC}}$	4.25 4.30 ^(a) $\approx$
	Sp1 vs. SS2	0.00100 50.0 ^(b)	0.00167 34.6	0.00100 50.0 ^(b)	0.00100 50.0 ^(b)	0.00100 50.0 ^(b)	$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (95%)	0 2.78 $\approx$
							$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (98%)	1.51 2.78 $\approx$
							$\bar{\varepsilon}_{\text{MCM}}$ (95%) vs. $\bar{\varepsilon}_{\text{SC}}$	0 2.78 $\approx$
							$\bar{\varepsilon}_{\text{MCM}}$ (98%) vs. $\bar{\varepsilon}_{\text{SC}}$	1.51 2.78 $\approx$
Sp2 vs. SS2	0.73 98.4	1.33 92.8	1.07 92.4	1.93 84.4	0.00100 50.0 ^(b)	$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (95%)	0.477 2.78 $\approx$	
						$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (98%)	0.507 2.78 $\approx$	
						$\bar{\varepsilon}_{\text{MCM}}$ (95%) vs. $\bar{\varepsilon}_{\text{SC}}$	1.76 4.30 ^(a) $\approx$	
						$\bar{\varepsilon}_{\text{MCM}}$ (98%) vs. $\bar{\varepsilon}_{\text{SC}}$	1.87 4.30 ^(a) $\approx$	
Sp1 vs. SS3	0.00100 50.0 ^(b)	0.00300 89.2	0.00100 50.0 ^(b)	0.00100 50.0 ^(b)	0.00100 50.0 ^(b)	$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (95%)	0 2.78 $\approx$	
						$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (98%)	1.29 2.78 $\approx$	
						$\bar{\varepsilon}_{\text{MCM}}$ (95%) vs. $\bar{\varepsilon}_{\text{SC}}$	0 2.78 $\approx$	
						$\bar{\varepsilon}_{\text{MCM}}$ (98%) vs. $\bar{\varepsilon}_{\text{SC}}$	1.29 2.78 $\approx$	
Sp2 vs. SS3	1.27 45.9	2.42 31.2	1.79 47.3	3.31 39.4	0.00100 50.0 ^(b)	$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (95%)	0.876 2.78 $\approx$	
						$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (98%)	1.02 2.78 $\approx$	
						$\bar{\varepsilon}_{\text{MCM}}$ (95%) vs. $\bar{\varepsilon}_{\text{SC}}$	3.77 4.30 ^(a) $\approx$	
						$\bar{\varepsilon}_{\text{MCM}}$ (98%) vs. $\bar{\varepsilon}_{\text{SC}}$	5.54 4.30 ^(a) >	

RSD – Relative standard deviation.

t_{exp} – t -value determined as the ratio between the absolute difference of $\bar{\delta}$ or $\bar{\varepsilon}$ and the standard deviation of the difference calculated from statistically equivalent or different standard deviations of compared $\bar{\delta}$ or $\bar{\varepsilon}$.

t_{cr} – critical value of the Student's t statistics for 95% confidence level. Compared $\bar{\delta}$ or $\bar{\varepsilon}$ are statistically different ($\bar{\delta}_{\text{MCM}}$ less than $\bar{\delta}_{\text{S-t}}$ or $\bar{\delta}_{\text{SC}}$ (<), or $\bar{\varepsilon}_{\text{MCM}}$ less than $\bar{\varepsilon}_{\text{S-t}}$ or $\bar{\varepsilon}_{\text{SC}}$ (<), or $\bar{\delta}_{\text{MCM}}$ greater than $\bar{\delta}_{\text{S-t}}$ or $\bar{\delta}_{\text{SC}}$ (>), or $\bar{\varepsilon}_{\text{MCM}}$ greater than $\bar{\varepsilon}_{\text{S-t}}$ or $\bar{\varepsilon}_{\text{SC}}$ (>)) for 95% confidence level ($t_{\text{exp}} > t_{\text{cr}}$), otherwise are statistically equivalent (≈).

(a) $t_{\text{cr}} = 4.30$ used for $\bar{\delta}$ or $\bar{\varepsilon}$ comparisons with different standard deviations.

(b) For statistical comparison of $\bar{\varepsilon}$ estimated by different approaches, a ε equal to zero was assumed as half of one compositional equivalence claim in 50,000 analysed *DR* sets (*i.e.*, 0.00100%). Additionally, a standard deviation of 0.000500% (RSD of 50.0%) was assumed if the estimated ε in the three trials was zero.

Table 5.1 (cont.).

	$\bar{\delta}$ or $\bar{\varepsilon}$ RSD (%)				SC	Comparison	t_{exp} t_{cr} <; ≈; >	
	MCM		S-t					
	95%	98%	95%	98%				
EN 15522-2 scenario	Sp1 vs. SS1	83.5 0.50	93.1 0.27	81.0 0.64	92.1 0.53	68.5 2.1	$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (95%)	6.46 2.78 >
							$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (98%)	4.65 2.78 >
							$\bar{\delta}_{\text{MCM}}$ (95%) vs. $\bar{\delta}_{\text{SC}}$	17.4 2.78 >
							$\bar{\delta}_{\text{MCM}}$ (98%) vs. $\bar{\delta}_{\text{SC}}$	30.0 2.78 >
	Sp2 vs. SS1	87.8 0.66	95.4 0.26	85.6 1.4	94.2 0.52	64.5 13.1	$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (95%)	2.73 2.78 ≈
							$[\bar{\delta}_{\text{MCM}}$ vs. $\bar{\delta}_{\text{S-t}}$] (98%)	3.84 2.78 >
							$\bar{\delta}_{\text{MCM}}$ (95%) vs. $\bar{\delta}_{\text{SC}}$	4.78 4.30 ^(a) >
							$\bar{\delta}_{\text{MCM}}$ (98%) vs. $\bar{\delta}_{\text{SC}}$	6.37 4.30 ^(a) >
	Sp1 vs. SS2	0.00200 86.6	0.0173 85.1	0.123 56.0	0.677 31.7	0.00100 50.0 ^(b)	$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (95%)	3.06 4.30 ^(a) ≈
							$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (98%)	5.31 4.30 ^(a) <
							$\bar{\varepsilon}_{\text{MCM}}$ (95%) vs. $\bar{\varepsilon}_{\text{SC}}$	0.961 2.78 ≈
							$\bar{\varepsilon}_{\text{MCM}}$ (98%) vs. $\bar{\varepsilon}_{\text{SC}}$	1.92 4.30 ^(a) ≈
	Sp2 vs. SS2	0.953 123	1.73 110	2.84 86.7	8.54 48.4	0.00100 50.0 ^(b)	$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (95%)	1.20 2.78 ≈
							$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (98%)	2.59 2.78 ≈
							$\bar{\varepsilon}_{\text{MCM}}$ (95%) vs. $\bar{\varepsilon}_{\text{SC}}$	1.41 4.30 ^(a) ≈
							$\bar{\varepsilon}_{\text{MCM}}$ (98%) vs. $\bar{\varepsilon}_{\text{SC}}$	1.58 4.30 ^(a) ≈
	Sp1 vs. SS3	0.00100 50.0 ^(b)	0.00300 57.7	0.0733 83.6	0.459 25.0	0.00100 50.0 ^(b)	$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (95%)	2.04 4.30 ^(a) ≈
							$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (98%)	6.88 4.30 ^(a) <
							$\bar{\varepsilon}_{\text{MCM}}$ (95%) vs. $\bar{\varepsilon}_{\text{SC}}$	0 2.78 ≈
							$\bar{\varepsilon}_{\text{MCM}}$ (98%) vs. $\bar{\varepsilon}_{\text{SC}}$	1.92 2.78 ≈
	Sp2 vs. SS3	2.14 34.6	4.19 24.2	8.33 20.9	22.5 11.6	0.00100 50.0 ^(b)	$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (95%)	5.68 2.78 <
							$[\bar{\varepsilon}_{\text{MCM}}$ vs. $\bar{\varepsilon}_{\text{S-t}}$] (98%)	11.3 2.78 <
							$\bar{\varepsilon}_{\text{MCM}}$ (95%) vs. $\bar{\varepsilon}_{\text{SC}}$	5.00 4.30 ^(a) >
							$\bar{\varepsilon}_{\text{MCM}}$ (98%) vs. $\bar{\varepsilon}_{\text{SC}}$	7.16 4.30 ^(a) >

RSD – Relative standard deviation.

t_{exp} – t -value determined as the ratio between the absolute difference of $\bar{\delta}$ or $\bar{\varepsilon}$ and the standard deviation of the difference calculated from statistically equivalent or different standard deviations of compared $\bar{\delta}$ or $\bar{\varepsilon}$.

t_{cr} – critical value of the Student's t statistics for 95% confidence level. Compared $\bar{\delta}$ or $\bar{\varepsilon}$ are statistically different ($\bar{\delta}_{\text{MCM}}$ less than $\bar{\delta}_{\text{S-t}}$ or $\bar{\delta}_{\text{SC}}$ (<), or $\bar{\varepsilon}_{\text{MCM}}$ less than $\bar{\varepsilon}_{\text{S-t}}$ or $\bar{\varepsilon}_{\text{SC}}$ (<), or $\bar{\delta}_{\text{MCM}}$ greater than $\bar{\delta}_{\text{S-t}}$ or $\bar{\delta}_{\text{SC}}$ (>), or $\bar{\varepsilon}_{\text{MCM}}$ greater than $\bar{\varepsilon}_{\text{S-t}}$ or $\bar{\varepsilon}_{\text{SC}}$ (>)) for 95% confidence level ($t_{\text{exp}} > t_{\text{cr}}$), otherwise are statistically equivalent (≈).

(a) $t_{\text{cr}} = 4.30$ used for $\bar{\delta}$ or $\bar{\varepsilon}$ comparisons with different standard deviations.

(b) For statistical comparison of $\bar{\varepsilon}$ estimated by different approaches, a ε equal to zero was assumed as half of one compositional equivalence claim in 50,000 analysed *DR* sets (*i.e.*, 0.00100%). Additionally, a standard deviation of 0.000500% (RSD of 50.0%) was assumed if the estimated ε in the three trials was zero.

For both comparisons of Sp1 and Sp2 with SS1, the $\bar{\delta}$ obtained by the MCM approach was similar for the two tested scenarios because this approach adapts to the statistical characteristics of processed data. At the same time the SC approach estimated higher $\bar{\delta}$ in the Nordtest scenario than in the EN 15522-2 scenario. On the contrary, due to a greater number of degrees of freedom of data from the Nordtest scenario than from the EN 15522-2 scenario, the S-t approach determined lower $\bar{\delta}$ in the first one. In some cases, it can be observed wider $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals determined by the S-t or MCM approaches in Nordtest scenario than in EN 15522-2 scenario when the third replicate considered is significantly different from the first two, with the DR dispersion influencing more the size of the intervals than the degrees of freedom. Regardless the scenario and P used, the MCM approach exhibited a tendency to estimate $\bar{\delta}$ equivalent or greater to the S-t approach. However, when comparing the $\bar{\delta}$ calculated by the MCM and SC approaches, the scenario and P have a major effect. In the Nordtest scenario, the SC approach tends to estimate similar or even lower $\bar{\delta}$ than the MCM approach, but in the EN 15522-2 scenario, the SC approach estimated $\bar{\delta}$ much lower than the MCM approach. **Table 5.1** also demonstrates that the $\bar{\varepsilon}$ estimated by the MCM and S-t approaches is often higher in the EN 15522-2 scenario than in the Nordtest scenario, and null $\bar{\varepsilon}$ was obtained by the SC approach in both tested conditions. This is owing to the dimension of the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals defined by the MCM and S-t approaches that varies with the degrees of freedom and the variability of the simulated input data (**Equations 5.6** and **5.7**), while the width of the confidence intervals produced by the SC approach only depends on the $\overline{DR}_d$ value (**Equation 5.10**). Thus, it is more unlikely that the zero value will be included in the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals produced by the SC approach. To compare statistically all $\bar{\varepsilon}$ estimated by the MCM approach with the other approaches, when simulated ε equal zero it was considered a pessimistic ε value of a half one false equivalence claim in 50,000 DR sets evaluated (0.00100%). In addition, it was assumed that this pessimistic value has a standard deviation of 0.000500% (RSD of 50.0%). **Table 5.1** shows that the $\bar{\varepsilon}$ found by the MCM approach, for P of 95% and 98%, tends to be equivalent or lower to those estimated by S-t approach in the EN 15522-2 scenario, but equivalent to those estimated by the S-t approach in the Nordtest scenario and by the SC approach in both scenarios. The exception is observed for the Sp2 and SS3 comparison (comparison of 8 DR and with SS with a more similar composition to Sp), with the $\bar{\varepsilon}$ estimated by the MCM approach significantly higher than the $\bar{\varepsilon}$ obtained by the SC approach in both scenarios and especially for P of 98%. Additionally, when comparing Sp2 with SS2 under the EN 15522-2 scenario conditions, the $\bar{\varepsilon}$ estimated by the

MCM approach (0.953% and 1.73% for P of 95% and 98%) seems to be somewhat different than the $\bar{\varepsilon}$ found by the other approaches (0.00100% by the SC approach and 2.84% and 8.54% by the S-t approach for P of 95% and 98%), but are statistically equivalent due to the large variability among $\bar{\varepsilon}$ replicates and reduced degrees of freedom.

In brief, the degrees of freedom and variability of the simulated DR used as input data to estimate δ and ε affect the ability to distinguish assessed approaches. The MCM approach was shown to be noticeably more promising considering δ values than the other approaches in the DR comparison conditions for which they were designed (S-t approach for the Nordtest scenario and SC approach for the EN 15522-2 scenario). However, under these same conditions, the MCM approach produced ε equal to those obtained by the S-t and SC approaches, but it tended to find greater ε than the SC approach when comparing Sp and SS with more compositional similarity and/or fewer DR . The fragilities of the SC approach in detecting true compositional equivalence are beneficial in avoiding false compositional equivalence claims.

5.3.3. Combined effect of different diagnostic ratio comparison trials

Table 5.2 presents the δ^{1T} , δ^{2T} and δ^{3T} (with jT representing the number of trials considered) estimated by the MCM, S-t and SC approaches in the Nordtest and EN 15522-2 scenarios with a P of 98% for MCM and S-t, for the comparison of Sp1 or Sp2 with SS1. Likewise, **Table 5.2** shows the ε^{1T} , ε^{2T} and ε^{3T} estimated by the same approaches and conditions when SS2 or SS3 are the alternative and less likely spill sources.

Table 5.2. Probabilities of true (δ) and false (ε) compositional equivalence claim, likelihood ratios (LR) and probability of prosecutor's claim being correct given the evidence (posterior probability, $P(H_p|E)$) estimated by the SC approach and by the MCM and S-t approaches for 98% confidence level applying the Nordtest and EN 15522-2 scenarios. Assessments from one DR comparison trial (1T) or from a combination of two (2T) or three (3T) DR comparison trials. Comparison of spill samples 1 and 2 (Sp1 and Sp2) with the suspected source known as being the origin of the spill (SS1) and not being the spill source (SS2 and SS3).

Nordtest scenario					EN 15522-2 scenario				
	δ (%)	ε (%)	LR	$P(H_p E)$ (%) ^(a)	δ (%)	ε (%)	LR	$P(H_p E)$ (%) ^(a)	
MCM	Sp1 vs. SS1 and SS2								
	1T	94.1	0.00200	47,050	99.9979	93.8	0.00600	15,633	99.9936
	2T	99.8	0.00600	16,633	99.9940	99.7	0.0580	1,719	99.9419
	3T	99.1	0.00100 ^(b)	99,100	99.9990	99.1	0.00100 ^(b)	99,100	99.9990
	Sp1 vs. SS1 and SS3								
	1T	94.1	0.00100 ^(b)	94,100	99.9989	93.8	0.00100 ^(b)	93,800	99.9989
	2T	99.8	0.00600	16,633	99.9940	99.7	0.0160	6,231	99.9840
	3T	99.1	0.00100 ^(b)	99,100	99.9990	99.1	0.00100 ^(b)	99,100	99.9990
	Sp2 vs. SS1 and SS2								
	1T	95.4	0.678	141	99.29	95.5	0.694	138	99.28
	2T	99.8	1.36	73.4	98.66	99.9	1.65	60.5	98.38
	3T	99.6	0.0240	4,150	99.98	99.5	0.0860	1,157	99.91
S-t	Sp2 vs. SS1 and SS3								
	1T	95.4	2.10	45.4	97.8	95.5	3.78	25.3	96.2
	2T	99.8	4.11	24.3	96.0	99.9	7.79	12.8	92.8
	3T	99.6	0.174	572	99.8	99.5	0.606	164	99.4
	Sp1 vs. SS1 and SS2								
	1T	78.1	0.00100 ^(b)	78,100	99.99872	92.1	0.912	101	99.02
	2T	96.2	0.00600	16,033	99.99376	99.6	6.63	15.0	93.76
	3T	91.0	0.00100 ^(b)	91,000	99.99890	98.8	0.284	348	99.71
	Sp1 vs. SS1 and SS3								
	1T	78.1	0.00100 ^(b)	78,100	99.99872	92.1	0.460	200	99.50
	2T	96.2	0.0100	9,620	99.98961	99.6	2.18	45.7	97.86
	3T	91.0	0.00100 ^(b)	91,000	99.99890	98.8	0.0540	1,830	99.95
SC	Sp2 vs. SS1 and SS2								
	1T	81.8	0.942	86.8	98.9	94.8	6.60	14.4	93.5
	2T	98.2	2.14	45.9	97.9	99.8	30.2	3.30	76.8
	3T	95.0	0.0720	1,319	99.9	99.3	9.48	10.5	91.3
	Sp2 vs. SS1 and SS3								
	1T	81.8	2.72	30.1	96.8	94.8	19.6	4.84	82.9
	2T	98.2	5.43	18.1	94.8	99.8	55.1	1.81	64.4
	3T	95.0	0.408	233	99.6	99.3	29.4	3.38	77.2
	Sp1 vs. SS1 and SS2								
	1T	84.9	0.00100 ^(b)	84,900	99.998822	70.0	0.00100 ^(b)	70,000	99.99857
	2T	99.1	0.00100 ^(b)	99,100	99.998991	95.2	0.00100 ^(b)	95,200	99.99895
	3T	97.4	0.00100 ^(b)	97,400	99.998973	87.8	0.00100 ^(b)	87,800	99.99886
SC	Sp1 vs. SS1 and SS3								
	1T	84.9	0.00100 ^(b)	84,900	99.998822	70.0	0.00100 ^(b)	70,000	99.99857
	2T	99.1	0.00100 ^(b)	99,100	99.998991	95.2	0.00100 ^(b)	95,200	99.99895
	3T	97.4	0.00100 ^(b)	97,400	99.998973	87.8	0.00100 ^(b)	87,800	99.99886
	Sp2 vs. SS1 and SS2								
	1T	86.9	0.00100 ^(b)	86,900	99.998849	69.8	0.00100 ^(b)	69,800	99.99857
	2T	99.0	0.00100 ^(b)	99,000	99.998990	94.6	0.00100 ^(b)	94,600	99.99894
	3T	95.9	0.00100 ^(b)	95,900	99.998957	82.4	0.00100 ^(b)	82,400	99.99879
	Sp2 vs. SS1 and SS3								
	1T	86.9	0.00100 ^(b)	86,900	99.998849	69.8	0.00100 ^(b)	69,800	99.99857
	2T	99.0	0.00100 ^(b)	99,000	99.998990	94.6	0.00100 ^(b)	94,600	99.99894
	3T	95.9	0.00100 ^(b)	95,900	99.998957	82.4	0.00100 ^(b)	82,400	99.99879

(a) Adjusted to at least three significant digits. However, in some cases, the number of significant digits has been raised allowing to observe variations in at least the last two significant digits.

(b) A ε equal to zero was assumed as half of one compositional equivalence claim in 50,000 analysed DR sets (*i.e.*, 0.00100%) for LR and $P(H_p|E)$ calculation purposes.

The Sp and SS compositional equivalence considering two and three *DR* comparison trials was assumed when each *DR*, from the *DR* set, was identified as equivalent in at least one or two of the two or three trials, respectively. Applying this criterion, for both scenarios and all approaches, it was observed that the δ and ε estimated considering two trials, varying from 94.6% to 99.9% and 0% to 55.1%, respectively, are larger than those obtained considering one trial, ranging from 69.8% to 95.5% and 0% to 19.6%, respectively, because the second trial provided a second chance of being reported compositional equivalence ($\delta^{2T} > \delta^{1T}$ and $\varepsilon^{2T} > \varepsilon^{1T}$). Whenever three trials are considered, the δ reduces slightly ($\delta^{2T} > \delta^{3T}$) and proportionally more the ε ($\varepsilon^{2T} \gg \varepsilon^{3T}$), varying from 82.4% to 99.6% and 0% to 29.4%, respectively. The option of only reporting compositional equivalence if at least two trials, and not only one, indicate *DR* equivalence for all *DR*, decreases both δ^{3T} and ε^{3T} but the ratio between these ($\delta^{3T}/\varepsilon^{3T}$) is larger than if compositional equivalence is considered if only one trial indicates *DR* equivalence (e.g., comparison of Sp2 with SS1 and SS2 by the MCM approach applying the Nordtest scenario estimated δ^{3T} of 100% and ε^{3T} of 4.74% producing a $\delta^{3T}/\varepsilon^{3T} = 21.1$, instead of $\delta^{3T}/\varepsilon^{3T} = 99.6\%/0.0240\% = 4,150$ from **Table 5.2**).

Briefly, for all approaches and both scenarios, the $\delta^{1T} < \delta^{2T} > \delta^{3T}$ and $\varepsilon^{1T} < \varepsilon^{2T} > \varepsilon^{3T}$ trends were observed, with $\delta^{1T} < \delta^{3T}$ and $\varepsilon^{1T} > \varepsilon^{3T}$. However, for the S-t approach in the EN 15522-2 scenario and for the comparison of only eight *DR*, estimated ε^{3T} is higher than ε^{1T} due to probabilistic inconsistencies of the S-t approach. These inconsistencies are owing to the wider *DR* confidence intervals defined by S-t compared to the other approaches (**Figures D.9** and **D.10** of the **Annex D** for the Sp2 and SS2, and Sp2 and SS3 *DR* comparisons, respectively) which are a result of the very low degrees of freedom employed, as determined by **Equation 5.9** with duplicate analysis of Sp and SS. Thus, given the more tolerant *DR* comparison criteria for some *DR* and a fewer number of *DR* to be compared, the chance of claiming false compositional equivalence between Sp and SS combining the *DR* comparison assessments of three trials is greater than just considering one trial. Additionally, having assumed the worst-case ε value for calculating purposes when zero ε is observed, it is not able to observe the ε variation trend (e.g., all the comparisons performed by the SC approach).

5.3.4. Distinguishing and identifying the spill source

In oil spill source identification, the *LR* expresses the ability to distinguish two possible alternative sources of the spill. Taking the most probable (SS_α) and an alternative (SS_γ) spill

sources, the ratio between the probability of oil pattern equivalence claim between Sp and SS_α ($P_{Sp|SS_\alpha}$), and Sp and SS_γ ($P_{Sp|SS_\gamma}$), *i.e.*, $P_{Sp|SS_\alpha}/P_{Sp|SS_\gamma}$, is an *LR* (**Equation 5.1**). Assuming there is not additional information indicating that SS_α or SS_γ is the most likely source of the spill, an *LR* of 10 or 1,000 indicates that SS_α is 10 or 1,000 times more likely the spill source than SS_γ . In the present study where the spill origin is known, $P_{Sp|SS_\alpha}$ and $P_{Sp|SS_\gamma}$ are the described δ and ε , respectively. **Table 5.2** shows the *LR* and the $P(H_p|E)$ determined for the studied approaches and scenarios, considering δ and ε estimated from one, two or three trials. The *LR* obtained under the conditions of the Nordtest and EN 15522-2 scenarios, respectively, vary from 24.3 to 99,100 and 12.8 to 99,100 for the MCM approach, 18.1 to 91,000 and 1.81 to 1,830 for the S-t approach, and 84,900 to 99,100 and 69,800 to 95,200 for the SC approach. These values reflect the impact, in the δ and ε , of the size of the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals, the number of *DR* compared, the compositional similarity between Sp and SS_γ , and the combination of trials, as previously discussed. The *LR* determined for the S-t approach in the Nordtest scenario were higher than those obtained for the EN 15522-2 scenario due to differences in the estimated δ and ε caused by the size of $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals. On the other hand, the MCM approach estimated similar δ and ε , and thus analogous *LR*, in the Nordtest and EN 15522-2 scenarios due to the more consistent identification criteria. Lower *LR* is obtained as a result of proportionally higher ε than δ , not only when fewer *DR* are compared but also when SS_γ and Sp are more compositionally similar. For all approaches and sample comparisons, in both tested scenarios, LR^{2T} decreases compared to LR^{1T} since the estimated δ^{2T} and ε^{2T} are higher than δ^{1T} and ε^{1T} but, considering a third trial, LR^{3T} rise considerably exceeding LR^{1T} due to a substantial decrease in the estimated ε^{3T} , regardless of the slight reduction in δ^{3T} . However, this *LR* tendency is not observed when fewer *DR* were compared by the S-t approach in the EN 15522-2 scenario, as already noted, due to statistical inconsistencies of the S-t approach. Furthermore, just as it was unable to recognise a ε trend with the number of trials considered for the SC approach, the *LR* trend cannot be assessed because it reflects only the δ variation. The $P(H_p|E)$, determined by **Equation 5.2** and assuming $P(H_p) = P(H_d) = 50.0\%$, indicates how likely SS_1 is the source of the spill given the compositional equivalence evidence of Sp_1 or Sp_2 and SS_1 . The $P(H_p|E)$ results reflect the same trend as observed for *LR*, ranging from 96.0% to 100% and 92.8% to 100% for the MCM approach, and 94.8% to 100% and 64.4% to 99.9% for the S-t approach, both applied to the Nordtest and EN 15522-2 scenarios, respectively. Nevertheless, the SC approach estimates

$P(H_p|E)$ approximately 100%, with very low variation, because of the null ε estimated in all Sp and SS comparisons.

The ability to distinguish a pair of spill sources expressed by the LR determined for the S-t approach proved to be lower than that observed for the MCM approach given that S-t tends to estimate lower δ and higher ε . In contrast, an analysis that adopts the SC approach instead of the MCM shows to distinguish better possible spill sources because estimates zero ε , but assesses the most likely spill source with lower δ . Thus, the MCM approach seems to be not as strong in distinguishing the spill source as the SC but provides more support in spill source identification. Additionally, and probably more importantly, the identification criteria used by the MCM approach are the only ones that are statistically sound and accurately adjusted to the performance of DR determination.

5.3.5. Strategy for reporting spill origin in real-world pollution case

The previously discussed differences in δ , ε , and, consequently, LR enabled the definition of a strategy to assess results from chemical analyses performed on Sp and SS from a real illicit pollution act. This strategy aims to improve the discrimination ability among SS and to produce a sound conclusion about spill origin, thereby strengthening the evidence that can be presented in court. **Figure 5.1** presents the diagram that assists the decision in the process of oil spill source identification by evaluating the strength of the evidence which, if necessary, can be substantially improved by performing additional trials. These decisions require a minimum threshold for LR , δ and ε so that it can be differentiated the chemical composition of alternative SS presented, as well as concluding that the compositions of the oil spilt and taken from the most probable spill source are equivalent. A minimum limit of 95.0% for δ appeared suitable, given that for a single DR comparison trial are studied confidence levels of 95% and 98%. For ε , a maximum limit of 0.50% was assumed, which can be a strict requirement when comparing Sp and SS using DR sets with few DR but keeps rather low the false claims of oil pattern equivalence. False equivalence claims are particularly critical because they involve the punishment of not-guilty entities. These limits yield an LR of 190, which is likewise regarded appropriate because it translates into moderately strong support for distinguishing chemical compositions from SS (ENFSI, 2015; Thompson *et al.*, 2018). Whenever the verbal equivalent to LR is considered unprecise, it can be decided to report the uncertainty of claiming compositional equivalence or difference to inform about how strong is the most probable claim.

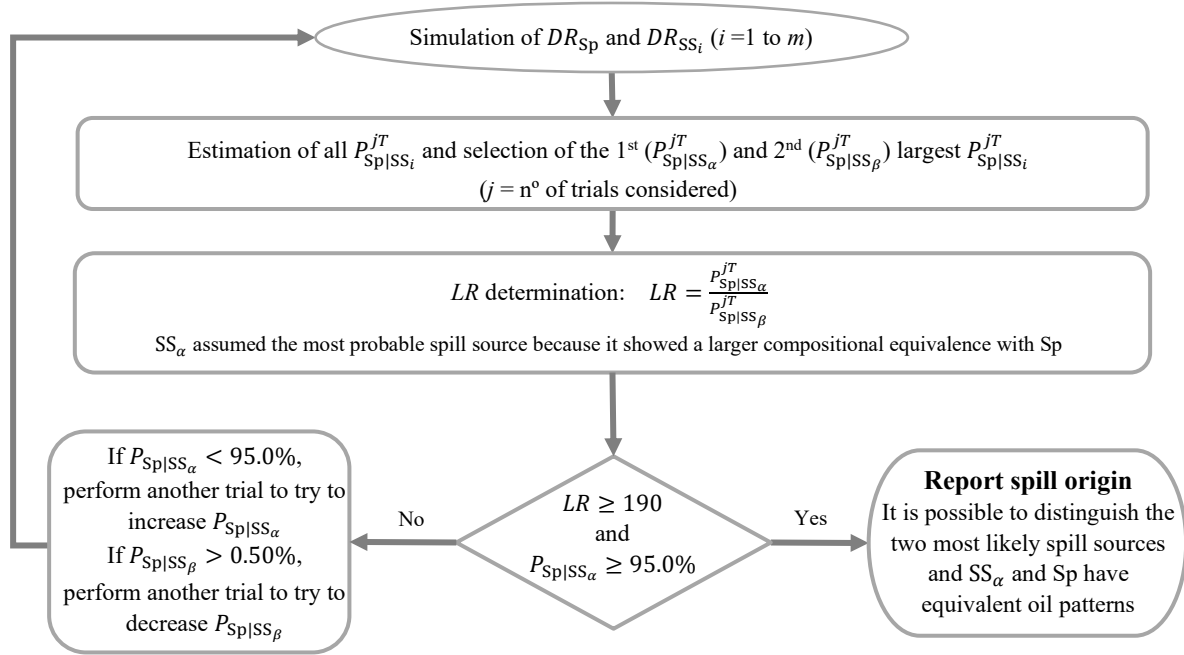


Figure 5.1. Strategy for oil spill identification through the assessment of the evidence strength using likelihood ratios (LR) and the probabilities of claiming compositional equivalence between the spill sample (Sp) and suspected source samples (SS_i), $P_{Sp|SS_i}^{jT}$, estimated from j comparison trials.

The analysis strategy for determining an oil spill source begins with a replicate GC-MS analysis (at least nine injections) of each Sp and SS . These nine injections allow the expert to run up to three Sp with SS comparison trials, each with three different injections for each sample. Based on processed chromatographic data, the DR for sample comparisons are selected, taking into account the weathering occurrence events that affect the abundance of specific compounds, particularly in the Sp . The selected DR are simulated for Sp and SS , by MCM, using the triplicate chromatographic signals and according to the desired DR comparison conditions (Nordtest or EN 15522-2 scenario). Simulated $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$ are used to define $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals to assess DR equivalence and, thus, compositional similarity between Sp and SS , as well as to estimate the probability of a compositional equivalence claim. The LR is determined as the ratio of the two highest estimated probabilities of compositional equivalence claim ($P_{Sp|SS_\alpha}^{jT}$ and $P_{Sp|SS_\beta}^{jT}$, with $P_{Sp|SS_\alpha}^{jT}$ as the highest probability and jT as the number of DR comparison trials considered), indicating that SS_α and SS_β represent the most likely suspects of the spill origin. For an LR and a $P_{Sp|SS_\alpha}^{jT}$ greater than or equal to 190 and 95.0%, respectively, it is reliable to report the most likely spill origin (*i.e.*, the SS_α) since it cannot only distinguish between the two most likely spill suspected sources but also identify the spill source with adequately low uncertainty. However, when these criteria are not met,

additional *DR* comparison trials should be conducted for the pairs *Sp* vs. *SS_α* and/or *Sp* vs. *SS_β*, to assess if it is possible to raise $P_{Sp|SS_{\alpha}}^{jT}$ and/or reduce $P_{Sp|SS_{\beta}}^{jT}$ to meet identification criteria. Nevertheless, in more complex spill cases or when the real spill source was not assessed, the use of three *DR* comparison trials may not be sufficient to ensure the identification of the spill source at the desired level of quality. In such instances, the provision of additional independent evidence might be useful because, if properly classified as an *LR*, it can be combined with the *LR* determined from the findings of chemical analyses, adding value to a judgment on polluter identification (Bettencourt da Silva and Ellison, 2021). The combination of non-analytical with analytical spill source information is beyond the scope of this paper. If analysts are somehow instructed to follow the Nordtest method or EN 15522-2 standard in spill source identification, they should be aware of the fragilities of these approaches that can be significantly mitigated by performing various comparison trials.

5.4. Conclusions

The origin of a spill was identified by assessing the compositional equivalence of samples stated from the *DR* comparison, as well as evaluating the evidence quality demonstrated by the probabilities of the compositional equivalence claim and the *LR*. The identification was performed by the MCM simulation approach and the conventional S-t and SC approaches according to the *DR* comparison conditions recommended by standard methodologies. Three *DR* comparison trials were conducted to validate the samples' declaration of compositional equivalence, as well as to enhance and/or to reduce the compositional equivalence rate when comparing samples with similar or distinct oil patterns, respectively.

The MCM and SC approaches state the compositional equivalence by performing a single trial regardless of the *DR* comparison conditions, confidence level employed, and number of *DR* compared. The stricter S-t approach, applied to the conditions for which it was projected, requires at least two trials to state compositional equivalence, especially when a large number of *DR* are compared. A compositional difference between samples characterised by a lower number of *DR* must also be verified with additional *DR* comparison trials to ensure that the false evaluation is unlikely. Once multiple trials' *DR* equivalence assessments are combined, the ability to differentiate oil patterns from competing suspected sources is improved, and the uncertainty in the identification of the most probable spill origin is reduced.

Compared to the others, the MCM approach proved to be notably more successful. The S-t approach is the one that leads to the lowest discriminations between suspect source compositions and to low-support spill source identifications. Even though the SC approach outperforms the MCM approach in estimating zero false compositional equivalence rates, it also does not offer as much support for spill source identification.

The findings of the study allowed to present an optimised and statistically sound strategy for identifying the origin of an oil spill based on target criteria for the *LR* and compositional equivalence rates, estimated by the comparison of the oil patterns of the spilt oil and the oils collected from suspected spill sources. The spill source identification is reported if a moderately strong discrimination between competing suspected sources is recognised ($LR \geq 190$) and the most likely spill source is identified with reduced uncertainty (compositional equivalence rate $\geq 95\%$). Otherwise, performing additional *DR* comparison trials is recommended to enhance the quality of the identification.

The MCM approach, which defines *DR* comparison criteria that are statistically sound and adjusted to the probabilistic nature of *DR*, as well as the presented oil spill source identification strategy that appropriately manages the quality of the identifications by performing additional *DR* comparison trials, proves to be a breakthrough in this field, in particular considering the shortcomings in the conventional methodologies. The success and benefit of the MCM in evaluating and optimising the uncertainty in identifying the most probable source of oil pollution incidents encourage its adoption in modelling the physical and chemical behaviour of spilt oils driven by multiple weathering mechanisms.

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6. Final conclusions and future research

The primary goal of the presented work was to assess and optimise the uncertainty in identifying sources of oil spills in the marine environment through chemical analyses. To achieve this, a novel method based on the Monte Carlo Method (MCM) simulation was developed to compare ratios between abundances of oil-discriminating compounds, *i.e.*, diagnostic ratios (*DR*). This method also enables the estimation of probabilities of compositional equivalence between spill samples (Sp) and samples from suspect sources (SS). The MCM approach was developed in a Microsoft Excel environment alongside the conventional methods Student's *t* statistics (S-t) and a maximum relative difference of 14% (single criterion, SC). The last two are suggested *DR* comparison approaches used in the field by the Nordtest and EN 15522-2 methodologies, respectively. Two user-friendly computational simulation tools were developed: *Single&Multi_DR_Modelling* and *Single&Multi_DR_Flex_Modelling_EN15522*. The first one applies the MCM and S-t approaches in the comparison of *DR* obtained from a replicated sample analysis with a single *DR* value from another sample (**Chapter 2**). This tool was improved, leading to the subsequent version, which considers *DR* comparisons using the MCM, S-t, and SC approaches, as well as greater flexibility in selecting *DR*, the number of sample replicates to compare, and *DR* calculation formats (**Chapter 3**). The *Single&Multi_DR_Modelling* tool was applied to chromatographic data from an unweathered mixture of four crude oils, proving that the assumption by the S-t approach of normal *DR* probability distributions is invalid. This finding was obtained by comparing the *DR* results from replicated analyses to a single analysis of the same mixture of crude oils (**Chapter 2**). These probability distributions exhibited both positive and negative skewness, with no discernible trend, resulting in confidence intervals, used as *DR* comparison criteria, that were wider than those obtained from normal distributions. Although not included in this thesis, another study conducted within its scope analysed the probability distributions of *DR* involving sesquiterpanes in various types of oils and found comparable findings (see **National publications in Annex E**).

The probability distributions of the differences between mean *DR* values, obtained from independent chromatographic analysis of the previously used mixture of crude oils, were also found to deviate from normality due to their flattening when using the optimised tool *Single&Multi_DR_Flex_Modelling_EN15522* (**Chapter 3**). Consequently, the confidence intervals derived from the real probability distributions of the differences in *DR* mean values were broader compared to those obtained by assuming normality. In both aforementioned cases,

as the number of chromatographic data replicates increased, there was an obvious tendency towards smaller confidence intervals.

In addition to the chromatographic data of a mixture of crude oils (**Chapters 2 and 3**), the "*Single&Multi_DR_Flex_Modelling_EN15522*" tool was used on chromatographic data from Sp and SS, which are known to be and not to be the origin of the spills represented by Sp (**Chapters 2 to 5**). These samples were obtained from four Round Robin Tests provided by the Oil Spill Network of Experts within the Bonn Agreement. This application was tested under a variety of *DR* comparison conditions, including distinct sets of *DR* unaffected by weathering, different replicated analyses, two calculation *DR* formats, and two confidence levels. This study allowed us to assess the impact of varying these conditions on the performance of the MCM approach in contrast to the traditional S-t and SC, based on the dimension of the confidence intervals produced to compare *DR* and the probabilities of true and false compositional equivalence claims. The various outcomes revealed consistent trends in the range of confidence limits, which were aligned with the previous findings from the assessment of the probability distributions of the *DR* and the differences between *DR* mean values. In contrast, the SC approach was more permissive and, when used under the *DR* comparison conditions for which it was designed, proved to be less restrictive than the MCM approach applied to 98% confidence. The MCM approach, regardless of the number of replicates or the *DR* format calculation, produced wider yet more robust confidence intervals, which narrowed as the statistical robustness conferred by the degrees of freedom increased.

Variations in the extent of the confidence intervals have a direct effect on both the declaration of compositional equivalence of the two samples, which is based on the equivalence of all the *DR* that characterise the fingerprint of the compared oils, and the probability (or total risk) of this being assumed. Both the claims of compositional equivalence and their respective probabilities vary depending on the *DR* comparison conditions and the number of *DR* used. The results obtained demonstrated that there is a proportional increase in the risk of falsely declaring a difference between *DR* with the number of *DR* considered. Such occurrences of a probabilistic nature can be recognised by performing additional *DR* comparison trials on independent chromatographic data for both samples. This new procedure, which is not advised by the usual Nordtest and EN 15522-2 methodologies, allows for the confirmation of sample compositional equivalence if each *DR* in both compared samples is statistically similar in at least one or two of the two or three *DR* comparison trials. In the studies conducted comparing Sp and SS known to be the source of the spills (**Chapters 4 and 5**), the S-t approach revealed that more than one

DR comparison trial is required to declare compositional equivalence, especially when applied to larger *DR* sets and under the conditions intended to be used. The MCM and SC approaches, regardless of the comparison conditions recommended by the Nordtest and EN 15522-2 methodologies or the number of *DR* analysed, can declare compositional equivalence using a single *DR* comparison trial. The declaration of compositional difference between samples, evaluated by comparing *Sp* with *SS* known not to be the source of the spills, was straightforward to establish due to the large number of non-equivalent *DR* identified by each approach, with the MCM approach matching or even outperforming the other approaches. However, when evaluating sets with a small number of *DR*, it is essential to take additional measures to verify the few inequalities among the identified *DR* pairs, ensuring low rates of false compositional equivalences.

The procedure for conducting additional *DR* comparison tests proved beneficial not only for deciding the compositional equivalence of two samples, but also in estimating the probability of compositional equivalence claims for oils. The probabilities of correct and incorrect claims of compositional equality were estimated based on the concluded compositional equivalence and difference evaluations, which were corroborated by prior information of the *SS* containing the same oil as the *Sp* (**Chapters 2 to 5**). The MCM approach was more effective when assessing accurate compositional equivalency, particularly under the *DR* comparison conditions specified by the Nordtest and EN 15522-2 practices. However, in relation to the probability of false compositional equivalence claim, the MCM approach prevailed over the S-t approach, while the SC approach outperformed the MCM approach, particularly when the competing *SS* have more similar chemical compositions and/or a reduced number of *DR* was compared.

The probabilities of true and false compositional equivalence claims considering two and three *DR* comparison trials were estimated by combining the assessments of the comparison of mean *DR* values from each performed trial, obtained by applying the tool "*Single&Multi_DR_Flex_Modelling_EN15522*" mentioned above and three additional computational tools, *i.e.*, "*MCM_False_Compositional_Equiv_Claim*", "*S-t_False_Compositional_Equiv_Claim*", and "*SC_False_Compositional_Equiv_Claim*" (**Chapter 5**). The results proved that performing additional *DR* comparison trials is beneficial, raising the chance of accurately declare compositional equivalence and lowering the chance of incorrect state compositional equivalence, particularly when two or three trials are employed, respectively. Applying such a procedure, the MCM approach also exhibited greater proficiency in identifying the pollution source by estimating probabilities of true compositional equivalence

claims compared to other approaches. Compared to the S-t approach, the MCM approach presented a lesser chance of affirming incorrect identifications, although it showed superiority to the SC approach. As a result, MCM outperforms the S-t approach by discriminating better between competing SS while falling short of the SC approach. However, this limitation of the MCM approach to SC is mitigated by identifying the polluting source with a lower level of uncertainty.

The strategy proposed to identify a spill source is founded on criteria for distinguishing competing suspected sources based on the *LR* value, as well as the degree of certainty of identifying the potential source, dependent on the probabilities of compositional equivalence claims between *Sp* and the two most probable SS (**Chapter 5**). The defined criteria of $\geq 95.0\%$ for the probability of compositional equivalence between *Sp* and the first most probable SS and $\leq 0.50\%$ for the second most probable SS produce an *LR* value ≥ 190 , with the value 190 pointing to moderately strong support in the differentiation of competing suspected sources, as indicated by the EN 15522-2 methodology and the European Network of Forensic Science Institutes. The inability to meet any of these requirements demands performing additional *DR* comparison trials using independent chromatographic analyses of the samples examined to adjust the quality of the identification to the required level. This prerequisite was proven by comparing two *Sp* with three SS, analysing *DR* sets with different ranges, and SS with distinct degrees of similarity.

All studies conducted emphasise the importance of selecting an appropriate approach for comparing oil patterns and, thus, ensuring accurate identification of pollutant sources of spills. The novel and innovative MCM approach differs from conventional ones as it is more reliable and robust, providing statistically strong control over comparisons, ensuring more accurate identifications. This research represents a major contribution to the subject by pioneering the statistically sound evaluation of the probabilistic aspects of *DR*, as well as giving a method for evaluating these indices adjusted to their statistical specificities. On the other hand, it provided an assessment of the influence that various *DR* comparison conditions have on the performance of the approaches when declaring the equivalence or difference between oil fingerprints. The user-friendly computational tools developed and made available to the scientific community address the shortage in the area, particularly those designed to estimate the rates of true and false identifications, which are essential to assess the probative value of the evidence in forensic science. Furthermore, the proposed strategy to identify the origin of an oil spill will contribute beneficially to more informed judicial decisions. The studies presented here provide resources

for improving forensic environmental analyses, but there is still an opportunity for progress in the presented domain, such as applying the tools developed to new and different cases of pollution offences, attempting to further deepen the performance of the suggested strategy, and conducting research on weathering, oil mixtures, sampling quality, and sample conservation.

Annexes

Annex A

Supplementary material of Chapter 2

Content:

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A.1. Experimental details

The experimental details present the operational conditions used in the GC-MS analysis and the list of diagnostic ratios studied.

▪ GC-MS conditions

One microliter of MixCrude solution was injected in on-column mode, by an ALS syringe of 10 μ L tapered, fixed needle, 23-26s/42/cone (Agilent Technologies, Santa Clara, USA) with a fast plunger and no pre- and post-injection dwell, with the injector operated 3 °C above oven temperature. The carrier gas was helium (purity $\geq$ 99.999%) at a constant flow of 1.1 mL/min. One meter of deactivated fused silica capillary pre-column, with 0.53 mm internal diameter (Agilent Technologies, Santa Clara, USA), was connected between the injector and a 30 m DB-5ms capillary column (non-polar phenyl arylene polymer capillary column virtually equivalent to (5%-phenyl)-methylpolysiloxane, 0.25 mm internal diameter, 0.25 μ m film thickness) (Agilent Technologies, Santa Clara, USA). The oven programme temperature was set to an initial temperature of 60 °C for 1 min, followed by a ramp I rate of 9 °C/min up to 100 °C and a ramp II rate of 5 °C/min until reaching a final temperature of 310 °C, which was held isothermal for 30 min. The quadrupole mass spectrometer detector was operated using 70 eV electron impact, with ion source, mass analyser and transfer line set to 230 °C, 150 °C and 300 °C, respectively. The analytical data were collected with 4.5 min of solvent delay, in the selected ion monitoring mode (SIM) according to the ion menu presented in **Table A.1**.

Table A.1. Compounds analysed and ions used for their identification and quantification.

Class of compounds	Compound	Abbreviation	Qion ⁽¹⁾	Cion ⁽²⁾
<i>n</i>-Alkanes	Decane to Hexatriacontane	C10 to C36 (Cx; x - carbon number)	85	57
Isoprenoids	Pristane Phytane	Pr Ph	85	57
PAH	Naphthalene Methylnaphthalenes Dimethylnaphthalenes Trimethylnaphthalenes Tetramethylnaphthalenes Acenaphthylene Acenaphthene Fluorene Methylfluorenes Dimethylfluorenes Trimethylfluorenes Phenanthrene Anthracene Methylphenanthrenes/anthracenes Dimethylphenanthrenes/anthracenes Trimethylphenanthrenes/anthracenes Tetramethylphenanthrenes/anthracenes Dibenzothiophene Methyldibenzothiophenes Dimethyldibenzothiophenes Trimethyldibenzothiophenes Tetramethyldibenzothiophenes Fluoranthene Pyrene Methylfluoranthenes/pyrenes Dimethylfluoranthenes/pyrenes Trimethylfluoranthenes/pyrenes Benzo(a)anthracene Chrysene Methylchrysenes Dimethylchrysenes Trimethylchrysenes Tetramethylchrysenes Benzo(b+k)fluoranthene Benzo(e)pyrene Benzo(a)pyrene Perylene Indeno(1,2,3-cd)pyrene Benzo(g,h,i)perylene Dibenzo(a,h)anthracene	N C1-N C2-N C3-N C4-N Acy Ace F C1-F C2-F C3-F Phe A C1-Phe/A C2-Phe/A C3-Phe/A C4-Phe/A Dbt C1-Dbt C2-Dbt C3-Dbt C4-Dbt Fluo P C1-Fluo/P C2-Fluo/P C3-Fluo/P BaA Chr C1-Chr C2-Chr C3-Chr C4-Chr B(b+k)F BeP BaP Per Ind BgHiP DBA	128 142 156 170 184 152 154 165 180 194 208 178 192 206 220 234 184 198 212 226 240 202 202 216 230 244 228 228 242 256 270 284 252 252 252 252 276 276 278	127 - - - - 153 153 165 - - - 176 - - - - 139 - - - - 101 101 - - - - 226 226 - - - 253 253 253 253 138 138 139
Methyldibenzothiophenes	4-Methyldibenzothiophene (2-/3)-Methyldibenzothiophenes 1-Methyldibenzothiophene	4-MDbt 2-/3-MDbt 1-MDbt	198	184

(1) Quantitation fragment.
(2) Confirmation fragment.

Table A.1 (cont.).

Class of compounds	Compound	Abbreviation	Qion ⁽¹⁾	Cion ⁽²⁾
Methylphenanthrenes	3-Methylphenanthrene	3-MPhe	192	-
	2-Methylphenanthrene	2-MPhe		
	(9-/4)-Methylphenanthrenes	9-/4-MPhe		
	1-Methylphenanthrene	1-MPhe		
Dimethylphenanthrenes	3,6-Dimethylphenanthrene	3,6-MPhe	206	-
	2,6-Dimethylphenanthrene	2,6-MPhe		
	2,7-Dimethylphenanthrene	2,7-MPhe		
	(1,3-/2,10-/3,9-/3,10)-Dimethylphenanthrenes	1,3-/2,10-/3,9-/3,10-MPhe		
	(1,6-/2,9)-Dimethylphenanthrenes	1,6-/2,9-MPhe		
	1,7-Dimethylphenanthrene	1,7-MPhe		
	(2,3-/1,9)-Dimethylphenanthrenes	2,3-/1,9-MPhe		
	1,8-Dimethylphenanthrene	1,8-MPhe		
	(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-Dimethylphenanthrenes	1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7-MPhe		
Hopanes	18 α (H)-22,29,30-Trisnorhopane	27Ts	191	412; 177
	17 α (H)-22,29,30-Trisnorhopane	27Tm		
	17 α (H),21 β (H)-25,28,30-Trisnorhopane	25nor30ab		
	17 α (H),21 β (H)-30-Norhopane	29ab		
	17 β (H),21 α (H)-Norhopane (Normoretane)	29ba		
	18 α (H)-Oleanane	30O		
	17 α (H),21 β (H)-Hopane (Hopane)	30ab		
	17 β (H),21 α (H)-Hopane (Moretane)	30ba		
	Gammacerane	30G		
	17 α (H),21 β (H),22S-Homohopane	31abS		
	17 α (H),21 β (H),22R-Homohopane	31abR		
	17 α (H),21 β (H),22S-Bishomohopane	32abS		
	17 α (H),21 β (H),22R-Bishomohopane	32abR		
	17 α (H),21 β (H),22S-Trishomohopane	33abS		
	17 α (H),21 β (H),22R-Trishomohopane	33abR		
	17 α (H),21 β (H),22S-Tetrakishomohopane	34abS		
	17 α (H),21 β (H),22R-Tetrakishomohopane	34abR		
	17 α (H),21 β (H),22S-Pentakishomohopane	35abS		
	17 α (H),21 β (H),22R-Pentakishomohopane	35abR		
Steranes	13 β (H),17 α (H),20S-Cholestane	27dbS	217	218
	13 β (H),17 α (H),20R-Cholestane	27dbR		
	24-Methyl-5 α (H),14 α (H),17 α (H),20R-cholestane	28aaR		
	24-Ethyl-5 α (H),14 α (H),17 α (H),20S-cholestane	29aaS		
	24-Ethyl-5 α (H),14 β (H),17 β (H),20R-cholestane	29bbR		
	24-Ethyl-5 α (H),14 β (H),17 β (H),20S-cholestane	29bbS		
	24-Ethyl-5 α (H),14 α (H),17 α (H),20R-cholestane	29aaR	218	217
	5 α (H),14 β (H),17 β (H),20(R+S)-Cholestane	27bb(R&S)		
	24-Methyl-5 α (H),14 β (H),17 β (H),20(R+S)-cholestane	28bb(R&S)		
	24-Ethyl-5 α (H),14 β (H),17 β (H), C20(R+S)-cholestane	29bb(R&S)		

(1) Quantitation fragment.

(2) Confirmation fragment.

Table A.1 (cont.).

Class of compounds	Compound	Abbreviation	Qion ⁽¹⁾	Cion ⁽²⁾
Triaromatic steranes				
	C20-Triaromatic sterane	TA20	231	-
	C21-Triaromatic sterane	TA21		
	C26,20S-Triaromatic sterane	TA26S		
	C26,20R- & C27,20S-Triaromatic steranes	TA26R&TA27S		
	C28,20S-Triaromatic sterane	TA28S		
	C27,20R-Triaromatic sterane	TA27R		
	C28,20R-Triaromatic sterane	TA28R		
Sesquiterpanes				
	C14 Sesquiterpane	SQ1	123	179
	Nordrimane	SQ2		
	C15 Sesquiterpane	SQ3		
	C15 Sesquiterpane	SQ4		193
	8β(H)-Drimane	SQ5		
	C15 Sesquiterpane	SQ6		207
	C16 Sesquiterpane	SQ7		
	C16 Sesquiterpane	SQ8		193
	C16 Sesquiterpane	SQ9		
	8β(H)-Homodrimane	SQ10		207
Adamantanes				
	Adamantane	Ad	136	135
	1-Methyladamantane	1-MAd	135	150
	1,3-Dimethyladamantane	1,3-MAd	149	164
	1,3,5-Trimethyladamantane	1,3,5-MAd	163	178
	1,3,5,7-Tetramethyladamantane	1,3,5,7-MAd	177	192
	2-Methyladamantane	2-MAd	135	150
	cis-1,4-Dimethyladamantane	1,4-MAd(cis)	149	164
	trans-1,4-Dimethyladamantane	1,4-MAd(trans)	149	164
	1,3,6-Trimethyladamantane	1,3,6-MAd	163	178
	1,2-Dimethyladamantane	1,2-MAd	149	164
	cis-1,3,4-Dimethyladamantane	1,3,4-MAd(cis)	163	178
	trans-1,3,4-Dimethyladamantane	1,3,4-MAd(trans)	163	178
	1,2,5,7-Tetramethyladamantane	1,2,5,7-MAd	177	192
	1-Ethyladamantane	1-EAd	135	164
	1-Ethyl-2-methyladamantane	1-E-3-MAd	149	178
	1-Ethyl-3,5-dimethyladamantane	1-E-3,5-MAd	163	192
	2-Ethyladamantane	2-EAd	135	164

(1) Quantitation fragment.

(2) Confirmation fragment.

Table A.2. List of studied diagnostic ratios, their corresponding *DR* code and the notation used in this work, as well as in the literature for their identification.

<i>DR</i> code	Current study ⁽²⁾	Biscaya (1997) ⁽¹⁾	Faksness <i>et al.</i> (2002) ⁽²⁾	CEN 2012 ⁽¹⁾	Yang <i>et al.</i> (2009) ⁽²⁾
<i>DR01</i>	<i>n</i> -Alkane and isoprenoid C18/Ph	-	n-C18/phytane	DR-n-C18/Phy	n-C18/Phy
	alkyl-PAH				
<i>DR02</i>	C2-Dbt/C2-Phe	-	C2-dbt/C2-phe (%)	DR - C2-dbt/C2-phe	-
<i>DR03</i>	4-MDbt/1-MDbt	-	4-MD/1-MD (%)	DR - 4-MDBT/1-MDBT	-
<i>DR04</i>	(2-/3)-MDbt/4-MDbt	$100 \times C'/C$	-	-	-
<i>DR05</i>	4-MDbt/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe	$100 \times C/D$	-	-	-
<i>DR06</i>	(2-/3)-MDbt/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe	$100 \times C'/D$	-	-	-
<i>DR07</i>	1-MDbt/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe	$100 \times C''/D$	-	-	-
<i>DR08</i>	3-MPhe/(9-/4-/1)-MPhe	$100 \times a/B$	-	-	-
<i>DR09</i>	2-MPhe/(9-/4-/1)-MPhe	$100 \times a'/B$	-	-	-
<i>DR10</i>	1-MPhe/(9-/4)-MPhe	$100 \times b'/b$	-	-	-
<i>DR11</i>	2-MPhe/1-MPhe	$100 \times a'/b'$	2-MP/1-MP (%)	DR - 2-MP/1-MP	-
<i>DR12</i>	3-MPhe/(1,3-/2,10-/3,9-/3,10/1,6-/2,9-/1,7)-MPhe	$100 \times a/D$	-	-	-
<i>DR13</i>	2-MPhe/(1,3-/2,10-/3,9-/3,10/1,6-/2,9-/1,7)-MPhe	$100 \times a'/D$	-	-	-
<i>DR14</i>	1-MPhe/(1,3-/2,10-/3,9-/3,10/1,6-/2,9-/1,7)-MPhe	$100 \times b'/D$	-	-	-
<i>DR15</i>	(9-/4-/1)-MPhe/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe	$100 \times B/D$	-	-	-
<i>DR16</i>	(9-/4)-MPhe/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe	$100 \times b/D$	-	-	-
<i>DR17</i>	(2-/3)-MPhe/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe	$100 \times A/D$	-	-	-
<i>DR18</i>	3,6-MPhe/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe	$100 \times e/D$	-	-	-
<i>DR19</i>	(2,6-/2,7)-MPhe/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe	$100 \times (e'+e'')/D$	-	-	-
<i>DR20</i>	(2,6-/2,7)-MPhe/(1,3-/2,10-/3,9-/3,10)-MPhe	$100 \times (e'+e'')/d$	-	-	-
<i>DR21</i>	(1,3-/2,10-/3,9-/3,10)-MPhe/(1,3-/2,10-/3,9-/3,10/1,6-/2,9-/1,7)-MPhe	$100 \times d/D$	-	-	-
<i>DR22</i>	(1,6-/2,9)-MPhe/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe	$100 \times d'/D$	-	-	-
<i>DR23</i>	1,7-MPhe/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe	$100 \times d''/D$	-	-	-
<i>DR24</i>	(1,6-/2,9)-MPhe/(1,3-/2,10-/3,9-/3,10)-MPhe	$100 \times d'/d$	-	-	-
<i>DR25</i>	1,7-MPhe/(1,3-/2,10-/3,9-/3,10)-MPhe	$100 \times d''/d$	-	-	-
<i>DR26</i>	((2,3-/1,9)-MPhe + 1,8-MPhe)/((1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe)	$100 \times (f+f')/D$	-	-	-

(1) Diagnostic ratio format: A/B .

(2) Diagnostic ratio format: $A/(A+B)$.

Table A.2 (cont.).

DR code	Current study ⁽²⁾	Biscaya (1997) ⁽¹⁾	Faksness <i>et al.</i> (2002) ⁽²⁾	CEN 2012 ⁽¹⁾	Yang <i>et al.</i> (2009) ⁽²⁾	Yang <i>et al.</i> (2011) ⁽¹⁾
Hopanes						
DR27	27Ts/27Tm	-	%27Ts	DR - Ts/Tm	-	Ts/Tm
DR28	27Ts/30ab	100 x H1/HOP	-	DR - 27Ts/30ab	-	-
DR29	27Tm/30ab	100 x H2/HOP	-	DR - 27Tm/30ab	-	-
DR30	30O/30ab	100 x OL/HOP	%30O	DR - 30O/30ab	-	-
DR31	30G/30ab	-	%30G	DR - 30G/30ab	-	-
DR32	29ab/30ab	100 x H4/HOP	%29ab	DR - 29ab/30ab	C29/C30ab-hopane	C29/C30
DR33	31abS/30ab	100 x H5/HOP	-	DR - 31abS/30ab	-	-
DR34	32abS/32abR	-	%32abS	-	-	C32(S)/C32(R)
Steranes						
DR35	29aaS/29aaR	-	%29aaS	DR - 29aaS/29aaR	-	-
DR36	27bb(R&S)/(28bb(R&S) + 29bb(R&S))	-	%27bbSTER	-	-	-
DR37	28bb(R&S)/(27bb(R&S) + 29bb(R&S))	-	%28bbSTER	-	-	-
DR38	29bb(R&S)/(27bb(R&S) + 28bb(R&S))	-	%29bbSTER	-	-	-
DR39	27bb(R&S)/29bb(R&S)	-	-	DR - 27bb/29bb (m/z 218)	C27 αββ/C29 αββ	C27 αββ/C29 αββ
Triaromatic steranes						
DR40	TA21/TA26R&TA27S	-	-	DR - C21TA/RC26 + SC27	-	-
DR41	TA21/TA28R	-	%TA21	DR - C21TA/RC28TA	-	-
DR42	TA27R/TA28R	-	%TA27	DR - RC27TA/RC28TA	-	-
DR43	TA27R/TA26R&TA27S	-	-	DR - RC27/RC26 + SC27	-	-
DR44	TA26S/TA28S	-	%TA26	DR - SC26TA/SC28TA	-	-
DR45	TA26S/TA26R&TA27S	-	-	DR - SC26/RC26 + SC27	-	-
DR46	TA28R/TA26R&TA27S	-	-	DR - RC28/RC26 + SC27	-	-
DR47	TA28S/TA26R&TA27S	-	-	DR - SC28/RC26 + SC27	-	-

(1) Diagnostic ratio format: A/B .(2) Diagnostic ratio format: $A/(A+B)$.

Table A.2 (cont.).

DR code	Current study ⁽²⁾	CEN (2012) ⁽¹⁾	Wang <i>et al.</i> (2005) ⁽¹⁾	Wang <i>et al.</i> (2006) ⁽¹⁾	Yang <i>et al.</i> (2006) ⁽¹⁾	Yang <i>et al.</i> (2009) ⁽¹⁾	Yang <i>et al.</i> (2011) ⁽¹⁾
Sesquiterpanes							
DR48	SQ3/SQ5	DR - SES 1/3	P3:P5	-	-	BS3/BS5	BS3/BS5
DR49	SQ3/SQ4	-	-	-	-	BS3/BS4	BS3/BS4
DR50	SQ4/SQ5	DR - SES 2/3	P4:P5	-	-	BS4/BS5	BS4/BS5
DR51	SQ6/SQ5	DR - SES 4/3	P6:P5	-	-	BS6/BS5	BS6/BS5
DR52	SQ8/SQ9	-	-	-	-	BS8/BS9	-
DR53	SQ8/SQ10	-	P8:P10	-	-	BS8/BS10	BS8/BS10
DR54	SQ1/SQ5	-	-	-	-	BS1/BS5	BS1/BS5
DR55	SQ3/SQ10	-	P3:P10	-	-	BS3/BS10	BS3/BS10
DR56	SQ9/SQ10	-	-	-	-	BS9/BS10	-
DR57	SQ10/SQ5	DR - SES 8/3	-	-	-	-	-
Adamantanes							
DR58	1-MAd/1,2-MAd	-	-	1-MA/1,2-DMA	1-MA/1,2-DMA	-	-
DR59	1-MAd/2-EAd	-	-	1-MA/2-EA	1-MA/2-EA	-	-
DR60	1-MAd/(1,3,4-MAd(cis) + 1,3,4-MAd(trans))	-	-	1-MA/1,3,4-TMA	1-MA/1,3,4-TMA	-	-
DR61	1-MAd/1,2,5,7-MAd	-	-	1-MA/1,2,5,7-TeMA	1-MA/1,2,5,7-TeMA	-	-
DR62	1,3,5-MAd/1,3,6-MAd	-	-	1,3,5-TMA/1,3,6-TMA	1,3,5-TMA/1,3,6-TMA	-	-
DR63	1,2-MAd/1,3,5-MAd	-	-	1,2-DMA/1,3,5-TMA	-	-	-
DR64	1,3,6-MAd/(1,3,4-MAd(cis) + 1,3,4-MAd(trans))	-	-	1,3,6-TMA/1,3,4-TMA	-	-	-
DR65	2-EAd/1,2-MAd	-	-	2-EA/1,2-DMA	2-EA/1,2-DMA	-	-
DR66	2-EAd/1,2,5,7-MAd	-	-	2-EA/1,2,5,7-TeMA	-	-	-
DR67	2-EAd/(1,3,4-MAd(cis) + 1,3,4-MAd(trans))	-	-	2-EA/1,3,4-TMA	-	-	-
DR68	1,2-MAd/(1,3,4-MAd(cis) + 1,3,4-MAd(trans))	-	-	1,2-DMA/1,3,4-TMA	-	-	-
DR69	(1,3,4-MAd(cis) + 1,3,4-MAd(trans))/1,2,5,7-MAd	-	-	1,3,4-TMA/1,2,5,7-TeMA	-	-	-

(1) Diagnostic ratio format: A/B .(2) Diagnostic ratio format: $A/(A+B)$.

A.2. Detailed results

Table A.3. Diagnostic ratio (*DR*) confidence intervals, defined by the MCM and S-t methods, from different replicate injections of extracts ($n = 3, 5, 8$) at 95% and 98% confidence levels. Quantification of *DR* skewness (A_P), interval range overlapping (η), and the probability of observing *DR* values beyond S-t limits (φ).

DR Code	n	Skewness		MCM confidence limits		S-t confidence limits		φ (%) ⁽²⁾		η (%) ⁽³⁾	
		A_P	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%	95%	98%
n-Alkane and isoprenoid											
DR01	3	-0.002	N - W	0.465 - 0.620	0.330 - 0.746	0.515 - 0.634	0.478 - 0.671	6.67	4.18	130	216
	5	-0.020	N - W	0.488 - 0.620	0.443 - 0.637	0.511 - 0.623	0.491 - 0.643	7.18	3.58	118	128
	8	-0.120	N - W	0.505 - 0.622	0.468 - 0.631	0.526 - 0.631	0.512 - 0.645	6.20	3.41	111	123
alkyl-PAH											
DR02	3	0.013	P - W	0.447 - 0.487	0.433 - 0.502	0.448 - 0.485	0.436 - 0.496	5.61	2.33	108	115
	5	0.032	P - W	0.455 - 0.492	0.451 - 0.502	0.453 - 0.487	0.447 - 0.494	4.40	1.89	109	109
	8	0.004	P - W	0.443 - 0.495	0.438 - 0.506	0.443 - 0.488	0.437 - 0.495	5.24	2.02	116	117
DR03	3	-0.011	N - W	0.610 - 0.632	0.602 - 0.639	0.612 - 0.631	0.606 - 0.637	5.32	2.33	116	119
	5	-0.051	N - W	0.607 - 0.629	0.600 - 0.631	0.610 - 0.629	0.606 - 0.633	4.61	1.92	116	115
	8	-0.022	N - W	0.607 - 0.630	0.603 - 0.633	0.609 - 0.629	0.606 - 0.632	6.33	2.82	115	115
DR04	3	0.018	P - W	0.397 - 0.456	0.374 - 0.486	0.396 - 0.447	0.380 - 0.462	5.09	2.30	116	137
	5	0.043	P - W	0.411 - 0.443	0.408 - 0.454	0.407 - 0.438	0.402 - 0.443	3.70	1.44	103	112
	8	0.038	P - W	0.408 - 0.441	0.404 - 0.446	0.410 - 0.438	0.406 - 0.442	5.99	2.68	118	117
DR05	3	-0.005	N - W	0.331 - 0.360	0.319 - 0.370	0.333 - 0.360	0.325 - 0.368	5.94	2.77	107	119
	5	-0.016	N - W	0.323 - 0.356	0.312 - 0.359	0.327 - 0.359	0.321 - 0.365	6.61	3.43	103	107
	8	0.013	P - W	0.292 - 0.384	0.283 - 0.402	0.296 - 0.372	0.286 - 0.382	6.15	2.78	121	124
DR06	3	-0.006	N - W	0.270 - 0.293	0.259 - 0.308	0.268 - 0.289	0.262 - 0.295	4.82	2.39	110	148
	5	-0.010	N - W	0.267 - 0.285	0.263 - 0.289	0.267 - 0.286	0.264 - 0.289	5.51	2.32	94.7	104
	8	0.023	P - W	0.242 - 0.305	0.236 - 0.318	0.243 - 0.296	0.236 - 0.303	5.38	2.32	119	122
DR07	3	-0.010	N - W	0.240 - 0.247	0.236 - 0.250	0.241 - 0.247	0.239 - 0.249	6.27	2.96	117	140
	5	-0.021	N - W	0.234 - 0.248	0.229 - 0.250	0.235 - 0.250	0.233 - 0.253	6.19	2.97	93.3	105
	8	0.022	P - W	0.201 - 0.281	0.192 - 0.297	0.204 - 0.268	0.196 - 0.276	8.53	4.24	125	131

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM area beyond S-t limits.

(3) MCM intervals relative to S-t intervals.

Table A.3 (cont.).

DR Code	n	Skewness		MCM confidence limits		S-t confidence limits		φ (%) ⁽²⁾		η (%) ⁽³⁾	
		A_P	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%	95%	98%
alkyl-PAH (continued)											
DR08	3	0.003	P - W	0.182 - 0.250	0.156 - 0.273	0.183 - 0.246	0.164 - 0.266	5.34	2.43	108	115
	5	-0.060	N - W	0.192 - 0.229	0.184 - 0.234	0.194 - 0.231	0.187 - 0.238	5.90	2.34	100	98.0
	8	-0.026	N - W	0.198 - 0.234	0.193 - 0.238	0.197 - 0.236	0.191 - 0.241	4.60	2.15	92.3	90.0
DR09	3	-0.007	N - W	0.261 - 0.282	0.253 - 0.289	0.262 - 0.282	0.256 - 0.288	5.39	2.33	105	113
	5	-0.004	N - W	0.259 - 0.295	0.254 - 0.302	0.259 - 0.293	0.253 - 0.299	5.71	2.58	106	104
	8	-0.031	N - W	0.261 - 0.288	0.258 - 0.291	0.262 - 0.288	0.259 - 0.291	5.08	2.02	104	103
DR10	3	0.012	P - W	0.469 - 0.569	0.446 - 0.622	0.463 - 0.554	0.435 - 0.582	6.40	2.98	110	120
	5	0.114	P - W	0.483 - 0.565	0.475 - 0.584	0.477 - 0.556	0.463 - 0.569	6.35	2.93	104	103
	8	0.239	P - M	0.478 - 0.556	0.471 - 0.574	0.474 - 0.546	0.465 - 0.556	7.02	3.58	108	113
DR11	3	-0.018	N - W	0.360 - 0.474	0.306 - 0.506	0.375 - 0.479	0.343 - 0.511	6.27	2.99	110	119
	5	-0.027	N - W	0.393 - 0.452	0.381 - 0.461	0.396 - 0.451	0.386 - 0.461	5.68	2.48	107	107
	8	-0.011	N - W	0.401 - 0.442	0.394 - 0.446	0.403 - 0.442	0.398 - 0.447	5.74	2.67	105	106
DR12	3	-0.012	N - W	0.165 - 0.256	0.122 - 0.307	0.162 - 0.241	0.137 - 0.266	4.97	2.30	115	143
	5	0.019	P - W	0.179 - 0.222	0.171 - 0.230	0.179 - 0.221	0.171 - 0.229	4.75	1.97	102	102
	8	0.168	P - M	0.186 - 0.224	0.182 - 0.232	0.182 - 0.221	0.177 - 0.227	3.54	1.32	97.4	100
DR13	3	-0.009	N - W	0.237 - 0.293	0.223 - 0.333	0.235 - 0.277	0.222 - 0.290	8.32	4.10	133	162
	5	0.055	P - W	0.240 - 0.291	0.234 - 0.306	0.239 - 0.283	0.232 - 0.290	7.41	3.50	116	124
	8	0.071	P - W	0.240 - 0.284	0.236 - 0.295	0.239 - 0.277	0.234 - 0.282	7.94	3.91	116	123
DR14	3	0.002	P - W	0.269 - 0.406	0.241 - 0.504	0.257 - 0.375	0.221 - 0.411	6.69	3.35	116	138
	5	0.044	P - W	0.281 - 0.382	0.269 - 0.410	0.281 - 0.368	0.265 - 0.384	6.89	3.21	116	118
	8	0.017	P - W	0.291 - 0.366	0.284 - 0.384	0.289 - 0.354	0.281 - 0.363	7.92	4.02	115	122
DR15	3	-0.003	N - W	0.459 - 0.524	0.447 - 0.576	0.452 - 0.507	0.435 - 0.524	7.46	3.90	118	145
	5	0.074	P - W	0.468 - 0.501	0.465 - 0.512	0.467 - 0.494	0.463 - 0.499	8.38	4.29	122	131
	8	0.207	P - M	0.464 - 0.502	0.462 - 0.514	0.463 - 0.493	0.458 - 0.497	9.28	5.22	127	133
DR16	3	-0.002	N - W	0.234 - 0.408	0.148 - 0.495	0.232 - 0.386	0.184 - 0.434	4.74	2.41	113	139
	5	0.017	P - W	0.265 - 0.357	0.248 - 0.373	0.267 - 0.354	0.252 - 0.369	5.33	2.48	106	107
	8	-0.002	N - W	0.283 - 0.343	0.275 - 0.351	0.283 - 0.343	0.275 - 0.350	4.83	2.29	100	101

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM area beyond S-t limits.

(3) MCM intervals relative to S-t intervals.

Table A.3 (cont.).

DR Code	n	Skewness		MCM confidence limits		S-t confidence limits		φ (%) ⁽²⁾		η (%) ⁽³⁾	
		A_P	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%	95%	98%
alkyl-PAH (continued)											
DR17	3	-0.016	N - W	0.361 - 0.379	0.346 - 0.385	0.367 - 0.380	0.362 - 0.385	4.85	2.34	138	170
	5	0.009	P - W	0.359 - 0.379	0.352 - 0.380	0.363 - 0.381	0.360 - 0.384	3.33	1.31	111	117
	8	0.055	P - W	0.350 - 0.394	0.346 - 0.404	0.351 - 0.385	0.346 - 0.390	8.98	4.83	129	132
DR18	3	-0.024	N - W	0.095 - 0.115	0.083 - 0.124	0.099 - 0.116	0.094 - 0.121	6.79	3.28	118	152
	5	-0.063	N - W	0.096 - 0.113	0.091 - 0.115	0.098 - 0.114	0.096 - 0.116	7.40	3.38	106	120
	8	-0.021	N - W	0.099 - 0.111	0.097 - 0.113	0.100 - 0.111	0.098 - 0.112	6.14	3.11	109	114
DR19	3	0.013	P - W	0.148 - 0.160	0.143 - 0.169	0.148 - 0.157	0.145 - 0.160	7.87	4.02	133	173
	5	-0.029	N - W	0.144 - 0.156	0.142 - 0.158	0.145 - 0.157	0.143 - 0.159	3.97	1.86	100	100
	8	0.017	P - W	0.140 - 0.164	0.137 - 0.168	0.142 - 0.162	0.139 - 0.164	7.43	3.73	120	124
DR20	3	0.000	N - W	0.216 - 0.366	0.174 - 0.460	0.209 - 0.334	0.171 - 0.372	7.16	3.26	120	142
	5	0.006	P - W	0.228 - 0.305	0.215 - 0.319	0.227 - 0.306	0.213 - 0.320	4.90	2.20	97.5	97.2
	8	-0.013	N - W	0.242 - 0.290	0.235 - 0.297	0.240 - 0.292	0.233 - 0.299	4.63	2.11	92.3	93.9
DR21	3	0.004	P - W	0.234 - 0.395	0.159 - 0.443	0.254 - 0.397	0.210 - 0.441	6.32	3.35	113	123
	5	0.055	P - W	0.291 - 0.370	0.278 - 0.384	0.290 - 0.368	0.276 - 0.382	5.27	2.30	101	100
	8	-0.003	N - W	0.304 - 0.360	0.297 - 0.369	0.303 - 0.358	0.295 - 0.366	5.53	2.40	102	101
DR22	3	0.008	P - W	0.143 - 0.222	0.087 - 0.260	0.162 - 0.228	0.141 - 0.249	7.22	3.73	120	160
	5	-0.034	N - W	0.177 - 0.216	0.168 - 0.223	0.178 - 0.218	0.171 - 0.225	5.71	2.50	97.5	102
	8	0.067	P - W	0.184 - 0.219	0.180 - 0.225	0.182 - 0.220	0.177 - 0.225	4.27	1.68	92.1	93.8
DR23	3	0.010	P - W	0.193 - 0.225	0.181 - 0.237	0.194 - 0.224	0.185 - 0.233	5.80	2.76	107	117
	5	0.009	P - W	0.198 - 0.218	0.195 - 0.222	0.199 - 0.217	0.195 - 0.220	5.86	2.56	111	108
	8	-0.021	N - W	0.201 - 0.214	0.199 - 0.215	0.201 - 0.214	0.199 - 0.216	5.19	2.03	100	94.1
DR24	3	-0.005	N - W	0.273 - 0.400	0.216 - 0.478	0.290 - 0.379	0.263 - 0.406	6.82	3.44	143	183
	5	-0.023	N - W	0.301 - 0.363	0.288 - 0.372	0.308 - 0.362	0.299 - 0.372	5.23	2.32	115	115
	8	-0.022	N - W	0.315 - 0.360	0.309 - 0.366	0.316 - 0.359	0.310 - 0.365	5.21	2.34	105	104
DR25	3	0.033	P - W	0.306 - 0.436	0.269 - 0.517	0.300 - 0.409	0.266 - 0.442	6.81	3.41	119	141
	5	-0.010	N - W	0.316 - 0.382	0.305 - 0.395	0.315 - 0.382	0.304 - 0.394	4.89	2.16	98.5	100
	8	-0.055	N - W	0.319 - 0.372	0.311 - 0.379	0.320 - 0.373	0.313 - 0.380	5.34	2.48	100	101

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM area beyond S-t limits.

(3) MCM intervals relative to S-t intervals.

Table A.3 (cont.).

DR Code	n	Skewness		MCM confidence limits		S-t confidence limits		φ (%) ⁽²⁾		η (%) ⁽³⁾	
		A_P	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%	95%	98%
Hopanes											
DR26	3	0.010	P - W	0.166 - 0.306	0.104 - 0.370	0.172 - 0.279	0.139 - 0.312	5.45	2.68	131	154
	5	0.018	P - W	0.191 - 0.282	0.178 - 0.303	0.193 - 0.272	0.180 - 0.286	5.52	2.12	115	118
	8	0.108	P - W	0.204 - 0.268	0.199 - 0.282	0.203 - 0.258	0.196 - 0.266	4.92	1.82	116	119
DR27	3	0.007	P - W	0.403 - 0.527	0.345 - 0.568	0.408 - 0.523	0.373 - 0.558	5.50	2.51	108	121
	5	0.008	P - W	0.423 - 0.528	0.404 - 0.546	0.426 - 0.524	0.409 - 0.542	5.66	2.50	107	107
	8	0.213	P - M	0.434 - 0.529	0.428 - 0.550	0.429 - 0.516	0.418 - 0.528	7.45	3.73	109	111
DR28	3	-0.017	N - W	0.134 - 0.193	0.110 - 0.211	0.136 - 0.193	0.118 - 0.210	5.52	2.24	104	110
	5	-0.007	N - W	0.149 - 0.182	0.143 - 0.188	0.150 - 0.182	0.145 - 0.188	5.48	2.29	103	105
	8	0.014	P - W	0.152 - 0.181	0.149 - 0.187	0.151 - 0.178	0.147 - 0.181	4.26	1.67	107	112
DR29	3	0.004	P - W	0.174 - 0.189	0.164 - 0.192	0.177 - 0.191	0.173 - 0.195	6.96	3.40	107	127
	5	-0.010	N - W	0.163 - 0.197	0.157 - 0.202	0.165 - 0.196	0.160 - 0.201	6.52	2.78	110	110
	8	-0.221	N - M	0.160 - 0.194	0.153 - 0.197	0.164 - 0.196	0.160 - 0.200	6.60	3.31	106	110
DR30	3	0.005	P - W	0.251 - 0.311	0.208 - 0.321	0.265 - 0.317	0.249 - 0.333	4.49	2.30	115	135
	5	-0.003	N - W	0.239 - 0.313	0.218 - 0.321	0.248 - 0.316	0.236 - 0.328	4.63	1.98	109	112
	8	-0.022	N - W	0.256 - 0.305	0.249 - 0.312	0.258 - 0.304	0.251 - 0.310	5.41	2.49	107	107
DR31	3	-0.003	N - W	0.168 - 0.234	0.138 - 0.258	0.176 - 0.236	0.158 - 0.255	6.49	2.89	110	124
	5	-0.129	N - W	0.174 - 0.222	0.162 - 0.228	0.178 - 0.225	0.170 - 0.233	6.46	3.01	102	105
	8	0.024	P - W	0.183 - 0.217	0.179 - 0.222	0.183 - 0.216	0.179 - 0.220	5.33	2.20	103	105
DR32	3	-0.026	N - W	0.357 - 0.441	0.295 - 0.456	0.378 - 0.449	0.357 - 0.471	4.25	2.04	118	141
	5	-0.071	N - W	0.385 - 0.428	0.371 - 0.432	0.393 - 0.430	0.387 - 0.437	3.91	1.50	116	122
	8	0.000	P - W	0.389 - 0.428	0.384 - 0.434	0.391 - 0.425	0.386 - 0.430	6.51	3.07	115	114
DR33	3	-0.006	N - W	0.200 - 0.294	0.136 - 0.310	0.225 - 0.300	0.201 - 0.324	7.54	3.69	125	141
	5	0.009	P - W	0.228 - 0.279	0.212 - 0.284	0.237 - 0.281	0.230 - 0.289	7.87	3.96	116	122
	8	-0.028	N - W	0.235 - 0.283	0.229 - 0.289	0.238 - 0.280	0.233 - 0.286	6.36	2.97	114	113
DR34	3	-0.007	N - W	0.483 - 0.618	0.433 - 0.665	0.494 - 0.616	0.457 - 0.653	5.29	2.63	111	118
	5	-0.055	N - W	0.522 - 0.584	0.511 - 0.595	0.527 - 0.582	0.517 - 0.592	5.20	2.37	113	112
	8	-0.054	N - W	0.526 - 0.575	0.518 - 0.580	0.529 - 0.576	0.523 - 0.583	4.56	1.97	104	103

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM area beyond S-t limits.

(3) MCM intervals relative to S-t intervals.

Table A.3 (cont.).

DR Code	n	Skewness		MCM confidence limits		S-t confidence limits		φ (%) ⁽²⁾		η (%) ⁽³⁾	
		A_P	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%	95%	98%
Steranes											
DR35	3	-0.019	N - W	0.466 - 0.666	0.337 - 0.735	0.518 - 0.666	0.472 - 0.711	7.28	3.89	135	167
	5	0.009	P - W	0.550 - 0.642	0.531 - 0.660	0.557 - 0.638	0.543 - 0.652	6.65	3.30	114	118
	8	-0.091	N - W	0.559 - 0.624	0.547 - 0.632	0.563 - 0.623	0.555 - 0.631	5.71	2.66	108	112
DR36	3	0.018	P - W	0.302 - 0.360	0.281 - 0.391	0.299 - 0.350	0.283 - 0.366	4.92	2.38	114	133
	5	0.102	P - W	0.314 - 0.345	0.311 - 0.354	0.313 - 0.340	0.308 - 0.345	4.07	1.62	115	116
	8	0.145	P - W	0.315 - 0.339	0.313 - 0.344	0.314 - 0.336	0.311 - 0.338	4.72	1.79	109	115
DR37	3	0.018	P - W	0.305 - 0.331	0.299 - 0.348	0.304 - 0.324	0.297 - 0.331	6.24	3.14	130	144
	5	0.016	P - W	0.299 - 0.325	0.295 - 0.329	0.300 - 0.323	0.296 - 0.328	5.66	2.57	113	106
	8	-0.067	N - W	0.303 - 0.320	0.300 - 0.322	0.304 - 0.319	0.302 - 0.321	6.30	2.98	113	116
DR38	3	-0.018	N - W	0.318 - 0.384	0.273 - 0.398	0.332 - 0.390	0.315 - 0.408	5.38	2.77	114	134
	5	-0.125	N - W	0.342 - 0.374	0.333 - 0.377	0.347 - 0.377	0.342 - 0.382	4.27	1.80	107	110
	8	-0.106	N - W	0.350 - 0.374	0.345 - 0.377	0.352 - 0.375	0.349 - 0.378	4.73	2.02	104	110
DR39	3	-0.008	N - W	0.441 - 0.530	0.415 - 0.586	0.434 - 0.512	0.410 - 0.537	7.03	3.57	114	135
	5	0.063	P - W	0.458 - 0.500	0.455 - 0.514	0.455 - 0.493	0.449 - 0.500	7.23	3.73	111	116
	8	0.165	P - M	0.458 - 0.491	0.455 - 0.498	0.457 - 0.487	0.453 - 0.491	6.99	3.59	110	113
Triaromatic steranes											
DR40	3	-0.013	N - W	0.137 - 0.191	0.112 - 0.211	0.146 - 0.190	0.133 - 0.203	6.73	3.28	123	141
	5	-0.173	N - M	0.153 - 0.179	0.147 - 0.182	0.157 - 0.180	0.153 - 0.184	7.01	3.51	113	113
	8	-0.097	N - W	0.154 - 0.176	0.150 - 0.178	0.157 - 0.177	0.154 - 0.180	6.38	3.28	110	108
DR41	3	-0.017	N - W	0.131 - 0.292	0.071 - 0.355	0.151 - 0.286	0.110 - 0.328	6.82	3.01	119	130
	5	-0.039	N - W	0.176 - 0.250	0.159 - 0.261	0.184 - 0.251	0.173 - 0.263	5.87	2.79	110	113
	8	-0.006	N - W	0.191 - 0.242	0.183 - 0.249	0.193 - 0.239	0.187 - 0.245	6.05	2.93	111	114
DR42	3	-0.019	N - W	0.417 - 0.539	0.361 - 0.579	0.437 - 0.538	0.406 - 0.569	5.53	2.72	121	134
	5	-0.033	N - W	0.422 - 0.519	0.395 - 0.529	0.436 - 0.521	0.421 - 0.536	4.61	1.98	114	117
	8	0.058	P - W	0.444 - 0.514	0.434 - 0.525	0.446 - 0.509	0.437 - 0.517	6.31	3.01	111	114

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM area beyond S-t limits.

(3) MCM intervals relative to S-t intervals.

Table A.3 (cont.).

DR Code	n	Skewness		MCM confidence limits		S-t confidence limits		φ (%) ⁽²⁾		η (%) ⁽³⁾	
		A _P	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%	95%	98%
Triaromatic steranes (continued)											
DR43	3	0.007	P - W	0.394 - 0.423	0.383 - 0.433	0.395 - 0.420	0.388 - 0.427	5.48	2.46	116	128
	5	-0.032	N - W	0.364 - 0.432	0.350 - 0.443	0.369 - 0.432	0.359 - 0.443	6.56	2.95	108	111
	8	-0.040	N - W	0.372 - 0.425	0.364 - 0.431	0.375 - 0.423	0.368 - 0.430	6.04	2.73	110	108
DR44	3	0.016	P - W	0.261 - 0.346	0.243 - 0.392	0.258 - 0.330	0.236 - 0.352	5.10	2.49	118	128
	5	0.112	P - W	0.274 - 0.349	0.268 - 0.375	0.268 - 0.335	0.256 - 0.347	3.97	1.63	112	118
	8	0.173	P - M	0.281 - 0.331	0.276 - 0.340	0.281 - 0.327	0.274 - 0.333	5.00	2.07	109	108
DR45	3	0.006	P - W	0.177 - 0.270	0.157 - 0.329	0.172 - 0.249	0.149 - 0.273	5.62	2.99	121	139
	5	0.025	P - W	0.194 - 0.242	0.190 - 0.258	0.191 - 0.233	0.184 - 0.240	3.98	1.58	114	121
	8	0.186	P - M	0.197 - 0.233	0.194 - 0.239	0.197 - 0.228	0.193 - 0.233	5.00	2.01	116	113
DR46	3	0.021	P - W	0.359 - 0.504	0.307 - 0.568	0.360 - 0.479	0.324 - 0.516	6.77	3.14	122	136
	5	0.034	P - W	0.394 - 0.461	0.385 - 0.479	0.392 - 0.451	0.382 - 0.461	7.56	3.62	114	119
	8	-0.112	N - W	0.392 - 0.446	0.384 - 0.451	0.396 - 0.446	0.389 - 0.453	4.91	2.06	108	105
DR47	3	0.008	P - W	0.378 - 0.414	0.371 - 0.438	0.376 - 0.405	0.367 - 0.414	5.30	2.66	124	143
	5	-0.071	N - W	0.354 - 0.409	0.341 - 0.417	0.358 - 0.410	0.349 - 0.419	6.15	2.98	106	109
	8	0.017	P - W	0.359 - 0.407	0.353 - 0.413	0.361 - 0.404	0.356 - 0.410	6.31	2.67	112	111
Sesquiterpanes											
DR48	3	0.004	P - W	0.367 - 0.578	0.222 - 0.707	0.412 - 0.589	0.357 - 0.643	6.20	3.55	119	170
	5	-0.014	N - W	0.439 - 0.545	0.405 - 0.562	0.453 - 0.546	0.437 - 0.562	5.27	2.60	114	126
	8	-0.031	N - W	0.454 - 0.530	0.440 - 0.540	0.459 - 0.531	0.449 - 0.540	5.05	2.37	106	110
DR49	3	-0.015	N - W	0.290 - 0.425	0.233 - 0.498	0.309 - 0.406	0.279 - 0.436	7.52	3.50	139	169
	5	0.011	P - W	0.315 - 0.396	0.297 - 0.417	0.321 - 0.390	0.309 - 0.403	6.52	3.03	117	128
	8	-0.095	N - W	0.306 - 0.397	0.282 - 0.405	0.320 - 0.400	0.310 - 0.410	7.59	3.87	114	123
DR50	3	0.004	P - W	0.491 - 0.746	0.346 - 0.838	0.534 - 0.750	0.467 - 0.817	5.63	3.25	118	141
	5	-0.039	N - W	0.580 - 0.692	0.550 - 0.710	0.594 - 0.694	0.576 - 0.711	4.99	2.35	112	119
	8	0.089	P - W	0.586 - 0.694	0.573 - 0.715	0.588 - 0.682	0.575 - 0.695	6.81	3.47	115	118

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM area beyond S-t limits.

(3) MCM intervals relative to S-t intervals.

Table A.3 (cont.).

DR Code	n	Skewness		MCM confidence limits		S-t confidence limits		φ (%) ⁽²⁾		η (%) ⁽³⁾	
		A_P	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%	95%	98%
Sesquiterpanes (continued)											
DR51	3	-0.024	N - W	0.334 - 0.466	0.220 - 0.528	0.371 - 0.475	0.338 - 0.508	7.91	4.00	127	181
	5	0.002	P - W	0.378 - 0.444	0.348 - 0.450	0.397 - 0.446	0.388 - 0.455	9.16	4.92	135	152
	8	-0.019	N - W	0.383 - 0.447	0.372 - 0.457	0.391 - 0.442	0.385 - 0.449	7.65	3.93	125	133
DR52	3	0.037	P - W	0.522 - 0.738	0.460 - 0.836	0.516 - 0.711	0.456 - 0.771	5.87	2.80	111	119
	5	0.024	P - W	0.571 - 0.691	0.556 - 0.727	0.569 - 0.669	0.551 - 0.686	7.54	4.01	120	127
	8	-0.042	N - W	0.577 - 0.673	0.563 - 0.686	0.585 - 0.667	0.574 - 0.678	6.33	3.17	117	118
DR53	3	0.015	P - W	0.230 - 0.287	0.218 - 0.329	0.225 - 0.273	0.210 - 0.288	4.18	2.02	119	142
	5	0.025	P - W	0.230 - 0.272	0.224 - 0.286	0.228 - 0.267	0.221 - 0.274	4.29	1.93	108	117
	8	0.015	P - W	0.235 - 0.264	0.232 - 0.270	0.234 - 0.261	0.230 - 0.265	4.15	1.71	107	109
DR54	3	0.001	P - W	0.346 - 0.442	0.279 - 0.495	0.364 - 0.445	0.339 - 0.471	5.42	2.83	119	164
	5	0.001	P - W	0.371 - 0.445	0.358 - 0.462	0.370 - 0.443	0.357 - 0.455	5.43	2.39	101	106
	8	0.045	P - W	0.379 - 0.438	0.373 - 0.451	0.376 - 0.431	0.369 - 0.438	6.98	3.34	107	113
DR55	3	-0.017	N - W	0.282 - 0.419	0.165 - 0.490	0.321 - 0.432	0.286 - 0.467	6.24	3.70	123	180
	5	-0.011	N - W	0.329 - 0.408	0.302 - 0.419	0.342 - 0.409	0.331 - 0.421	7.36	3.80	118	130
	8	-0.112	N - W	0.343 - 0.397	0.328 - 0.402	0.353 - 0.401	0.346 - 0.408	7.21	4.06	113	119
DR56	3	-0.010	N - W	0.118 - 0.227	0.077 - 0.263	0.123 - 0.223	0.092 - 0.254	6.26	2.73	109	115
	5	0.004	P - W	0.128 - 0.204	0.112 - 0.217	0.136 - 0.201	0.125 - 0.213	6.73	3.17	117	119
	8	0.068	P - W	0.138 - 0.197	0.131 - 0.208	0.139 - 0.190	0.132 - 0.197	5.56	2.20	116	118
DR57	3	-0.011	N - W	0.581 - 0.667	0.551 - 0.704	0.584 - 0.663	0.560 - 0.687	5.29	2.45	109	120
	5	-0.009	N - W	0.604 - 0.644	0.595 - 0.651	0.606 - 0.642	0.600 - 0.648	5.72	2.67	111	117
	8	0.030	P - W	0.597 - 0.647	0.591 - 0.659	0.596 - 0.640	0.590 - 0.646	7.23	3.74	114	121
Adamantanes											
DR58	3	0.017	P - W	0.667 - 0.746	0.615 - 0.807	0.661 - 0.725	0.642 - 0.745	7.69	4.07	123	186
	5	0.011	P - W	0.679 - 0.717	0.674 - 0.732	0.678 - 0.709	0.672 - 0.715	7.72	4.07	123	135
	8	0.007	P - W	0.667 - 0.720	0.663 - 0.737	0.666 - 0.709	0.661 - 0.715	8.45	4.59	123	137

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM area beyond S-t limits.

(3) MCM intervals relative to S-t intervals.

Table A.3 (cont.).

DR Code	n	Skewness		MCM confidence limits		S-t confidence limits		φ (%) ⁽²⁾		η (%) ⁽³⁾	
		A _P	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%	95%	98%
Adamantanes (continued)											
DR59	3	-0.009	N - W	0.704 - 0.847	0.593 - 0.968	0.691 - 0.805	0.656 - 0.841	7.11	4.16	125	203
	5	-0.004	N - W	0.687 - 0.793	0.667 - 0.818	0.689 - 0.787	0.672 - 0.804	5.83	2.86	108	114
	8	0.011	P - W	0.681 - 0.794	0.665 - 0.820	0.680 - 0.780	0.667 - 0.793	7.05	3.71	113	123
DR60	3	0.014	P - W	0.591 - 0.685	0.507 - 0.768	0.582 - 0.655	0.560 - 0.677	4.82	3.26	129	223
	5	0.012	P - W	0.596 - 0.644	0.588 - 0.659	0.595 - 0.636	0.588 - 0.643	4.79	2.10	117	129
	8	0.022	P - W	0.587 - 0.642	0.581 - 0.656	0.586 - 0.634	0.580 - 0.640	4.86	2.09	115	125
DR61	3	0.017	P - W	0.828 - 0.861	0.816 - 0.876	0.829 - 0.858	0.819 - 0.867	6.22	2.60	114	125
	5	0.037	P - W	0.835 - 0.855	0.832 - 0.861	0.836 - 0.853	0.833 - 0.856	6.98	3.26	118	126
	8	0.021	P - W	0.827 - 0.858	0.823 - 0.865	0.828 - 0.855	0.824 - 0.859	6.69	3.17	115	120
DR62	3	-0.018	N - W	0.399 - 0.476	0.361 - 0.515	0.414 - 0.469	0.397 - 0.486	6.95	3.25	140	173
	5	-0.060	N - W	0.404 - 0.457	0.383 - 0.461	0.414 - 0.461	0.406 - 0.470	7.52	4.00	113	122
	8	0.005	P - W	0.420 - 0.457	0.414 - 0.462	0.421 - 0.457	0.417 - 0.461	5.21	2.45	103	109
DR63	3	0.010	P - W	0.591 - 0.676	0.520 - 0.743	0.616 - 0.683	0.595 - 0.704	4.76	3.09	127	205
	5	-0.058	N - W	0.624 - 0.662	0.605 - 0.665	0.634 - 0.665	0.629 - 0.670	3.97	1.90	123	146
	8	-0.014	N - W	0.625 - 0.671	0.609 - 0.676	0.634 - 0.674	0.628 - 0.679	4.29	1.76	115	131
DR64	3	0.010	P - W	0.281 - 0.423	0.155 - 0.539	0.280 - 0.378	0.249 - 0.408	5.65	3.05	145	242
	5	0.043	P - W	0.303 - 0.384	0.296 - 0.420	0.297 - 0.361	0.286 - 0.373	4.03	1.71	127	143
	8	0.016	P - W	0.301 - 0.356	0.295 - 0.370	0.298 - 0.352	0.291 - 0.359	4.24	1.64	102	110
DR65	3	-0.015	N - W	0.360 - 0.461	0.262 - 0.566	0.393 - 0.470	0.369 - 0.494	5.96	3.90	131	243
	5	0.012	P - W	0.376 - 0.513	0.342 - 0.540	0.386 - 0.505	0.365 - 0.526	6.63	3.21	115	123
	8	-0.062	N - W	0.382 - 0.504	0.357 - 0.522	0.395 - 0.502	0.381 - 0.516	5.92	2.74	114	122
DR66	3	0.005	P - W	0.537 - 0.686	0.389 - 0.849	0.589 - 0.700	0.554 - 0.734	4.94	3.51	134	256
	5	-0.051	N - W	0.582 - 0.720	0.544 - 0.742	0.597 - 0.719	0.575 - 0.740	5.50	2.72	113	120
	8	-0.021	N - W	0.578 - 0.721	0.543 - 0.739	0.601 - 0.723	0.584 - 0.739	5.15	2.54	117	126
DR67	3	-0.011	N - W	0.289 - 0.394	0.213 - 0.454	0.313 - 0.392	0.289 - 0.416	7.47	3.52	133	190
	5	0.001	P - W	0.314 - 0.408	0.290 - 0.428	0.320 - 0.404	0.306 - 0.418	5.57	2.48	112	123
	8	-0.029	N - W	0.301 - 0.420	0.275 - 0.437	0.315 - 0.418	0.301 - 0.432	7.00	3.42	116	124

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM area beyond S-t limits.

(3) MCM intervals relative to S-t intervals.

Table A.3 (cont.).

DR Code	<i>n</i>	Skewness		MCM confidence limits		S-t confidence limits		φ (%) ⁽²⁾		η (%) ⁽³⁾	
		<i>A_P</i>	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%	95%	98%
Adamantanes (continued)											
DR68	3	-0.002	N - W	0.394 - 0.446	0.366 - 0.474	0.400 - 0.435	0.390 - 0.445	7.67	3.94	149	196
	5	0.012	P - W	0.391 - 0.436	0.382 - 0.447	0.395 - 0.433	0.388 - 0.440	6.20	2.88	118	125
	8	-0.026	N - W	0.394 - 0.432	0.386 - 0.437	0.400 - 0.431	0.395 - 0.435	5.87	2.76	123	128
DR69	3	0.009	P - W	0.717 - 0.800	0.657 - 0.864	0.742 - 0.795	0.726 - 0.812	5.64	3.21	157	241
	5	-0.011	N - W	0.746 - 0.793	0.734 - 0.801	0.752 - 0.792	0.746 - 0.799	5.64	2.64	118	126
	8	-0.003	N - W	0.756 - 0.786	0.749 - 0.790	0.759 - 0.786	0.756 - 0.789	5.38	2.49	111	124
Max.		-0.221	Max.				9.28	5.22	157	256	
Min.		0.239	Min.				3.33	1.31	92.1	90.0	
			Mode				6.20	2.02	116	119	
Max. (<i>n</i> = 3)		0.037	Max. (<i>n</i> = 3)				8.32	4.18	157	256	
Min. (<i>n</i> = 3)		-0.026	Min. (<i>n</i> = 3)				4.18	2.02	104	110	
Max. (<i>n</i> = 5)		0.114	Max. (<i>n</i> = 5)				9.16	4.92	135	152	
Min. (<i>n</i> = 5)		-0.173	Min. (<i>n</i> = 5)				3.33	1.31	93.3	97.2	
Max. (<i>n</i> = 8)		0.239	Max. (<i>n</i> = 8)				9.28	5.22	129	137	
Min. (<i>n</i> = 8)		-0.221	Min. (<i>n</i> = 8)				3.54	1.32	92.1	90.0	

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM area beyond S-t limits.

(3) MCM intervals relative to S-t intervals.

Table A.4. Diagnostic ratio (*DR*) confidence intervals, defined by the MCM and S-t methods, from triplicate injections of extracts used in the experimental assessment of these limits at 95% and 98% confidence levels. Quantification of *DR* skewness (*A_P*) and interval range overlapping (η).

DR Code	n	Skewness		MCM confidence limits		S-t confidence limits		η (%) ⁽²⁾	
		A_P	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%
n-Alkane and isoprenoid									
DR01	3	-0.091	N - W	0.450 - 0.636	0.276 - 0.764	0.503 - 0.661	0.454 - 0.710	118	191
alkyl-PAH									
DR02	3	-0.104	N - W	0.446 - 0.477	0.427 - 0.492	0.453 - 0.478	0.446 - 0.485	127	167
DR03	3	0.062	P - W	0.594 - 0.648	0.578 - 0.677	0.598 - 0.638	0.585 - 0.650	134	153
DR04	3	0.057	P - W	0.411 - 0.449	0.403 - 0.481	0.407 - 0.440	0.396 - 0.451	113	143
DR05	3	0.057	P - W	0.307 - 0.382	0.274 - 0.425	0.314 - 0.369	0.297 - 0.386	137	169
DR06	3	0.030	P - W	0.248 - 0.324	0.207 - 0.370	0.247 - 0.305	0.229 - 0.322	130	173
DR07	3	0.058	P - W	0.234 - 0.254	0.227 - 0.264	0.236 - 0.250	0.231 - 0.254	143	163
DR08	3	0.081	P - W	0.207 - 0.240	0.199 - 0.263	0.203 - 0.233	0.193 - 0.242	109	132
DR09	3	-0.059	N - W	0.236 - 0.293	0.195 - 0.315	0.252 - 0.295	0.239 - 0.308	132	174
DR10	3	-0.120	N - W	0.460 - 0.532	0.410 - 0.562	0.478 - 0.535	0.460 - 0.552	126	164
DR11	3	-0.041	N - W	0.365 - 0.468	0.324 - 0.519	0.380 - 0.463	0.355 - 0.489	124	145
DR12	3	0.062	P - W	0.180 - 0.256	0.150 - 0.321	0.169 - 0.237	0.148 - 0.258	112	156
DR13	3	0.050	P - W	0.231 - 0.285	0.210 - 0.309	0.235 - 0.277	0.222 - 0.290	128	147
DR14	3	0.069	P - W	0.261 - 0.405	0.223 - 0.489	0.261 - 0.380	0.224 - 0.417	120	138
DR15	3	0.085	P - W	0.456 - 0.523	0.419 - 0.568	0.448 - 0.508	0.429 - 0.526	113	154
DR16	3	0.091	P - W	0.267 - 0.405	0.214 - 0.510	0.259 - 0.371	0.225 - 0.405	124	164
DR17	3	0.048	P - W	0.343 - 0.408	0.323 - 0.435	0.346 - 0.395	0.331 - 0.411	133	141
DR18	3	-0.041	N - W	0.096 - 0.115	0.087 - 0.124	0.100 - 0.113	0.096 - 0.118	140	168
DR19	3	-0.041	N - W	0.125 - 0.177	0.095 - 0.206	0.136 - 0.173	0.124 - 0.184	142	185
DR20	3	0.061	P - W	0.248 - 0.343	0.143 - 0.431	0.237 - 0.315	0.213 - 0.339	122	230
DR21	3	-0.066	N - W	0.213 - 0.374	0.095 - 0.487	0.262 - 0.386	0.223 - 0.424	130	195
DR22	3	-0.054	N - W	0.136 - 0.221	0.069 - 0.271	0.158 - 0.235	0.134 - 0.258	111	162
DR23	3	-0.055	N - W	0.202 - 0.209	0.197 - 0.213	0.203 - 0.211	0.203 - 0.211	128	190
DR24	3	0.052	P - W	0.305 - 0.378	0.275 - 0.414	0.314 - 0.361	0.299 - 0.375	156	182
DR25	3	0.060	P - W	0.296 - 0.468	0.147 - 0.610	0.290 - 0.415	0.252 - 0.454	138	229
DR26	3	0.054	P - W	0.178 - 0.272	0.145 - 0.340	0.189 - 0.256	0.168 - 0.277	139	180

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM intervals relative to S-t intervals.

Table A.4 (cont.).

DR Code	n	Skewness		MCM confidence limits		S-t confidence limits		η (%) ⁽²⁾	
		A _P	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%
Hopanes									
DR27	3	0.072	P - W	0.440 - 0.525	0.424 - 0.586	0.429 - 0.508	0.405 - 0.532	108	128
DR28	3	0.091	P - W	0.141 - 0.212	0.117 - 0.268	0.135 - 0.193	0.118 - 0.211	124	162
DR29	3	0.054	P - W	0.165 - 0.207	0.149 - 0.233	0.167 - 0.197	0.157 - 0.207	138	169
DR30	3	0.057	P - W	0.228 - 0.353	0.181 - 0.419	0.238 - 0.333	0.209 - 0.363	132	155
DR31	3	0.003	P - W	0.174 - 0.231	0.155 - 0.251	0.178 - 0.225	0.164 - 0.239	122	127
DR32	3	0.067	P - W	0.354 - 0.475	0.321 - 0.531	0.361 - 0.459	0.331 - 0.489	124	133
DR33	3	0.064	P - W	0.183 - 0.347	0.117 - 0.415	0.198 - 0.318	0.161 - 0.355	136	153
DR34	3	0.051	P - W	0.552 - 0.575	0.546 - 0.585	0.553 - 0.572	0.547 - 0.578	119	128
Steranes									
DR35	3	-0.086	N - W	0.532 - 0.640	0.476 - 0.685	0.558 - 0.635	0.535 - 0.659	140	169
DR36	3	0.086	P - W	0.303 - 0.365	0.290 - 0.409	0.297 - 0.352	0.280 - 0.368	113	134
DR37	3	0.063	P - W	0.307 - 0.325	0.304 - 0.337	0.305 - 0.321	0.300 - 0.326	112	132
DR38	3	-0.069	N - W	0.313 - 0.388	0.258 - 0.399	0.328 - 0.397	0.307 - 0.419	108	127
DR39	3	0.089	P - W	0.438 - 0.539	0.417 - 0.594	0.427 - 0.517	0.400 - 0.544	114	122
Triaromatic Steranes									
DR40	3	0.068	P - W	0.152 - 0.189	0.140 - 0.208	0.153 - 0.185	0.144 - 0.195	121	133
DR41	3	0.038	P - W	0.157 - 0.304	0.116 - 0.396	0.164 - 0.277	0.129 - 0.312	130	153
DR42	3	0.038	P - W	0.431 - 0.556	0.389 - 0.637	0.437 - 0.538	0.407 - 0.569	125	153
DR43	3	-0.045	N - W	0.400 - 0.412	0.395 - 0.416	0.402 - 0.411	0.399 - 0.414	129	136
DR44	3	0.038	P - W	0.239 - 0.359	0.206 - 0.423	0.250 - 0.343	0.221 - 0.372	128	144
DR45	3	0.047	P - W	0.163 - 0.275	0.131 - 0.328	0.168 - 0.257	0.140 - 0.284	125	136
DR46	3	-0.070	N - W	0.349 - 0.479	0.276 - 0.517	0.366 - 0.471	0.333 - 0.504	123	140
DR47	3	0.058	P - W	0.378 - 0.410	0.365 - 0.431	0.377 - 0.403	0.369 - 0.411	123	159

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM intervals relative to S-t intervals.

Table A.4 (cont.).

DR Code	n	Skewness		MCM confidence limits		S-t confidence limits		η (%) ⁽²⁾	
		A_P	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%
Sesquiterpanes									
DR48	3	-0.046	N - W	0.370 - 0.562	0.227 - 0.686	0.416 - 0.570	0.369 - 0.618	124	184
DR49	3	0.037	P - W	0.299 - 0.458	0.254 - 0.546	0.314 - 0.430	0.278 - 0.465	137	156
DR50	3	-0.044	N - W	0.479 - 0.727	0.338 - 0.876	0.532 - 0.712	0.476 - 0.767	138	185
DR51	3	-0.045	N - W	0.304 - 0.498	0.205 - 0.551	0.335 - 0.493	0.286 - 0.542	123	135
DR52	3	0.051	P - W	0.583 - 0.705	0.551 - 0.793	0.578 - 0.677	0.547 - 0.708	123	150
DR53	3	0.051	P - W	0.225 - 0.289	0.210 - 0.336	0.218 - 0.276	0.200 - 0.294	109	133
DR54	3	-0.031	N - W	0.346 - 0.430	0.283 - 0.445	0.366 - 0.442	0.343 - 0.465	111	132
DR55	3	-0.062	N - W	0.279 - 0.420	0.168 - 0.501	0.319 - 0.439	0.281 - 0.477	116	170
DR56	3	-0.036	N - W	0.127 - 0.194	0.084 - 0.218	0.137 - 0.189	0.120 - 0.206	128	156
DR57	3	-0.044	N - W	0.570 - 0.655	0.532 - 0.675	0.579 - 0.650	0.558 - 0.672	120	125
Adamantanes									
DR58	3	0.046	P - W	0.636 - 0.754	0.598 - 0.814	0.639 - 0.741	0.607 - 0.772	116	131
DR59	3	0.041	P - W	0.688 - 0.846	0.588 - 0.986	0.691 - 0.806	0.655 - 0.841	138	215
DR60	3	0.069	P - W	0.537 - 0.703	0.488 - 0.786	0.537 - 0.683	0.492 - 0.728	114	126
DR61	3	-0.040	N - W	0.785 - 0.886	0.742 - 0.928	0.800 - 0.880	0.776 - 0.904	127	144
DR62	3	-0.038	N - W	0.412 - 0.467	0.383 - 0.491	0.423 - 0.462	0.411 - 0.475	139	168
DR63	3	-0.041	N - W	0.592 - 0.672	0.523 - 0.726	0.617 - 0.681	0.597 - 0.701	124	194
DR64	3	0.037	P - W	0.293 - 0.400	0.198 - 0.489	0.281 - 0.367	0.254 - 0.394	125	209
DR65	3	-0.040	N - W	0.347 - 0.470	0.260 - 0.592	0.387 - 0.469	0.361 - 0.494	149	249
DR66	3	-0.051	N - W	0.503 - 0.715	0.339 - 0.885	0.571 - 0.706	0.530 - 0.747	157	251
DR67	3	-0.064	N - W	0.258 - 0.404	0.156 - 0.500	0.301 - 0.389	0.274 - 0.416	167	243
DR68	3	0.055	P - W	0.394 - 0.438	0.377 - 0.457	0.396 - 0.430	0.385 - 0.441	126	142
DR69	3	-0.094	N - W	0.734 - 0.788	0.687 - 0.837	0.750 - 0.791	0.738 - 0.803	132	231

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM intervals relative to S-t intervals.

Table A.4 (cont.).

DR Code	n	Skewness		MCM confidence limits		S-t confidence limits		η (%) ⁽²⁾	
		A_P	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%
n-Alkane and isoprenoid									
DR01	3	-0.091	N - W	0.450 - 0.636	0.276 - 0.764	0.503 - 0.661	0.454 - 0.710	118	191
alkyl-PAH									
DR02	3	-0.104	N - W	0.446 - 0.477	0.427 - 0.492	0.453 - 0.478	0.446 - 0.485	127	167
DR03	3	0.062	P - W	0.594 - 0.648	0.578 - 0.677	0.598 - 0.638	0.585 - 0.650	134	153
DR04	3	0.057	P - W	0.411 - 0.449	0.403 - 0.481	0.407 - 0.440	0.396 - 0.451	113	143
DR05	3	0.057	P - W	0.307 - 0.382	0.274 - 0.425	0.314 - 0.369	0.297 - 0.386	137	169
DR06	3	0.030	P - W	0.248 - 0.324	0.207 - 0.370	0.247 - 0.305	0.229 - 0.322	130	173
DR07	3	0.058	P - W	0.234 - 0.254	0.227 - 0.264	0.236 - 0.250	0.231 - 0.254	143	163
DR08	3	0.081	P - W	0.207 - 0.240	0.199 - 0.263	0.203 - 0.233	0.193 - 0.242	109	132
DR09	3	-0.059	N - W	0.236 - 0.293	0.195 - 0.315	0.252 - 0.295	0.239 - 0.308	132	174
DR10	3	-0.120	N - W	0.460 - 0.532	0.410 - 0.562	0.478 - 0.535	0.460 - 0.552	126	164
DR11	3	-0.041	N - W	0.365 - 0.468	0.324 - 0.519	0.380 - 0.463	0.355 - 0.489	124	145
DR12	3	0.062	P - W	0.180 - 0.256	0.150 - 0.321	0.169 - 0.237	0.148 - 0.258	112	156
DR13	3	0.050	P - W	0.231 - 0.285	0.210 - 0.309	0.235 - 0.277	0.222 - 0.290	128	147
DR14	3	0.069	P - W	0.261 - 0.405	0.223 - 0.489	0.261 - 0.380	0.224 - 0.417	120	138
DR15	3	0.085	P - W	0.456 - 0.523	0.419 - 0.568	0.448 - 0.508	0.429 - 0.526	113	154
DR16	3	0.091	P - W	0.267 - 0.405	0.214 - 0.510	0.259 - 0.371	0.225 - 0.405	124	164
DR17	3	0.048	P - W	0.343 - 0.408	0.323 - 0.435	0.346 - 0.395	0.331 - 0.411	133	141
DR18	3	-0.041	N - W	0.096 - 0.115	0.087 - 0.124	0.100 - 0.113	0.096 - 0.118	140	168
DR19	3	-0.041	N - W	0.125 - 0.177	0.095 - 0.206	0.136 - 0.173	0.124 - 0.184	142	185
DR20	3	0.061	P - W	0.248 - 0.343	0.143 - 0.431	0.237 - 0.315	0.213 - 0.339	122	230
DR21	3	-0.066	N - W	0.213 - 0.374	0.095 - 0.487	0.262 - 0.386	0.223 - 0.424	130	195
DR22	3	-0.054	N - W	0.136 - 0.221	0.069 - 0.271	0.158 - 0.235	0.134 - 0.258	111	162
DR23	3	-0.055	N - W	0.202 - 0.209	0.197 - 0.213	0.203 - 0.211	0.203 - 0.211	128	190
DR24	3	0.052	P - W	0.305 - 0.378	0.275 - 0.414	0.314 - 0.361	0.299 - 0.375	156	182
DR25	3	0.060	P - W	0.296 - 0.468	0.147 - 0.610	0.290 - 0.415	0.252 - 0.454	138	229
DR26	3	0.054	P - W	0.178 - 0.272	0.145 - 0.340	0.189 - 0.256	0.168 - 0.277	139	180

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM intervals relative to S-t intervals.

Table A.4 (cont.).

DR Code	n	Skewness		MCM confidence limits		S-t confidence limits		η (%) ⁽²⁾	
		A _P	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%
Hopanes									
DR27	3	0.072	P - W	0.440 - 0.525	0.424 - 0.586	0.429 - 0.508	0.405 - 0.532	108	128
DR28	3	0.091	P - W	0.141 - 0.212	0.117 - 0.268	0.135 - 0.193	0.118 - 0.211	124	162
DR29	3	0.054	P - W	0.165 - 0.207	0.149 - 0.233	0.167 - 0.197	0.157 - 0.207	138	169
DR30	3	0.057	P - W	0.228 - 0.353	0.181 - 0.419	0.238 - 0.333	0.209 - 0.363	132	155
DR31	3	0.003	P - W	0.174 - 0.231	0.155 - 0.251	0.178 - 0.225	0.164 - 0.239	122	127
DR32	3	0.067	P - W	0.354 - 0.475	0.321 - 0.531	0.361 - 0.459	0.331 - 0.489	124	133
DR33	3	0.064	P - W	0.183 - 0.347	0.117 - 0.415	0.198 - 0.318	0.161 - 0.355	136	153
DR34	3	0.051	P - W	0.552 - 0.575	0.546 - 0.585	0.553 - 0.572	0.547 - 0.578	119	128
Steranes									
DR35	3	-0.086	N - W	0.532 - 0.640	0.476 - 0.685	0.558 - 0.635	0.535 - 0.659	140	169
DR36	3	0.086	P - W	0.303 - 0.365	0.290 - 0.409	0.297 - 0.352	0.280 - 0.368	113	134
DR37	3	0.063	P - W	0.307 - 0.325	0.304 - 0.337	0.305 - 0.321	0.300 - 0.326	112	132
DR38	3	-0.069	N - W	0.313 - 0.388	0.258 - 0.399	0.328 - 0.397	0.307 - 0.419	108	127
DR39	3	0.089	P - W	0.438 - 0.539	0.417 - 0.594	0.427 - 0.517	0.400 - 0.544	114	122
Triaromatic Steranes									
DR40	3	0.068	P - W	0.152 - 0.189	0.140 - 0.208	0.153 - 0.185	0.144 - 0.195	121	133
DR41	3	0.038	P - W	0.157 - 0.304	0.116 - 0.396	0.164 - 0.277	0.129 - 0.312	130	153
DR42	3	0.038	P - W	0.431 - 0.556	0.389 - 0.637	0.437 - 0.538	0.407 - 0.569	125	153
DR43	3	-0.045	N - W	0.400 - 0.412	0.395 - 0.416	0.402 - 0.411	0.399 - 0.414	129	136
DR44	3	0.038	P - W	0.239 - 0.359	0.206 - 0.423	0.250 - 0.343	0.221 - 0.372	128	144
DR45	3	0.047	P - W	0.163 - 0.275	0.131 - 0.328	0.168 - 0.257	0.140 - 0.284	125	136
DR46	3	-0.070	N - W	0.349 - 0.479	0.276 - 0.517	0.366 - 0.471	0.333 - 0.504	123	140
DR47	3	0.058	P - W	0.378 - 0.410	0.365 - 0.431	0.377 - 0.403	0.369 - 0.411	123	159

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM intervals relative to S-t intervals.

Table A.4 (cont.).

DR Code	n	Skewness		MCM confidence limits		S-t confidence limits		η (%) ⁽²⁾	
		A _P	Evaluation ⁽¹⁾	95%	98%	95%	98%	95%	98%
Sesquiterpanes									
DR48	3	-0.046	N - W	0.370 - 0.562	0.227 - 0.686	0.416 - 0.570	0.369 - 0.618	124	184
DR49	3	0.037	P - W	0.299 - 0.458	0.254 - 0.546	0.314 - 0.430	0.278 - 0.465	137	156
DR50	3	-0.044	N - W	0.479 - 0.727	0.338 - 0.876	0.532 - 0.712	0.476 - 0.767	138	185
DR51	3	-0.045	N - W	0.304 - 0.498	0.205 - 0.551	0.335 - 0.493	0.286 - 0.542	123	135
DR52	3	0.051	P - W	0.583 - 0.705	0.551 - 0.793	0.578 - 0.677	0.547 - 0.708	123	150
DR53	3	0.051	P - W	0.225 - 0.289	0.210 - 0.336	0.218 - 0.276	0.200 - 0.294	109	133
DR54	3	-0.031	N - W	0.346 - 0.430	0.283 - 0.445	0.366 - 0.442	0.343 - 0.465	111	132
DR55	3	-0.062	N - W	0.279 - 0.420	0.168 - 0.501	0.319 - 0.439	0.281 - 0.477	116	170
DR56	3	-0.036	N - W	0.127 - 0.194	0.084 - 0.218	0.137 - 0.189	0.120 - 0.206	128	156
DR57	3	-0.044	N - W	0.570 - 0.655	0.532 - 0.675	0.579 - 0.650	0.558 - 0.672	120	125
Adamantanes									
DR58	3	0.046	P - W	0.636 - 0.754	0.598 - 0.814	0.639 - 0.741	0.607 - 0.772	116	131
DR59	3	0.041	P - W	0.688 - 0.846	0.588 - 0.986	0.691 - 0.806	0.655 - 0.841	138	215
DR60	3	0.069	P - W	0.537 - 0.703	0.488 - 0.786	0.537 - 0.683	0.492 - 0.728	114	126
DR61	3	-0.040	N - W	0.785 - 0.886	0.742 - 0.928	0.800 - 0.880	0.776 - 0.904	127	144
DR62	3	-0.038	N - W	0.412 - 0.467	0.383 - 0.491	0.423 - 0.462	0.411 - 0.475	139	168
DR63	3	-0.041	N - W	0.592 - 0.672	0.523 - 0.726	0.617 - 0.681	0.597 - 0.701	124	194
DR64	3	0.037	P - W	0.293 - 0.400	0.198 - 0.489	0.281 - 0.367	0.254 - 0.394	125	209
DR65	3	-0.040	N - W	0.347 - 0.470	0.260 - 0.592	0.387 - 0.469	0.361 - 0.494	149	249
DR66	3	-0.051	N - W	0.503 - 0.715	0.339 - 0.885	0.571 - 0.706	0.530 - 0.747	157	251
DR67	3	-0.064	N - W	0.258 - 0.404	0.156 - 0.500	0.301 - 0.389	0.274 - 0.416	167	243
DR68	3	0.055	P - W	0.394 - 0.438	0.377 - 0.457	0.396 - 0.430	0.385 - 0.441	126	142
DR69	3	-0.094	N - W	0.734 - 0.788	0.687 - 0.837	0.750 - 0.791	0.738 - 0.803	132	231

(1) N - Negative skew; P - Positive skew; W - Weak skew; M - Moderate skew.

(2) MCM intervals relative to S-t intervals.

Table A.5. Diagnostic ratios (*DR*) observed in five independent injections of the MixCrude. Cells in red identify values outside MCM or S-t intervals defined from triplicate injections of the same extract presented in Table A.4. (“«” value in the left).

Single analysis ID	MixCrude_Inj02				MixCrude_Inj04				MixCrude_Inj05				MixCrude_Inj07				MixCrude_Inj08			
Confidence intervals	MCM 95%	S-t 95%	MCM 98%	S-t 98%	MCM 95%	S-t 95%	MCM 98%	S-t 98%	MCM 95%	S-t 95%	MCM 98%	S-t 98%	MCM 95%	S-t 95%	MCM 98%	S-t 98%	MCM 95%	S-t 95%	MCM 98%	S-t 98%
Number of "In"	67	67	68	67	65	66	69	69	65	66	68	68	65	64	66	66	65	63	67	67
Number of "Out"	2	2	1	2	4	3	0	0	4	3	1	1	4	5	3	3	4	6	2	2
<i>n</i> -Alkane and isoprenoid																				
<i>DR01</i>	0.574	«	«	«	0.576	«	«	«	0.535	«	«	«	0.596	«	«	«	0.602	«	«	«
alkyl-PAH																				
<i>DR02</i>	0.471	«	«	«	0.477	«	«	«	0.475	«	«	«	0.458	«	«	«	0.448	«	«	«
<i>DR03</i>	0.624	«	«	«	0.616	«	«	«	0.615	«	«	«	0.616	«	«	«	0.624	«	«	«
<i>DR04</i>	0.416	«	«	«	0.429	«	«	«	0.420	«	«	«	0.422	«	«	«	0.435	«	«	«
<i>DR05</i>	0.350	«	«	«	0.334	«	«	«	0.341	«	«	«	0.319	«	«	«	0.302	«	«	«
<i>DR06</i>	0.277	«	«	«	0.274	«	«	«	0.273	«	«	«	0.255	«	«	«	0.249	«	«	«
<i>DR07</i>	0.245	«	«	«	0.238	«	«	«	0.244	«	«	«	0.226	«	«	«	0.206	«	«	«
<i>DR08</i>	0.207	«	«	«	0.205	«	«	«	0.214	«	«	«	0.231	«	«	«	0.220	«	«	«
<i>DR09</i>	0.274	«	«	«	0.280	«	«	«	0.284	«	«	«	0.269	«	«	«	0.273	«	«	«
<i>DR10</i>	0.521	«	«	«	0.536	«	«	«	0.521	«	«	«	0.499	«	«	«	0.488	«	«	«
<i>DR11</i>	0.435	«	«	«	0.422	«	«	«	0.415	«	«	«	0.416	«	«	«	0.427	«	«	«
<i>DR12</i>	0.194	«	«	«	0.193	«	«	«	0.203	«	«	«	0.216	«	«	«	0.197	«	«	«
<i>DR13</i>	0.259	«	«	«	0.266	«	«	«	0.271	«	«	«	0.252	«	«	«	0.247	«	«	«
<i>DR14</i>	0.312	«	«	«	0.331	«	«	«	0.344	«	«	«	0.322	«	«	«	0.305	«	«	«
<i>DR15</i>	0.480	«	«	«	0.481	«	«	«	0.484	«	«	«	0.478	«	«	«	0.466	«	«	«
<i>DR16</i>	0.294	«	«	«	0.300	«	«	«	0.325	«	«	«	0.322	«	«	«	0.316	«	«	«
<i>DR17</i>	0.373	«	«	«	0.366	«	«	«	0.372	«	«	«	0.368	«	«	«	0.353	«	«	«
<i>DR18</i>	0.109	«	«	«	0.104	«	«	«	0.102	«	«	«	0.104	«	«	«	0.103	«	«	«
<i>DR19</i>	0.153	«	«	«	0.147	«	«	«	0.152	«	«	«	0.154	«	«	«	0.145	«	«	«
<i>DR20</i>	0.257	«	«	«	0.249	«	«	«	0.269	«	«	«	0.264	«	«	«	0.263	«	«	«
<i>DR21</i>	0.343	«	«	«	0.343	«	«	«	0.327	«	«	«	0.337	«	«	«	0.323	«	«	«
<i>DR22</i>	0.199	«	«	«	0.203	«	«	«	0.204	«	«	«	0.215	«	«	«	0.198	«	«	«
<i>DR23</i>	0.213	«	«	«	0.209	«	«	«	0.204	«	«	«	0.205	«	«	«	0.208	«	«	«
<i>DR24</i>	0.323	«	«	«	0.327	«	«	«	0.345	«	«	«	0.349	«	«	«	0.341	«	«	«
<i>DR25</i>	0.341	«	«	«	0.336	«	«	«	0.345	«	«	«	0.337	«	«	«	0.355	«	«	«
<i>DR26</i>	0.239	«	«	«	0.235	«	«	«	0.251	«	«	«	0.234	«	«	«	0.220	«	«	«

Table A.5 (cont.).

Single analysis ID	MixCrude Inj02				MixCrude Inj04				MixCrude Inj05				MixCrude Inj07				MixCrude Inj08			
Confidence intervals	MCM 95%	S-t 95%	MCM 98%	S-t 98%	MCM 95%	S-t 95%	MCM 98%	S-t 98%	MCM 95%	S-t 95%	MCM 98%	S-t 98%	MCM 95%	S-t 95%	MCM 98%	S-t 98%	MCM 95%	S-t 95%	MCM 98%	S-t 98%
Hopanes																				
DR27	0.452	«	«	«	0.479	«	«	«	0.500	«	«	«	0.494	«	«	«	0.450	«	«	«
DR28	0.157	«	«	«	0.167	«	«	«	0.172	«	«	«	0.166	«	«	«	0.160	«	«	«
DR29	0.184	«	«	«	0.179	«	«	«	0.172	«	«	«	0.169	«	«	«	0.188	«	«	«
DR30	0.290	«	«	«	0.268	«	«	«	0.271	«	«	«	0.282	«	«	«	0.276	«	«	«
DR31	0.212	«	«	«	0.193	«	«	«	0.195	«	«	«	0.199	«	«	«	0.194	«	«	«
DR32	0.411	«	«	«	0.406	«	«	«	0.412	«	«	«	0.404	«	«	«	0.402	«	«	«
DR33	0.258	«	«	«	0.251	«	«	«	0.258	«	«	«	0.266	«	«	«	0.266	«	«	«
DR34	0.539	«	«	«	0.554	«	«	«	0.554	«	«	«	0.538	«	«	«	0.552	«	«	«
Steranes																				
DR35	0.572	«	«	«	0.605	«	«	«	0.608	«	«	«	0.581	«	«	«	0.591	«	«	«
DR36	0.320	«	«	«	0.329	«	«	«	0.329	«	«	«	0.323	«	«	«	0.324	«	«	«
DR37	0.316	«	«	«	0.311	«	«	«	0.305	«	«	«	0.311	«	«	«	0.310	«	«	«
DR38	0.364	«	«	«	0.359	«	«	«	0.366	«	«	«	0.366	«	«	«	0.366	«	«	«
DR39	0.468	«	«	«	0.478	«	«	«	0.474	«	«	«	0.469	«	«	«	0.470	«	«	«
Triaromatic steranes																				
DR40	0.163	«	«	«	0.166	«	«	«	0.171	«	«	«	0.160	«	«	«	0.169	«	«	«
DR41	0.203	«	«	«	0.210	«	«	«	0.222	«	«	«	0.219	«	«	«	0.216	«	«	«
DR42	0.477	«	«	«	0.470	«	«	«	0.460	«	«	«	0.487	«	«	«	0.463	«	«	«
DR43	0.411	«	«	«	0.399	«	«	«	0.382	«	«	«	0.392	«	«	«	0.390	«	«	«
DR44	0.299	«	«	«	0.317	«	«	«	0.307	«	«	«	0.308	«	«	«	0.309	«	«	«
DR45	0.216	«	«	«	0.219	«	«	«	0.208	«	«	«	0.214	«	«	«	0.209	«	«	«
DR46	0.433	«	«	«	0.429	«	«	«	0.421	«	«	«	0.405	«	«	«	0.425	«	«	«
DR47	0.393	«	«	«	0.376	«	«	«	0.372	«	«	«	0.379	«	«	«	0.371	«	«	«

Table A.5 (cont.).

Single analysis ID	MixCrude Inj02				MixCrude Inj04				MixCrude Inj05				MixCrude Inj07				MixCrude Inj08			
Confidence intervals	MCM 95%	S-t 95%	MCM 98%	S-t 98%	MCM 95%	S-t 95%	MCM 98%	S-t 98%	MCM 95%	S-t 95%	MCM 98%	S-t 98%	MCM 95%	S-t 95%	MCM 98%	S-t 98%	MCM 95%	S-t 95%	MCM 98%	S-t 98%
Sesquiterpanes																				
<i>DR48</i>	0.512	«	«	«	0.510	«	«	«	0.487	«	«	«	0.476	«	«	«	0.493	«	«	«
<i>DR49</i>	0.345	«	«	«	0.366	«	«	«	0.340	«	«	«	0.341	«	«	«	0.373	«	«	«
<i>DR50</i>	0.666	«	«	«	0.644	«	«	«	0.649	«	«	«	0.637	«	«	«	0.621	«	«	«
<i>DR51</i>	0.425	«	«	«	0.418	«	«	«	0.420	«	«	«	0.411	«	«	«	0.419	«	«	«
<i>DR52</i>	0.590	«	«	«	0.622	«	«	«	0.632	«	«	«	0.637	«	«	«	0.644	«	«	«
<i>DR53</i>	0.248	«	«	«	0.253	«	«	«	0.238	«	«	«	0.252	«	«	«	0.248	«	«	«
<i>DR54</i>	0.410	«	«	«	0.424	«	«	«	0.392	«	«	«	0.402	«	«	«	0.390	«	«	«
<i>DR55</i>	0.378	«	«	«	0.386	«	«	«	0.364	«	«	«	0.369	«	«	«	0.381	«	«	«
<i>DR56</i>	0.186	«	«	«	0.171	«	«	«	0.154	«	«	«	0.161	«	«	«	0.154	«	«	«
<i>DR57</i>	0.633	«	«	«	0.624	«	«	«	0.624	«	«	«	0.608	«	«	«	0.612	«	«	«
Adamantanes																				
<i>DR58</i>	0.689	«	«	«	0.691	«	«	«	0.697	«	«	«	0.681	«	«	«	0.676	«	«	«
<i>DR59</i>	0.742	«	«	«	0.730	«	«	«	0.715	«	«	«	0.701	«	«	«	0.707	«	«	«
<i>DR60</i>	0.618	«	«	«	0.613	«	«	«	0.609	«	«	«	0.608	«	«	«	0.603	«	«	«
<i>DR61</i>	0.840	«	«	«	0.844	«	«	«	0.848	«	«	«	0.842	«	«	«	0.839	«	«	«
<i>DR62</i>	0.434	«	«	«	0.425	«	«	«	0.439	«	«	«	0.449	«	«	«	0.437	«	«	«
<i>DR63</i>	0.653	«	«	«	0.649	«	«	«	0.649	«	«	«	0.667	«	«	«	0.664	«	«	«
<i>DR64</i>	0.335	«	«	«	0.342	«	«	«	0.318	«	«	«	0.309	«	«	«	0.323	«	«	«
<i>DR65</i>	0.435	«	«	«	0.452	«	«	«	0.478	«	«	«	0.477	«	«	«	0.464	«	«	«
<i>DR66</i>	0.645	«	«	«	0.666	«	«	«	0.689	«	«	«	0.694	«	«	«	0.684	«	«	«
<i>DR67</i>	0.360	«	«	«	0.369	«	«	«	0.382	«	«	«	0.398	«	«	«	0.386	«	«	«
<i>DR68</i>	0.422	«	«	«	0.415	«	«	«	0.403	«	«	«	0.421	«	«	«	0.421	«	«	«
<i>DR69</i>	0.764	«	«	«	0.773	«	«	«	0.782	«	«	«	0.774	«	«	«	0.775	«	«	«

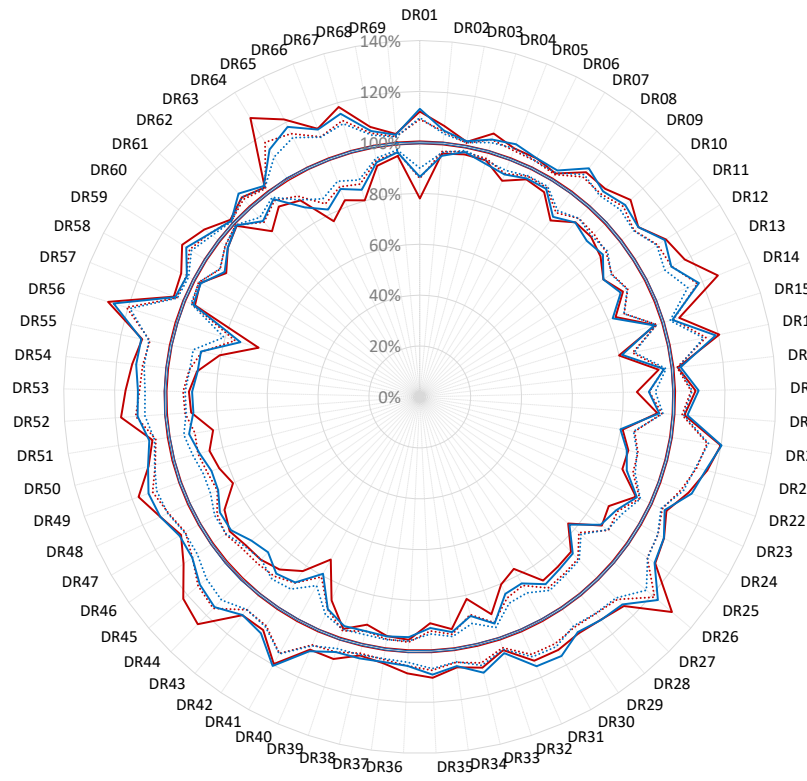


Figure A.1. Percentiles required to define 95% and 98% confidence limits by the MCM and S-t methods of all 69 *DR* studied, normalised to the 50th percentile simulated by MCM, for $n = 5$ injections: — $P50$ – MCM; — $P50$ – S-t; ... $P2.5$ and $P97.5$ – MCM; ... $P2.5$ and $P97.5$ – S-t; — $P1$ and $P99$ – MCM; — $P1$ and $P99$ – S-t.

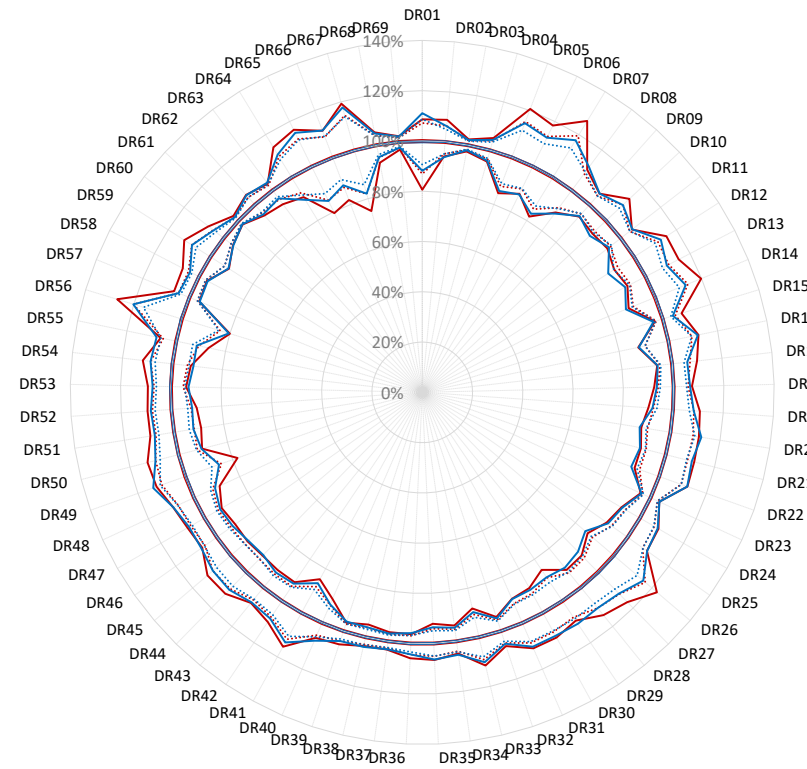
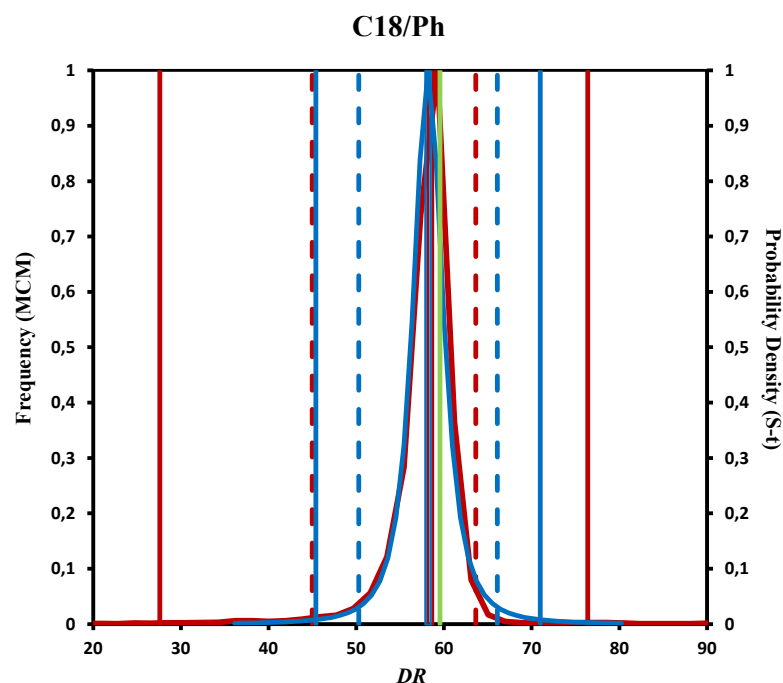
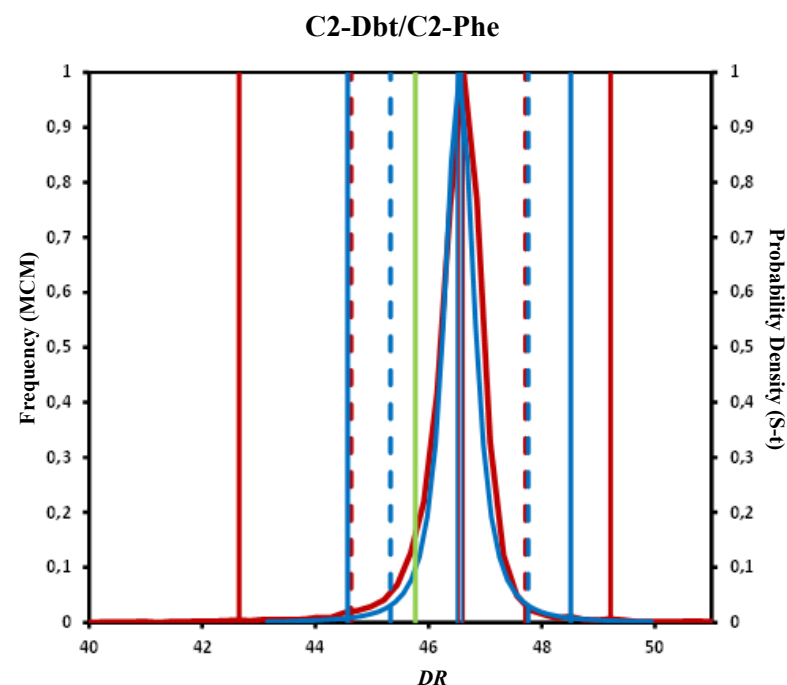


Figure A.2. Percentiles required to define 95% and 98% confidence limits by the MCM and S-t methods of all 69 *DR* studied, normalised to the 50th percentile simulated by MCM, for $n = 8$ injections: — $P50$ – MCM; — $P50$ – S-t; ... $P2.5$ and $P97.5$ – MCM; ... $P2.5$ and $P97.5$ – S-t; — $P1$ and $P99$ – MCM; — $P1$ and $P99$ – S-t.



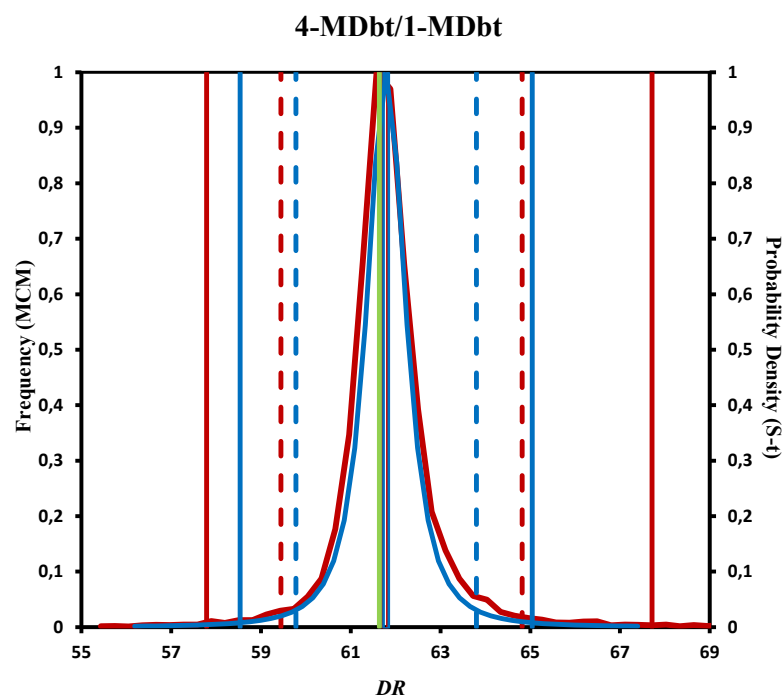
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.3. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



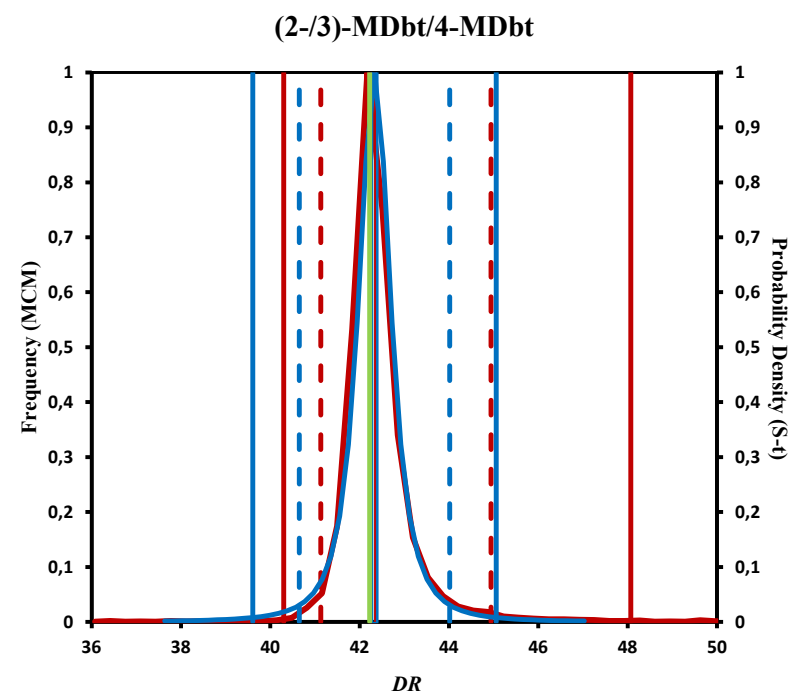
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.4. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

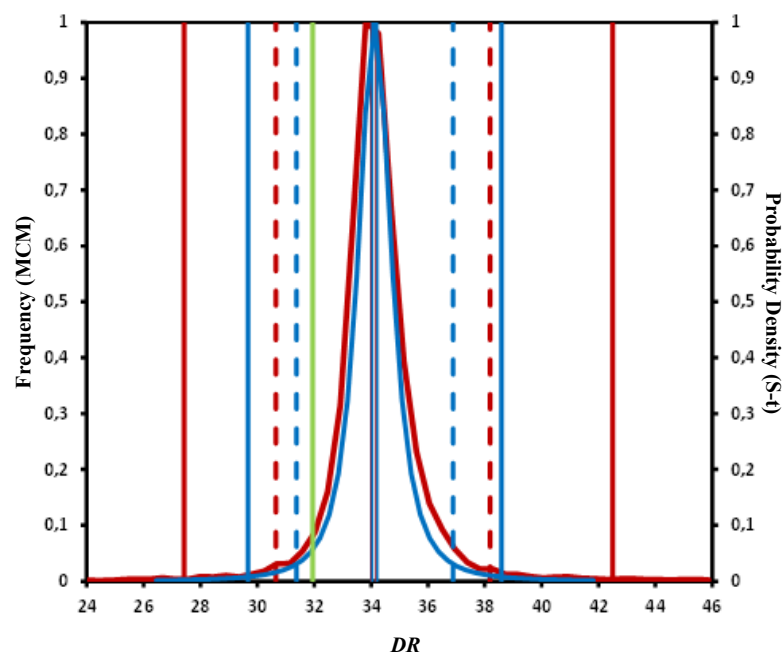
Figure A.5. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.6. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.

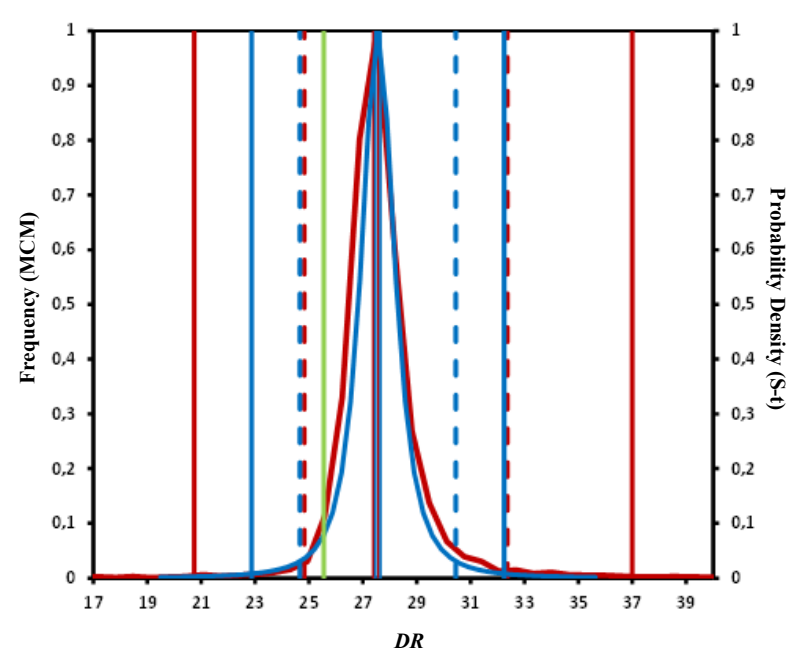
4-MDbt/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe



	Interval P2.5 to P97.5	Interval P1 to P99
MCM	In	In
S-t	In	In

Figure A.7. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.

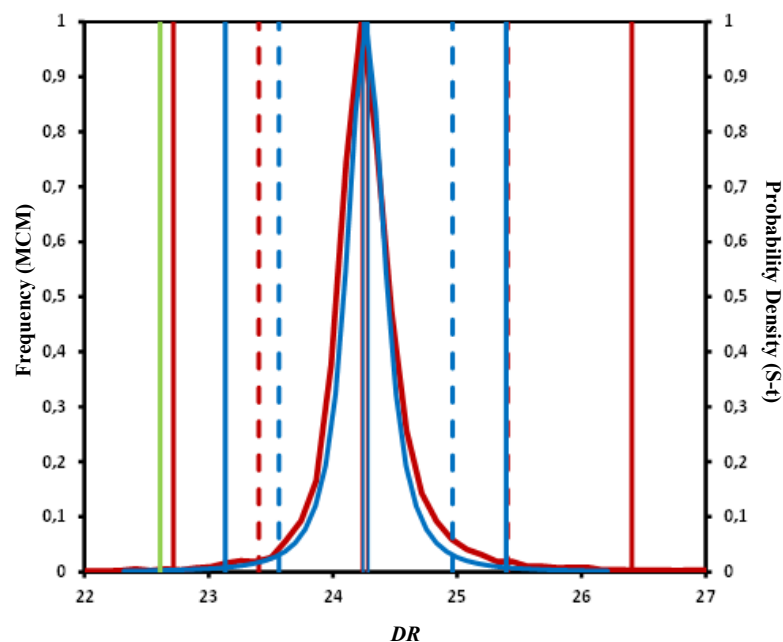
(2-/3)-MDbt/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe



	Interval P2.5 to P97.5	Interval P1 to P99
MCM	In	In
S-t	In	In

Figure A.8. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.

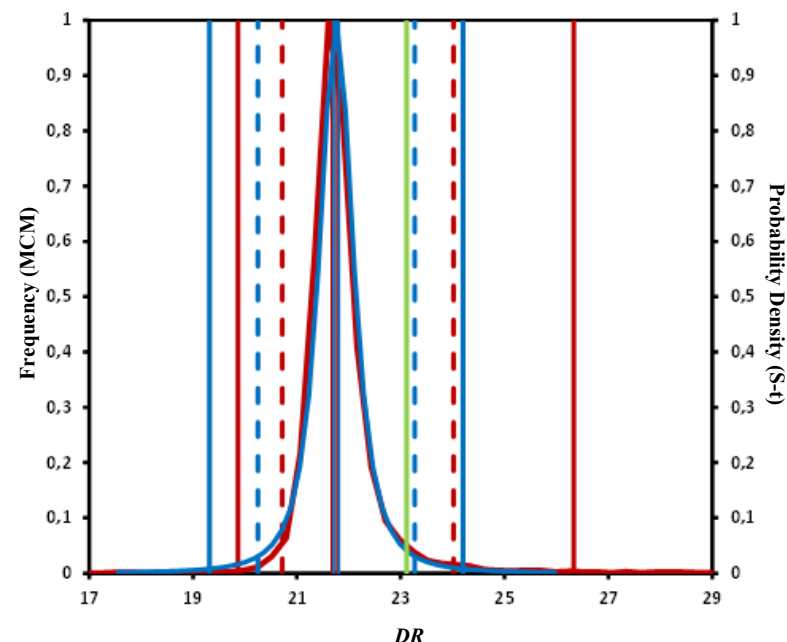
1-MDbt/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe



	Interval P2.5 to P97.5	Interval P1 to P99
MCM	Out	Out
S-t	Out	Out

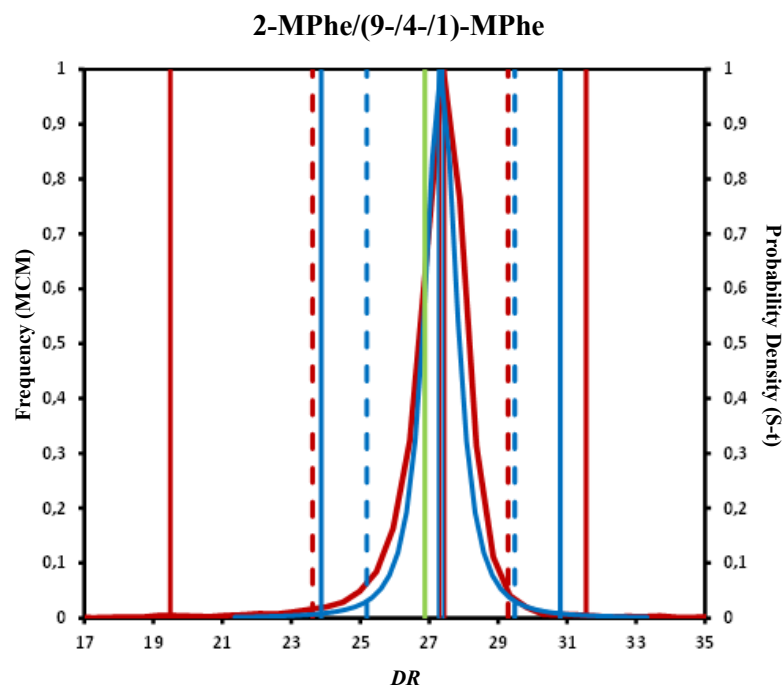
Figure A.9. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.

3-MPhe/(9-/4-/1)-MPhe



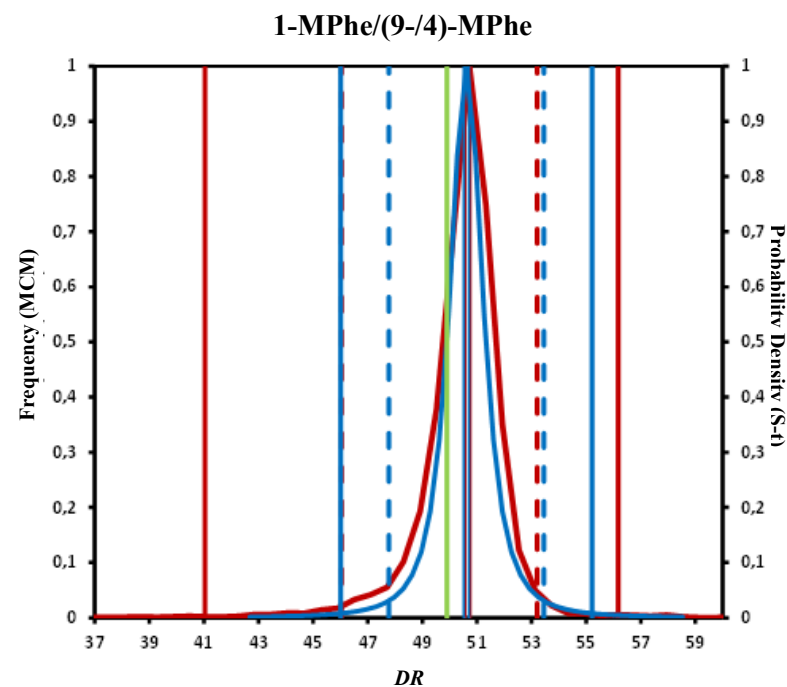
	Interval P2.5 to P97.5	Interval P1 to P99
MCM	In	In
S-t	In	In

Figure A.10. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.11. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.12. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.

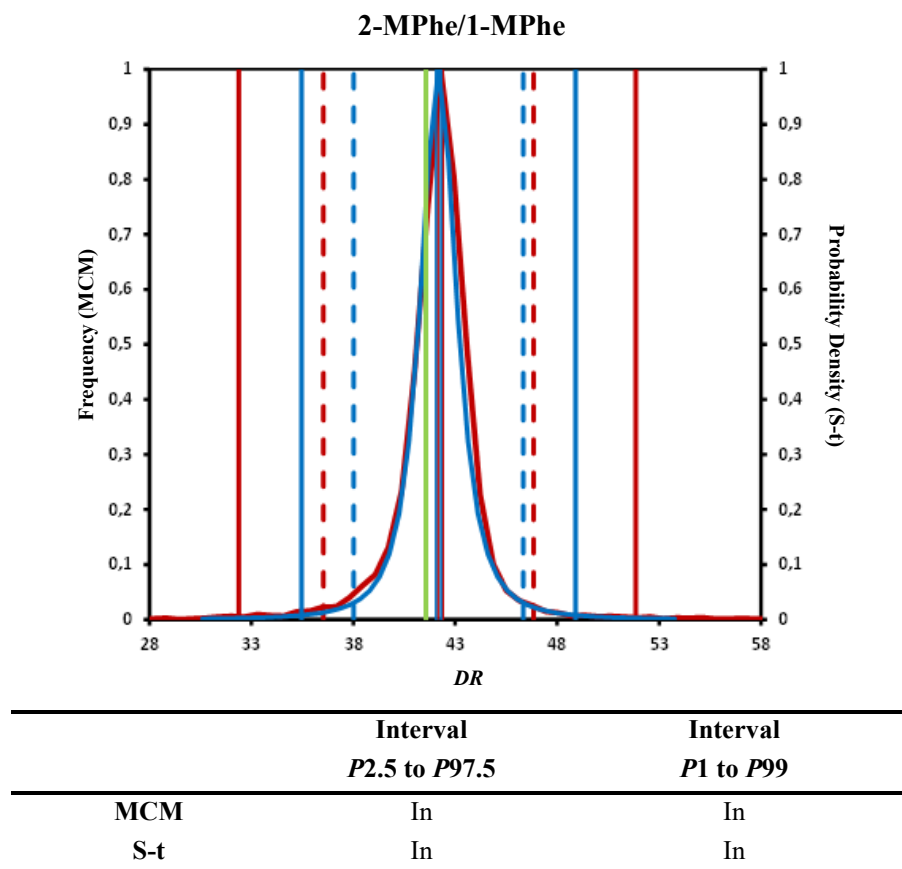


Figure A.13. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.

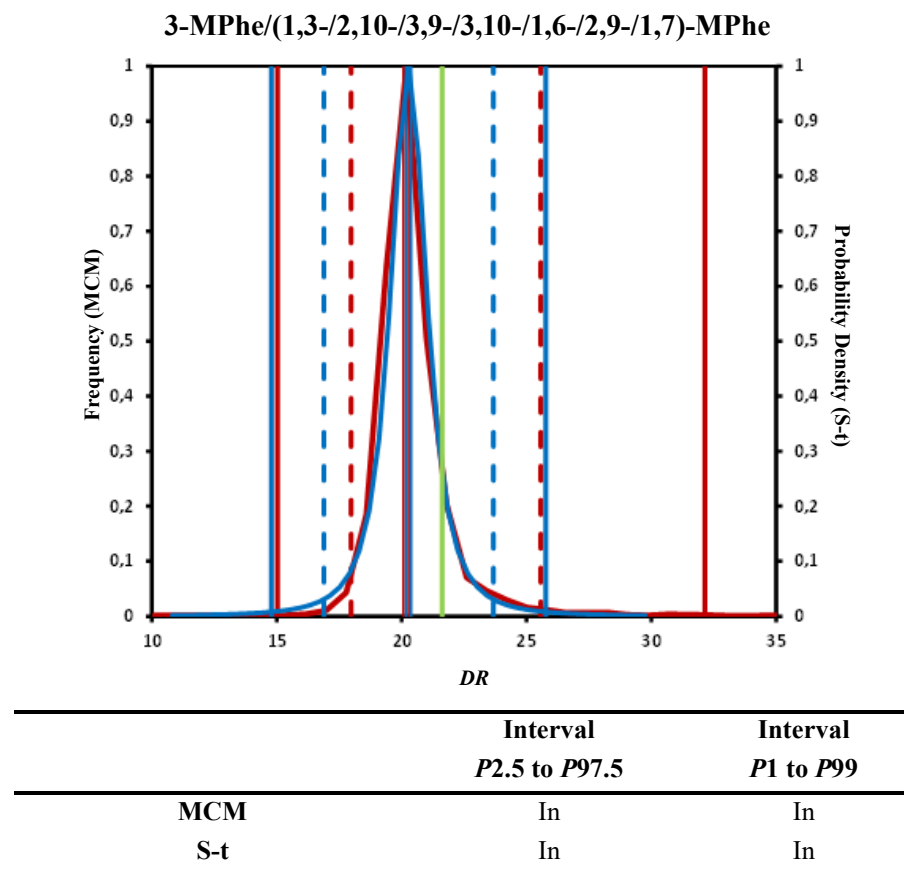
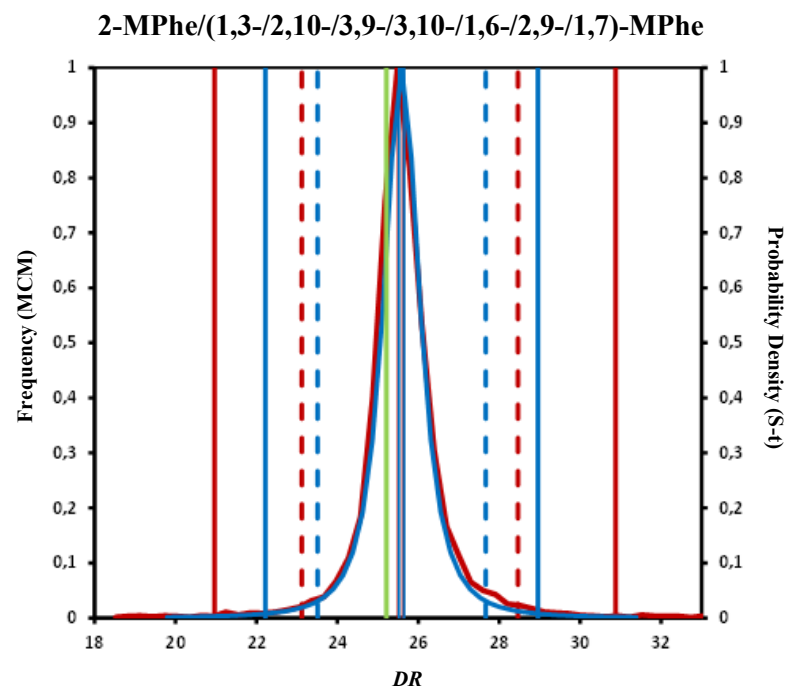
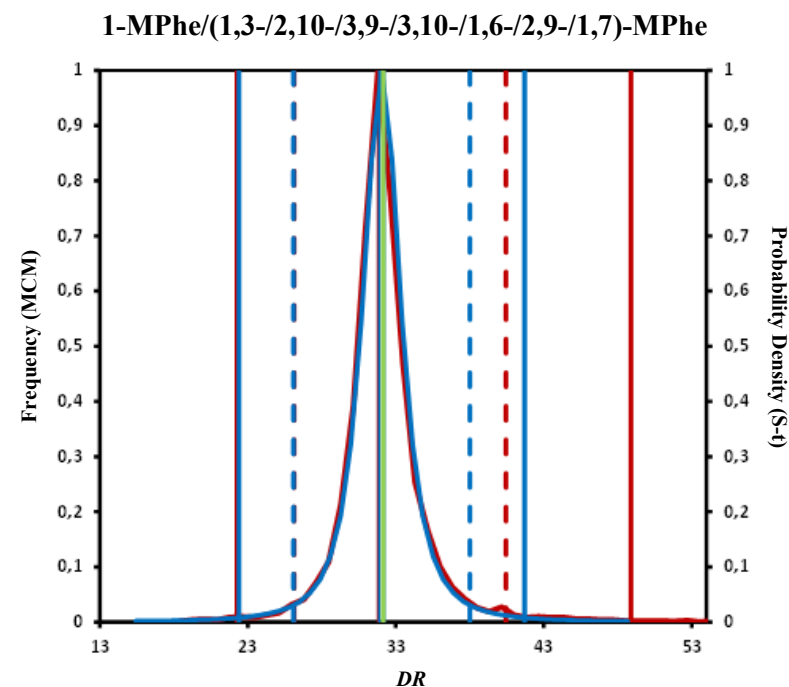


Figure A.14. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



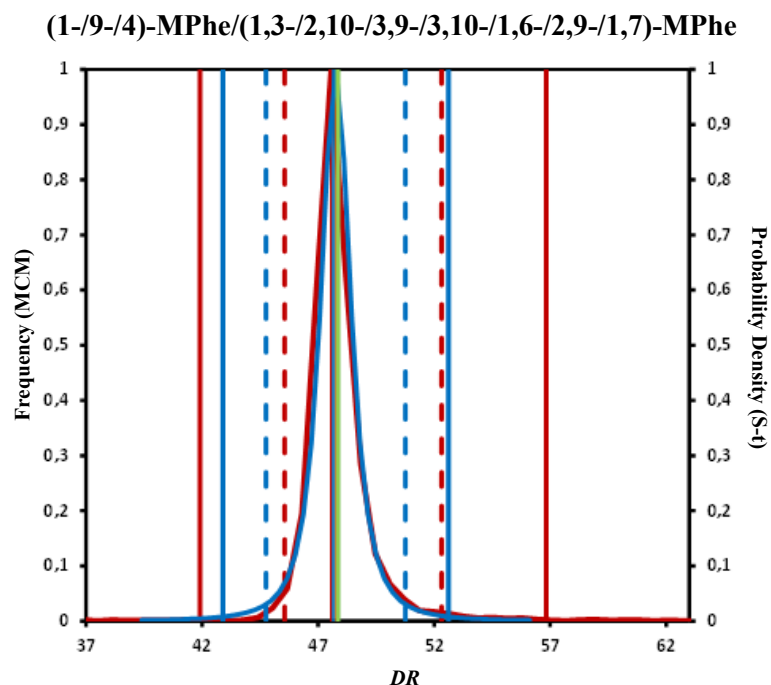
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.15. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



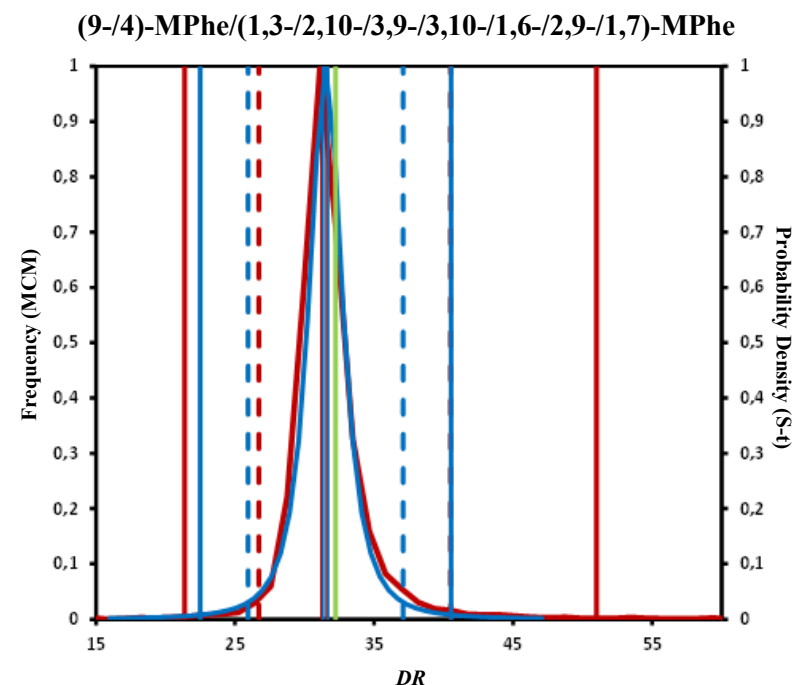
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.16. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



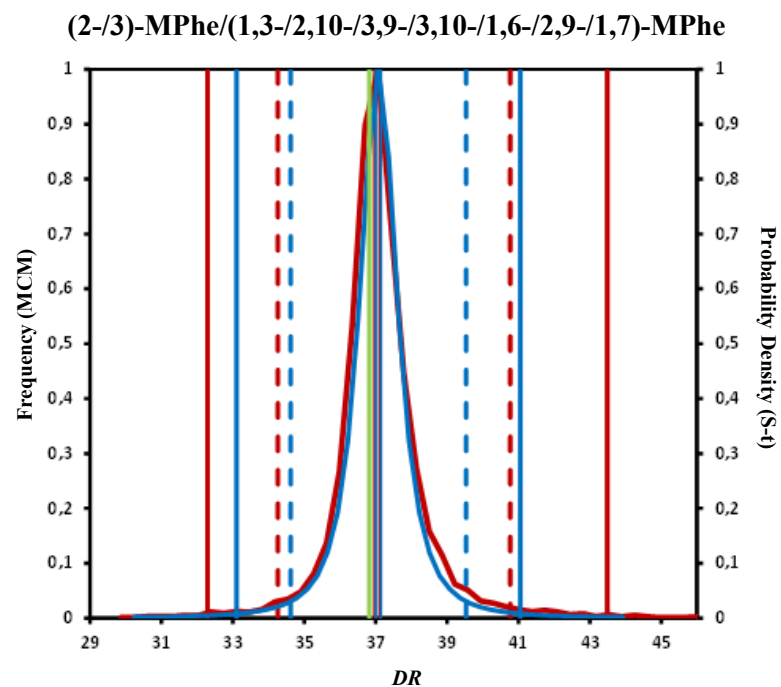
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.17. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



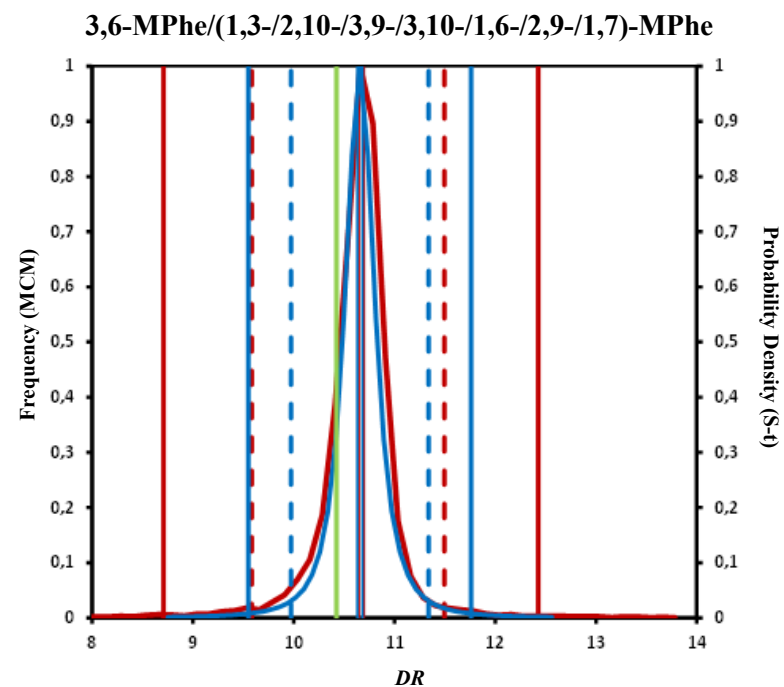
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.18. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



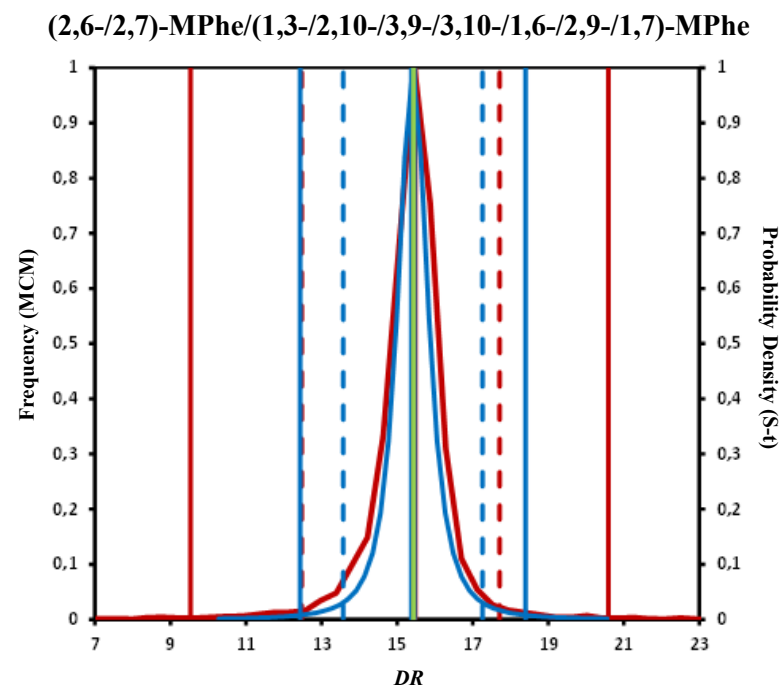
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.19. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



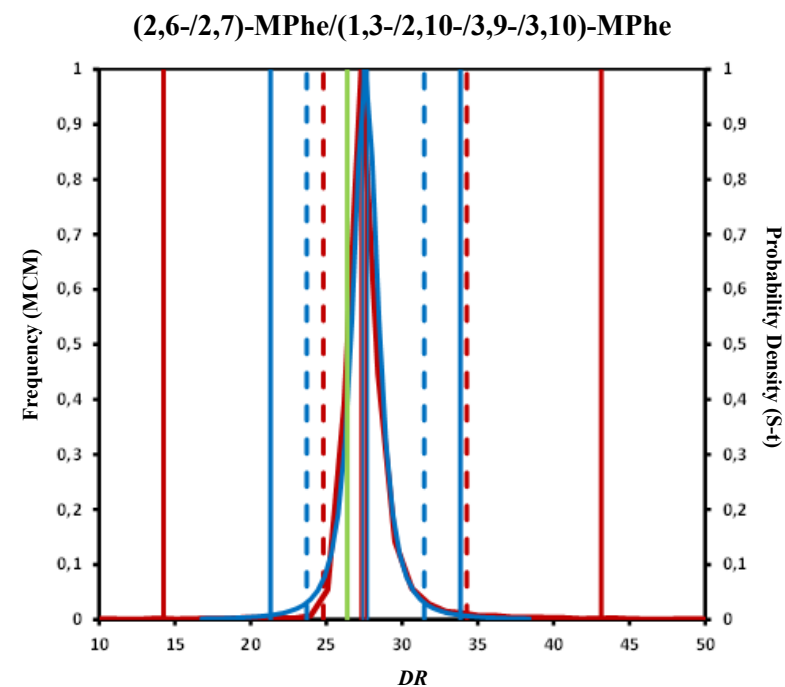
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.20. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

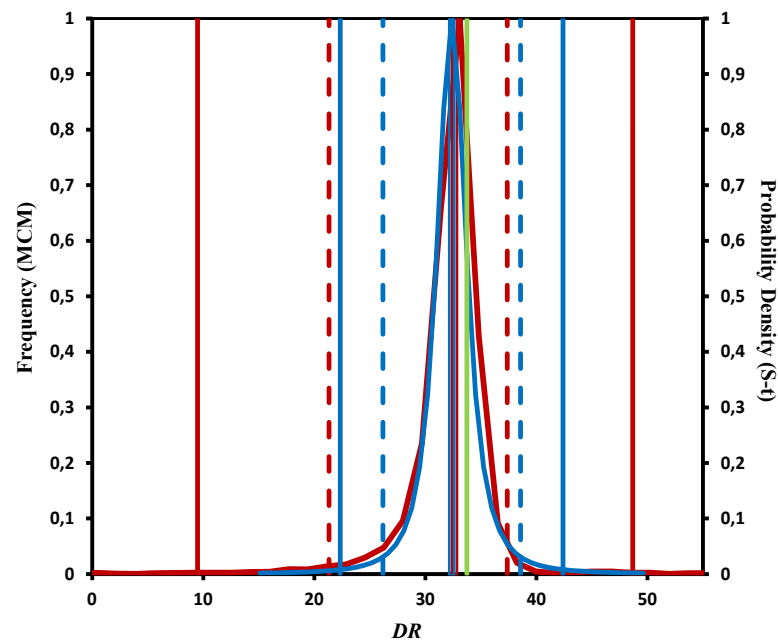
Figure A.21. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.22. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.

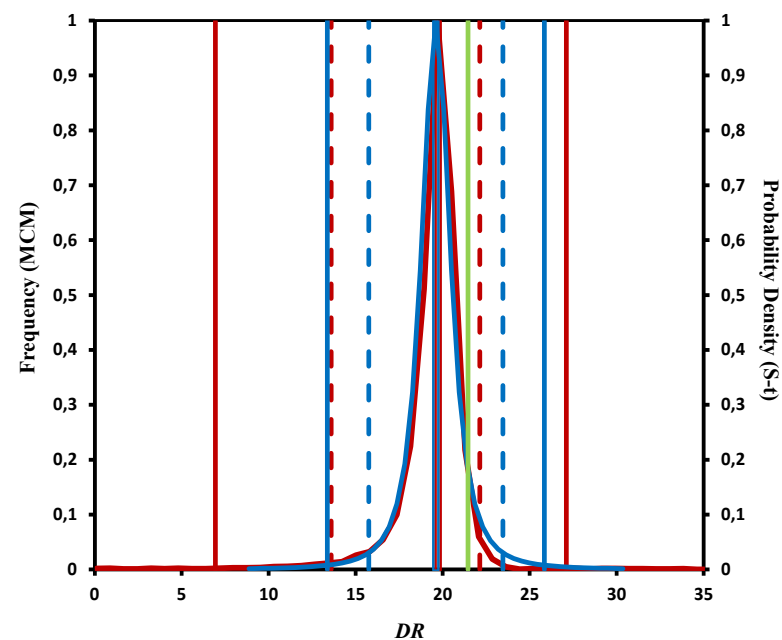
(1,3-/2,10-/3,9-/3,10)-MPhe/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe



	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

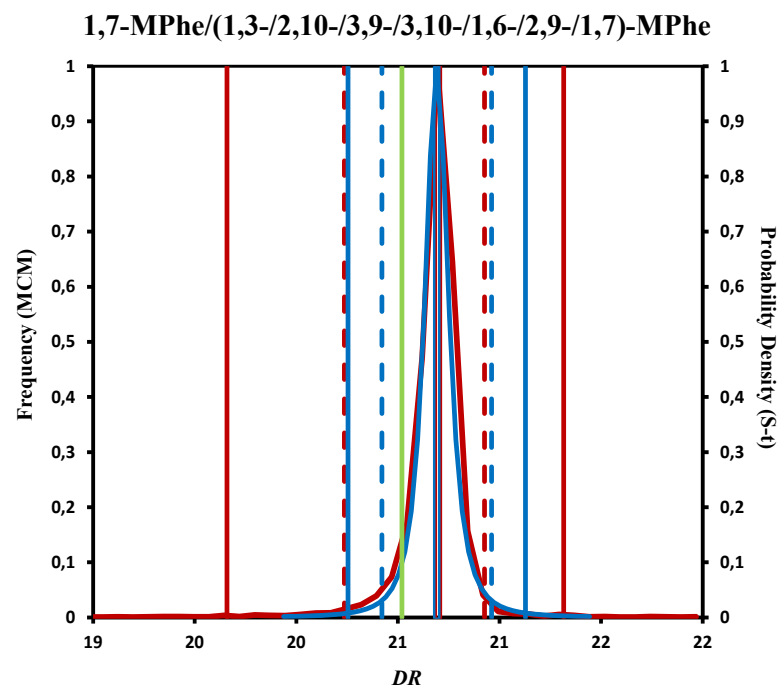
Figure A.23. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.

(1,6-/2,9)-MPhe/(1,3-/2,10-/3,9-/3,10-/1,6-/2,9-/1,7)-MPhe



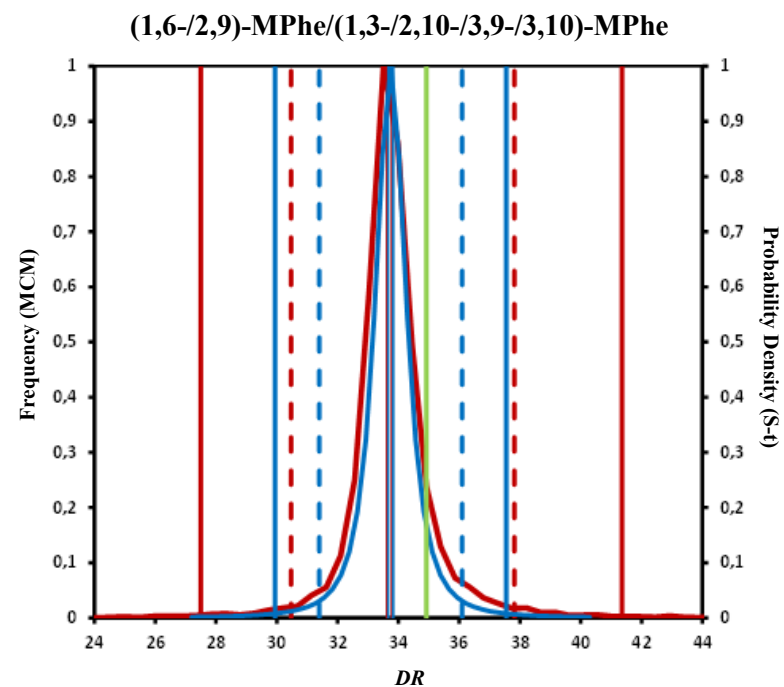
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.24. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



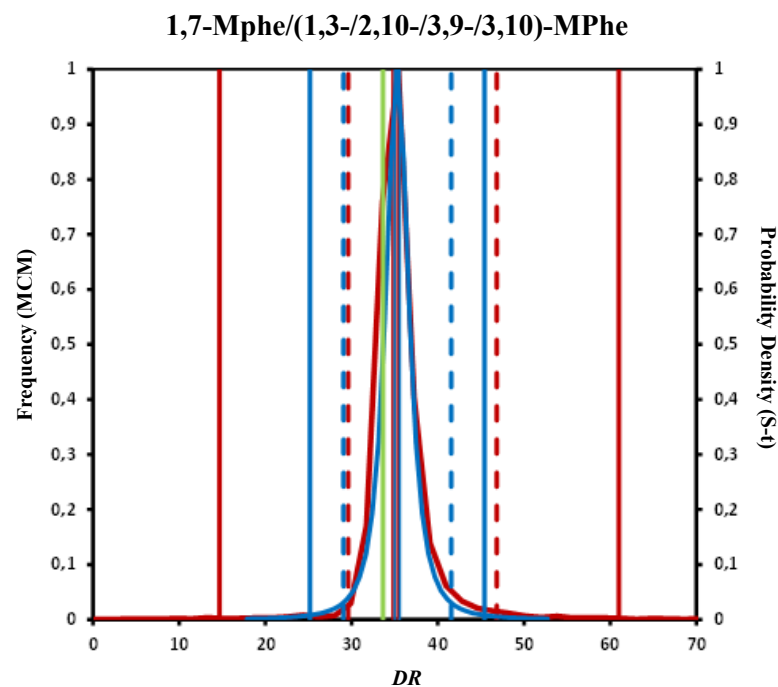
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.25. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



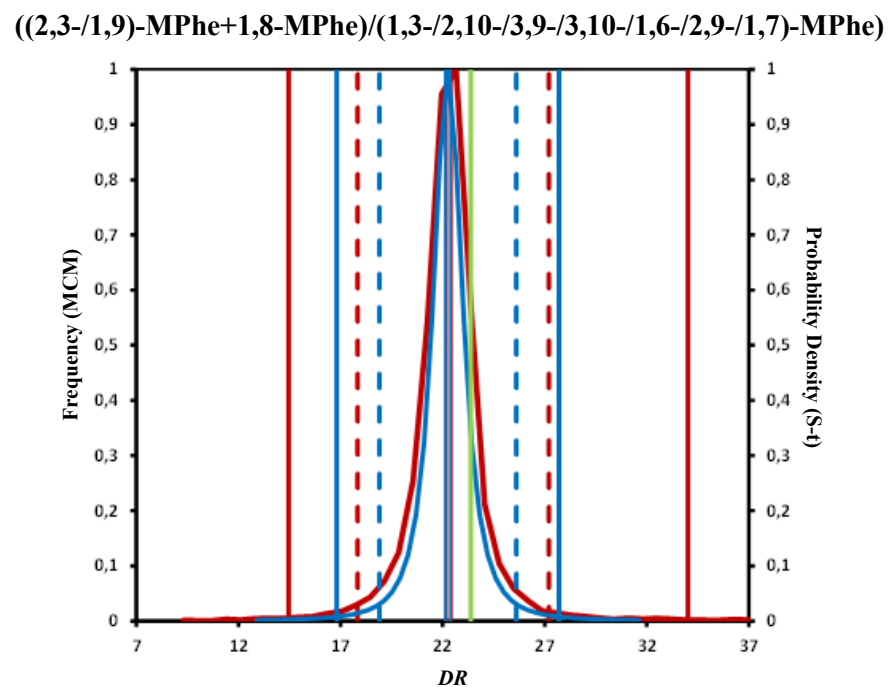
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.26. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



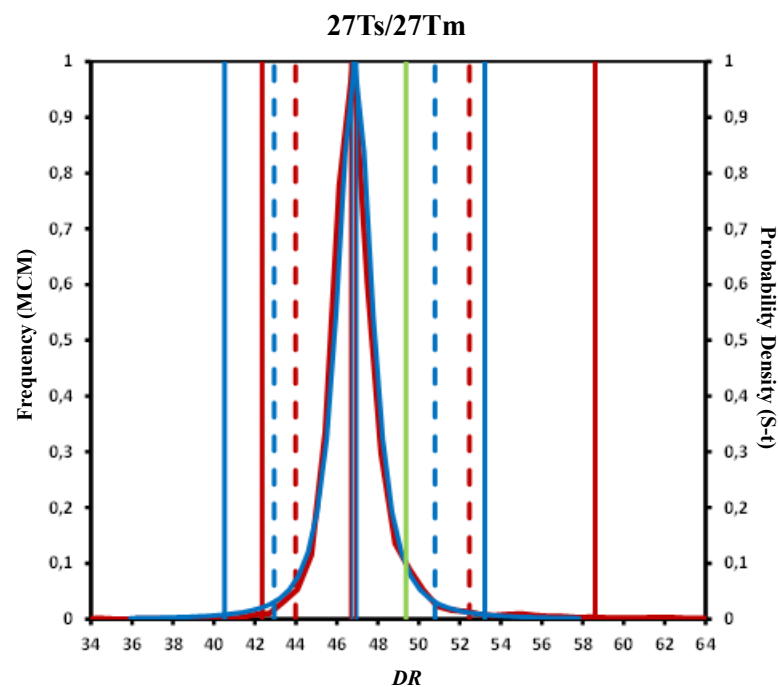
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.27. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



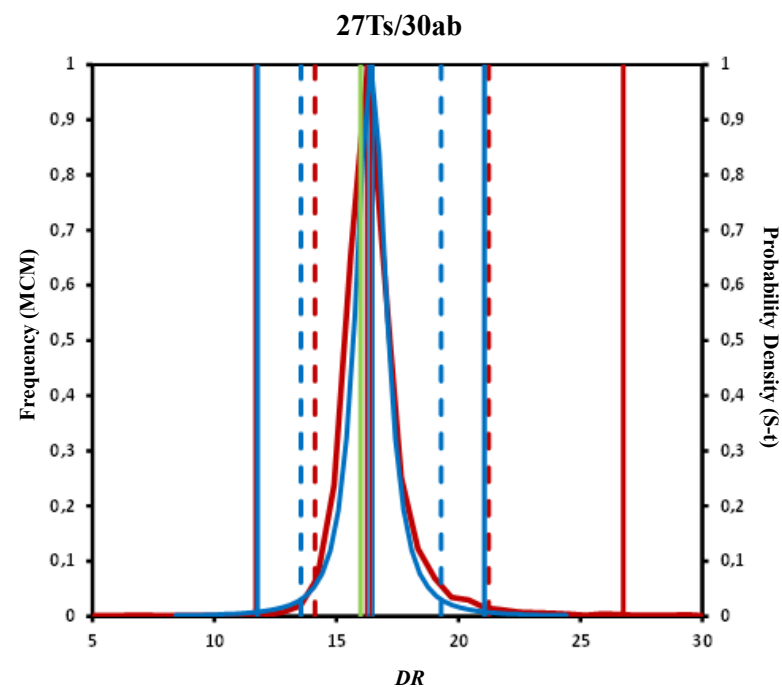
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.28. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



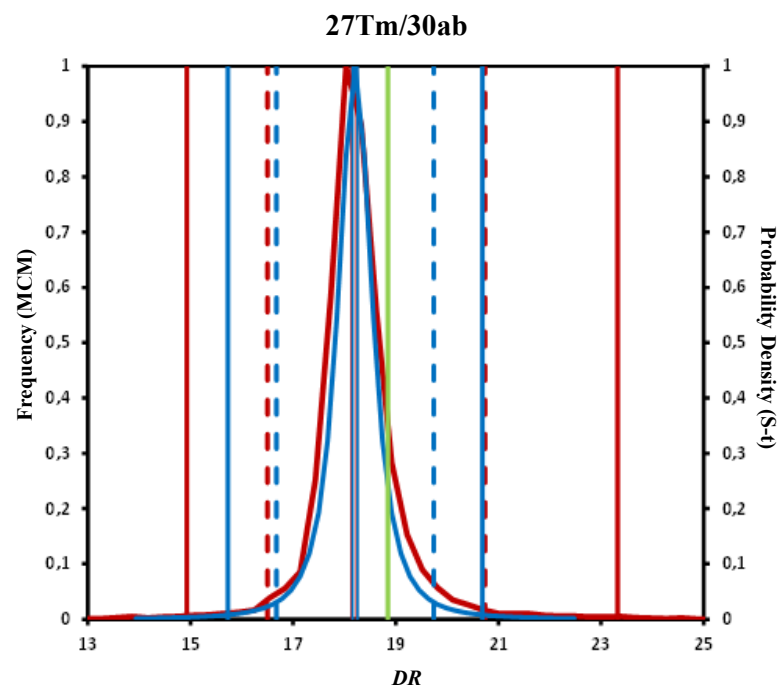
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.29. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



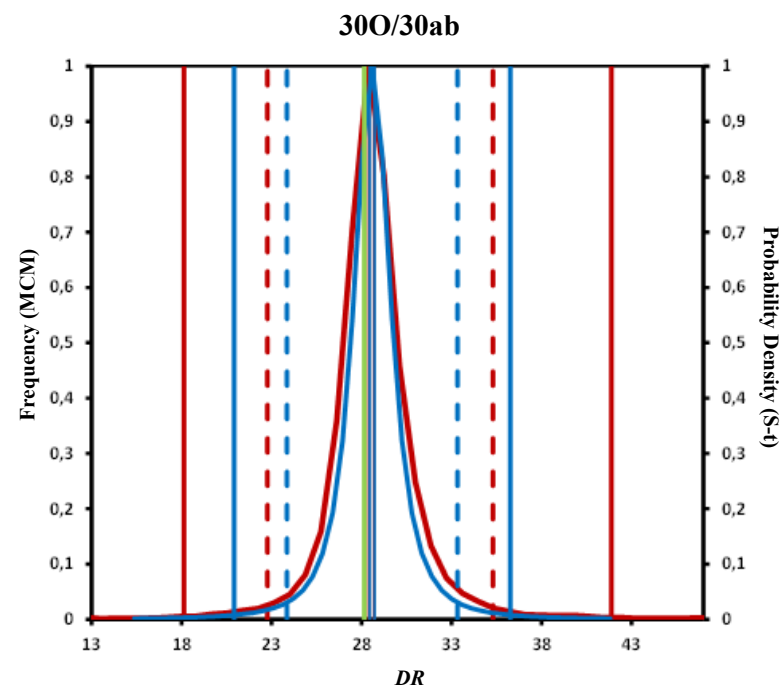
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.30. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



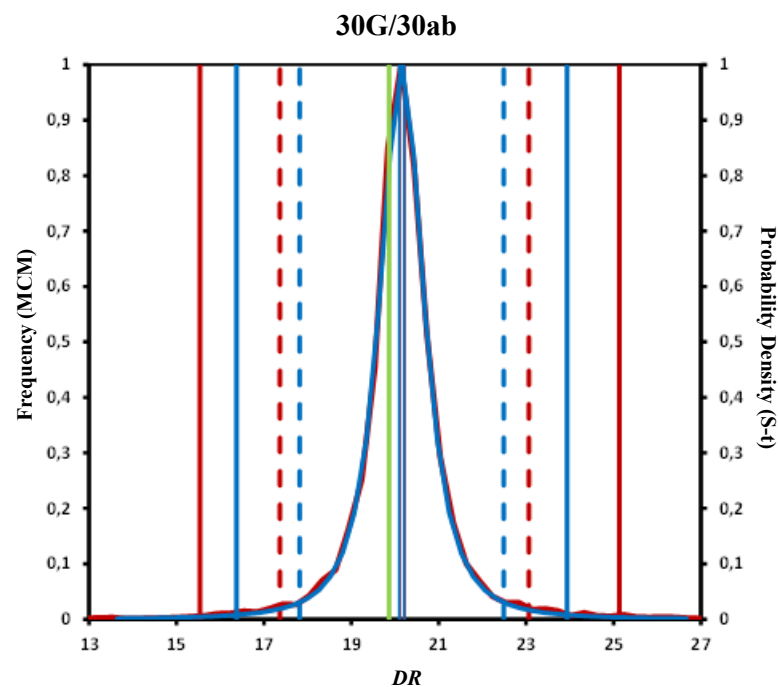
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.31. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



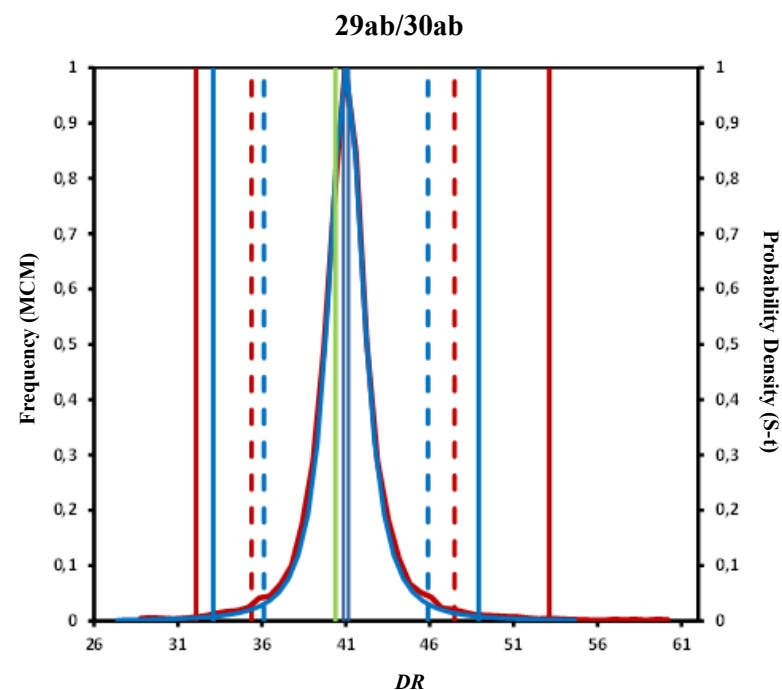
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.32. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



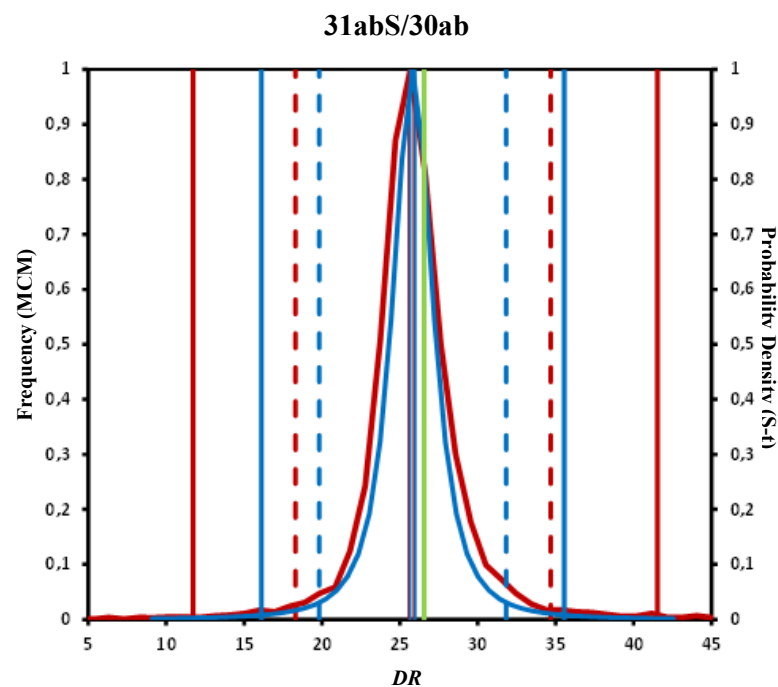
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.33. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



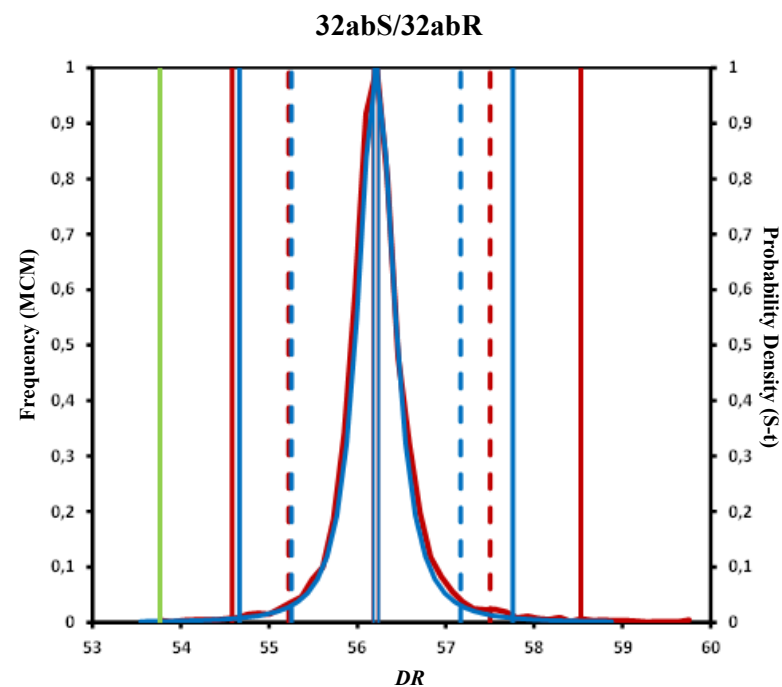
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.34. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



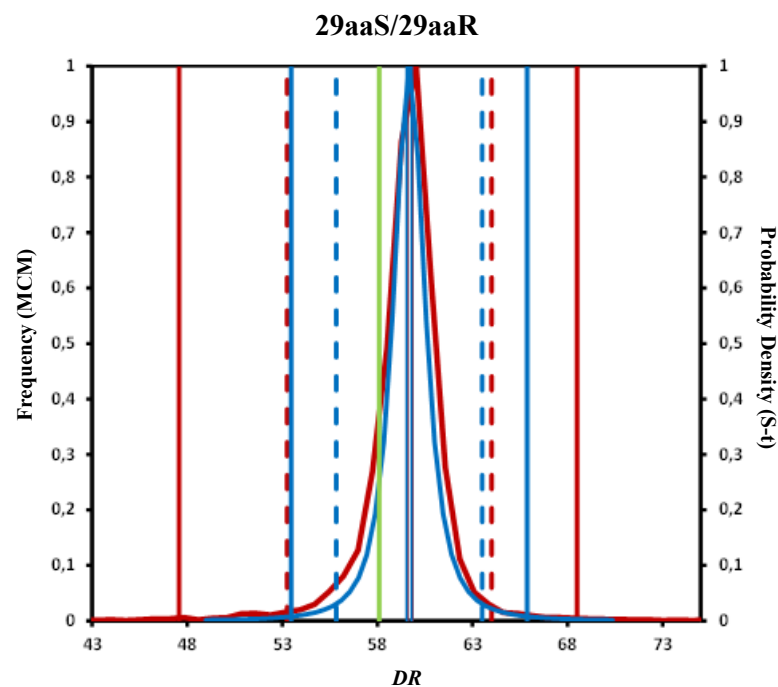
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.35. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P_{\chi^{\text{th}}}$): --- $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



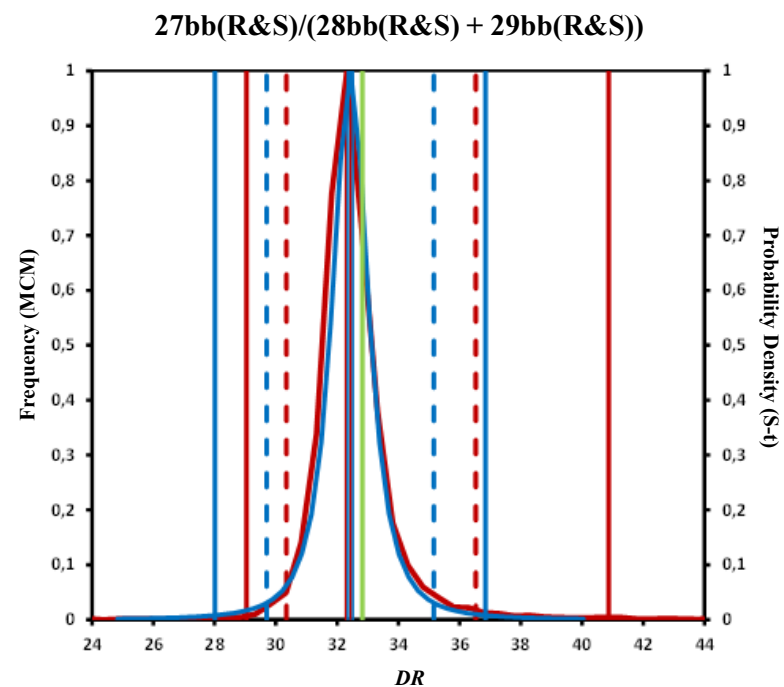
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	Out	Out
S-t	Out	Out

Figure A.36. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P_{\chi^{\text{th}}}$): --- $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



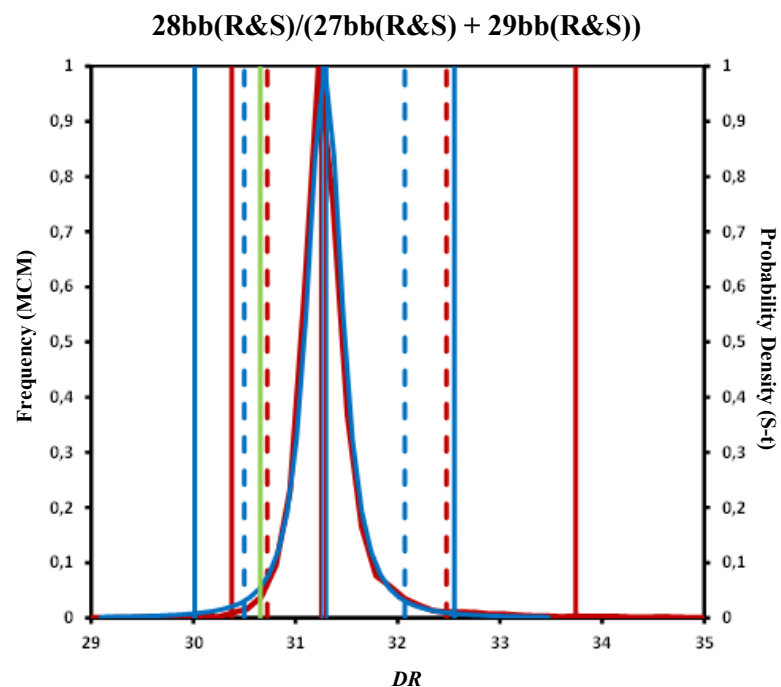
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.37. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



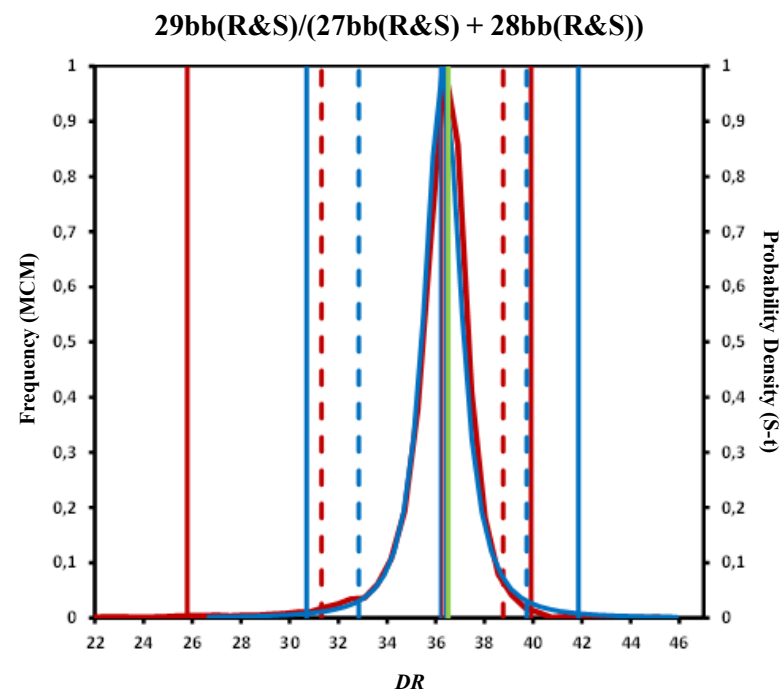
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.38. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



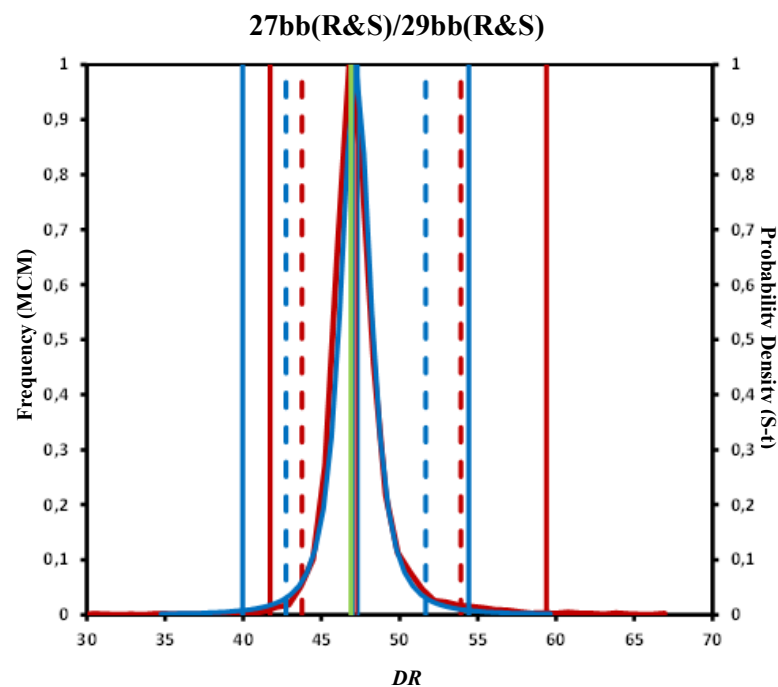
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	Out	In
S-t	In	In

Figure A.39. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



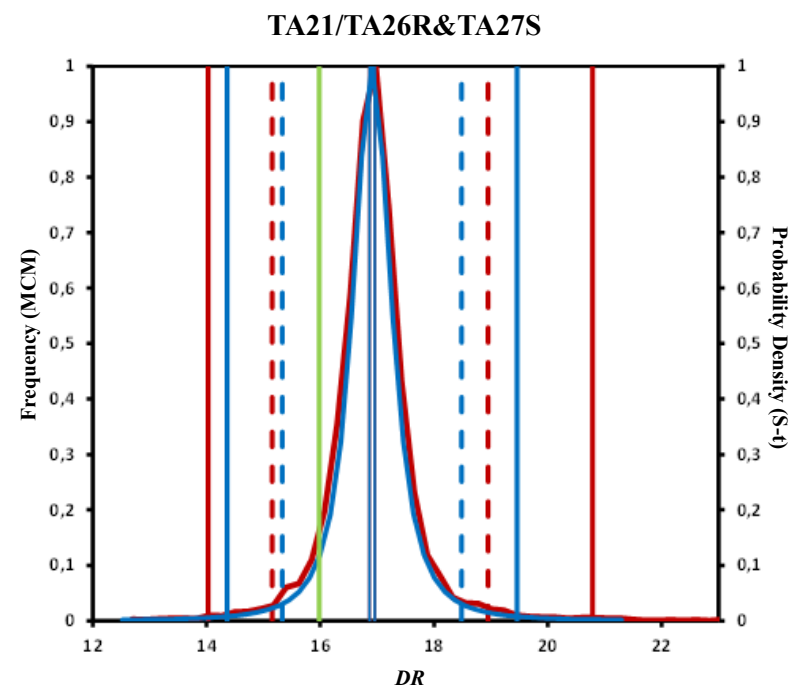
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.40. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



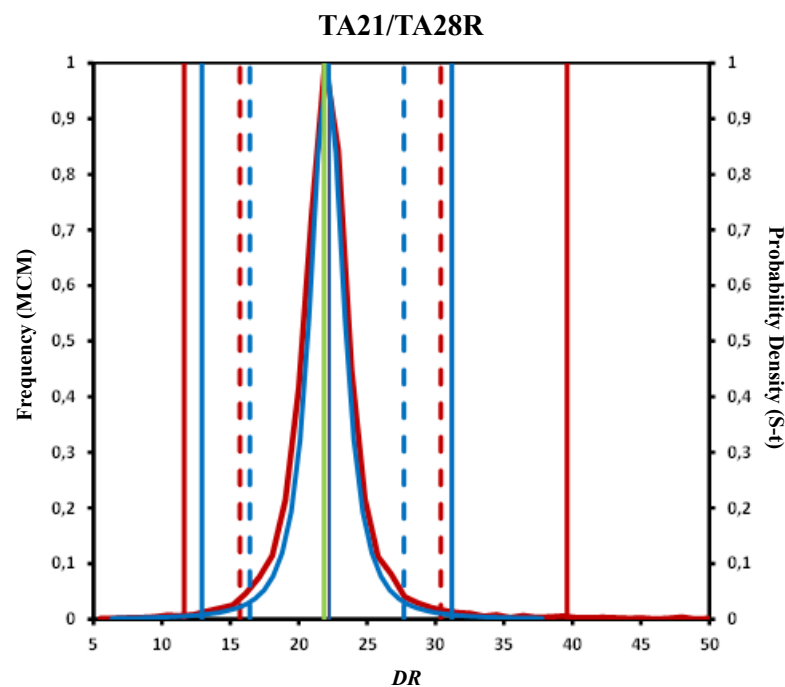
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.41. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



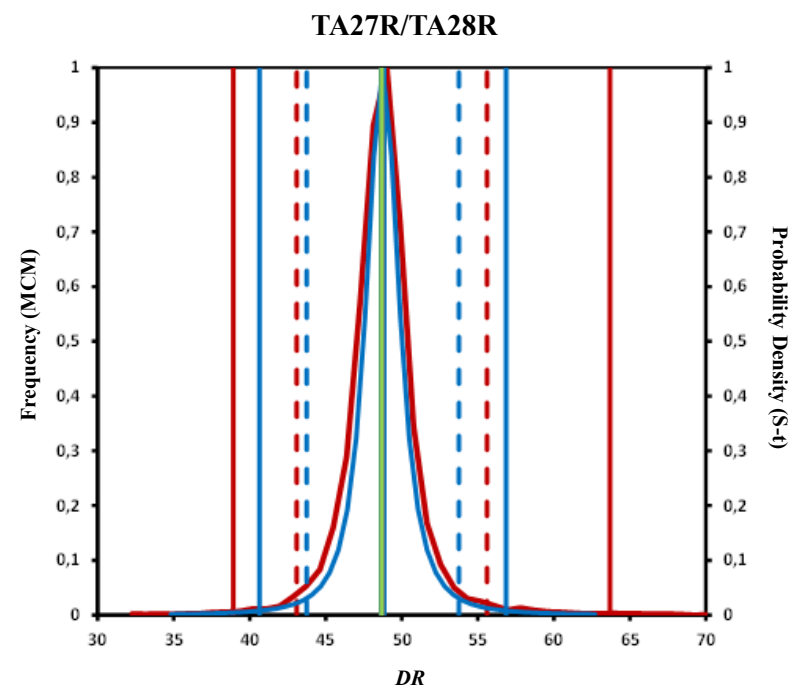
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.42. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



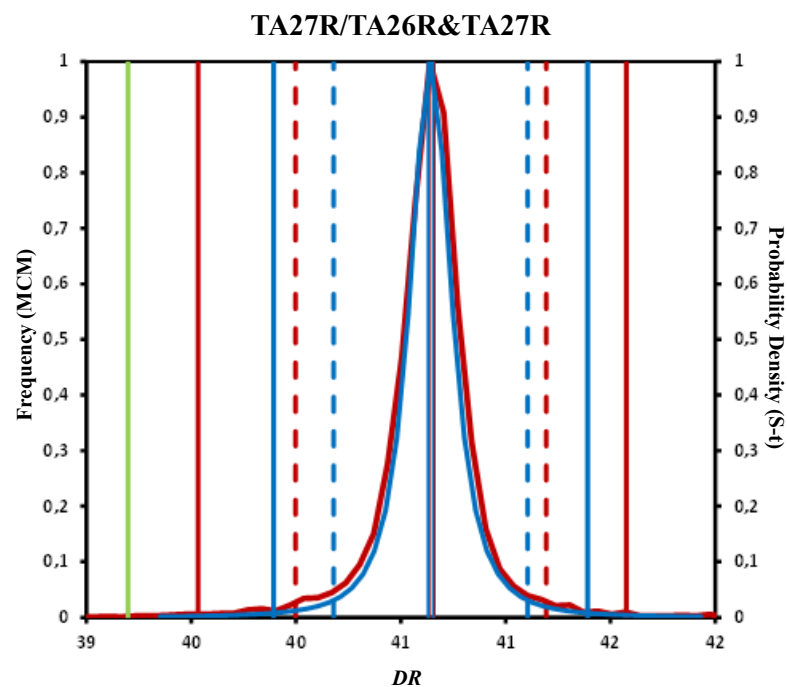
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.43. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



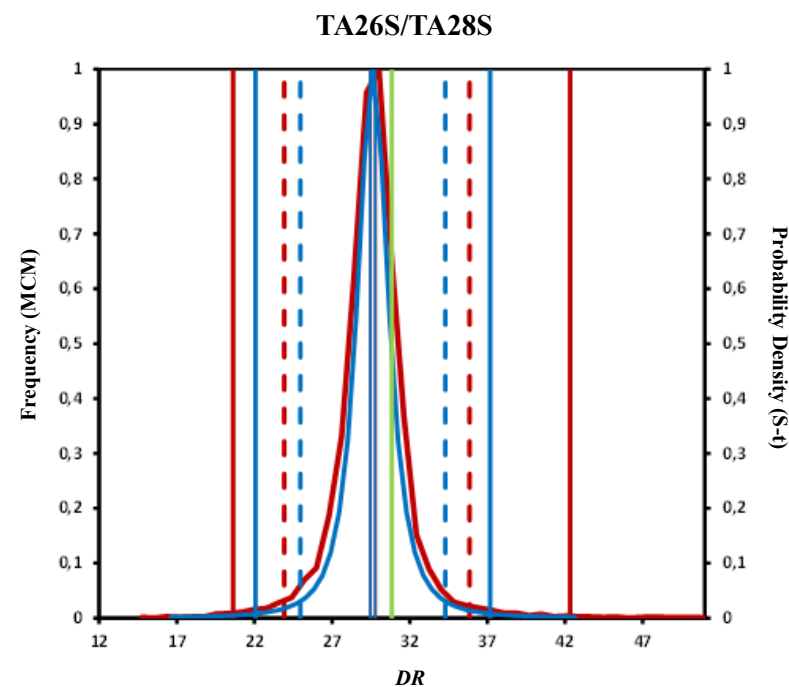
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.44. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



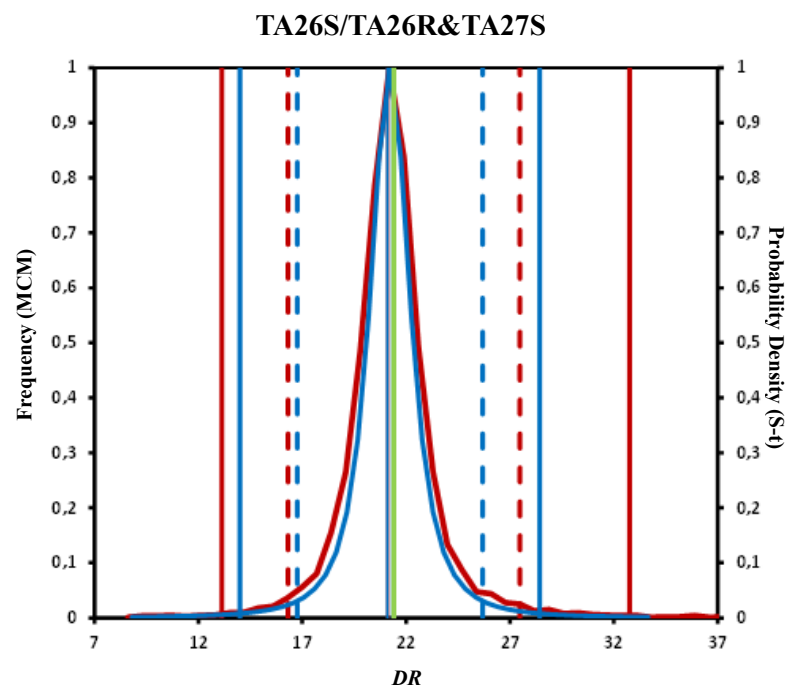
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	Out	Out
S-t	Out	Out

Figure A.45. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



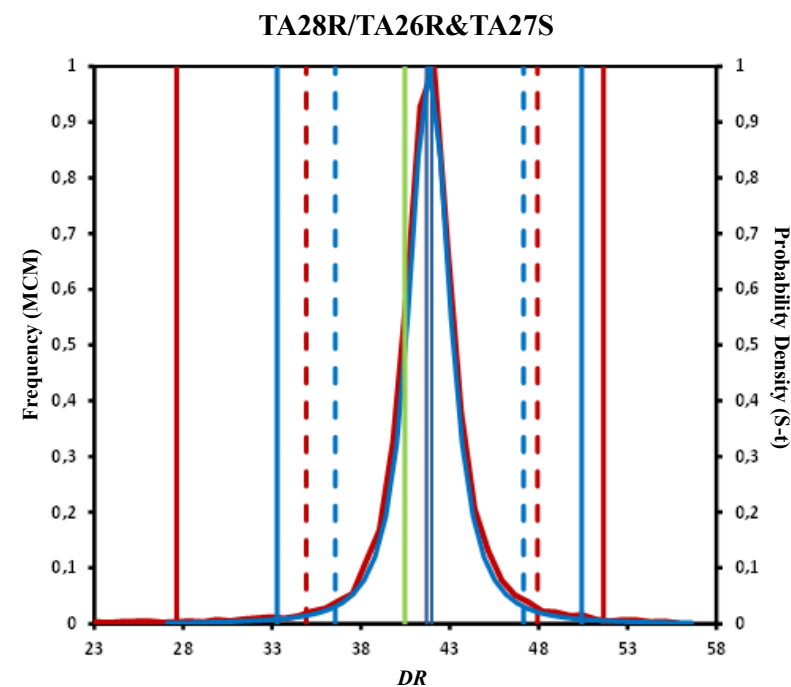
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.46. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



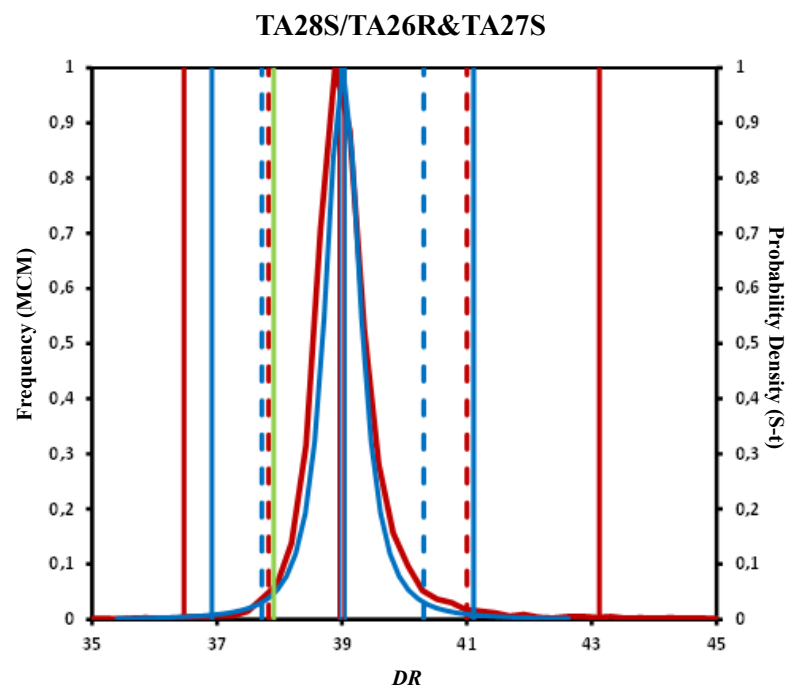
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.47. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



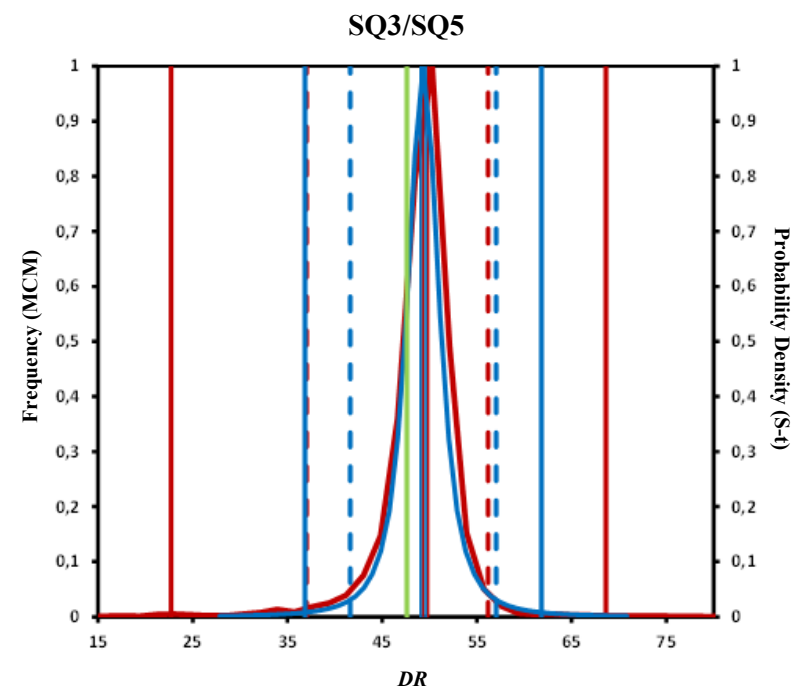
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.48. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



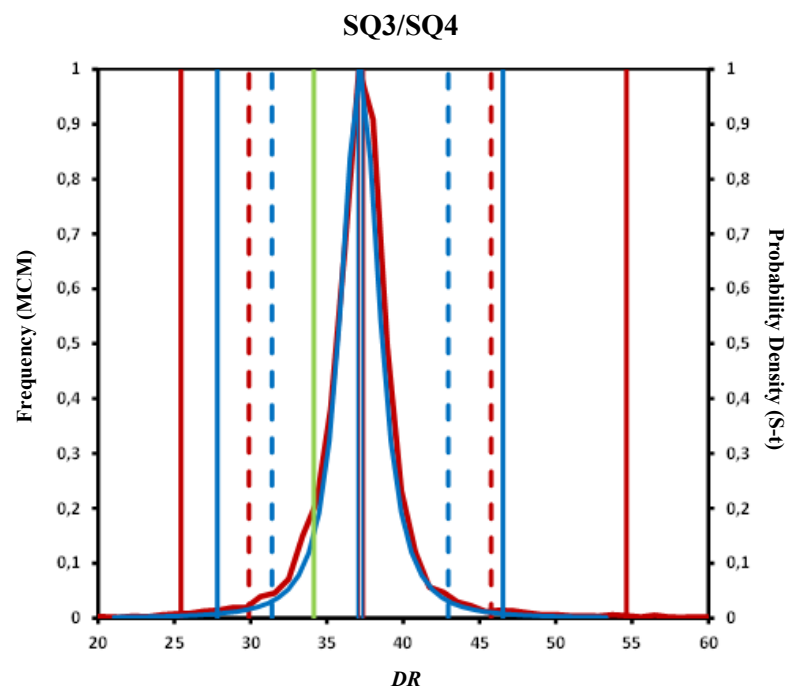
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.49. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



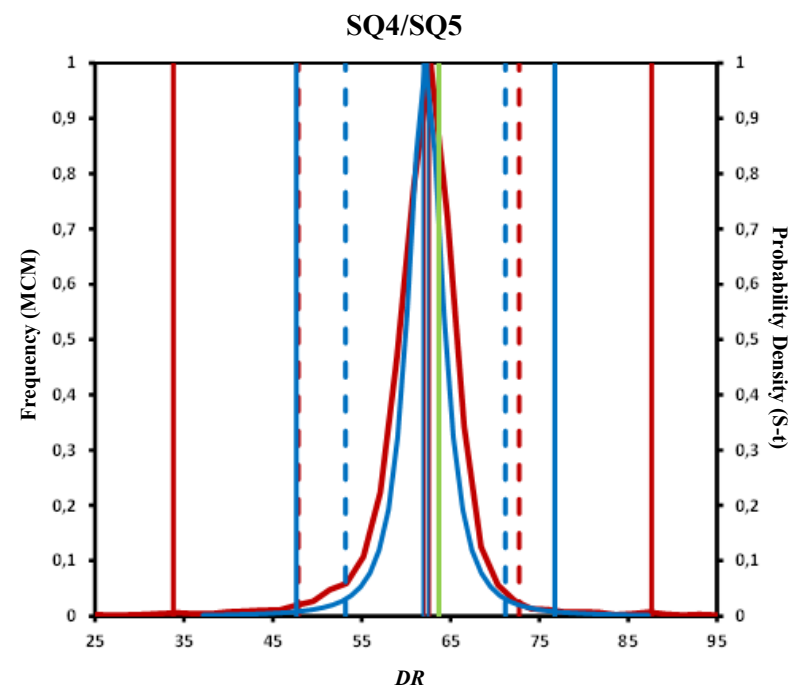
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.50. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



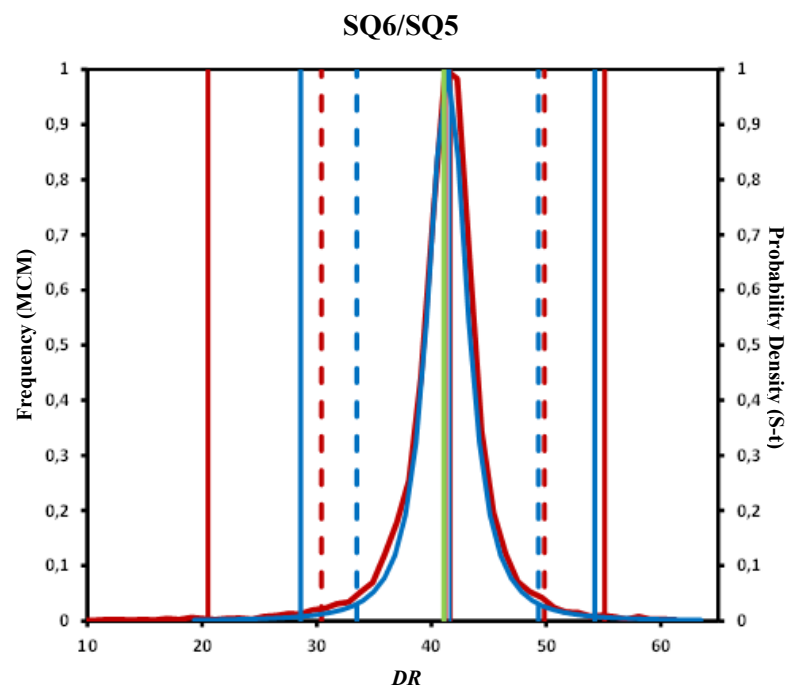
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.51. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



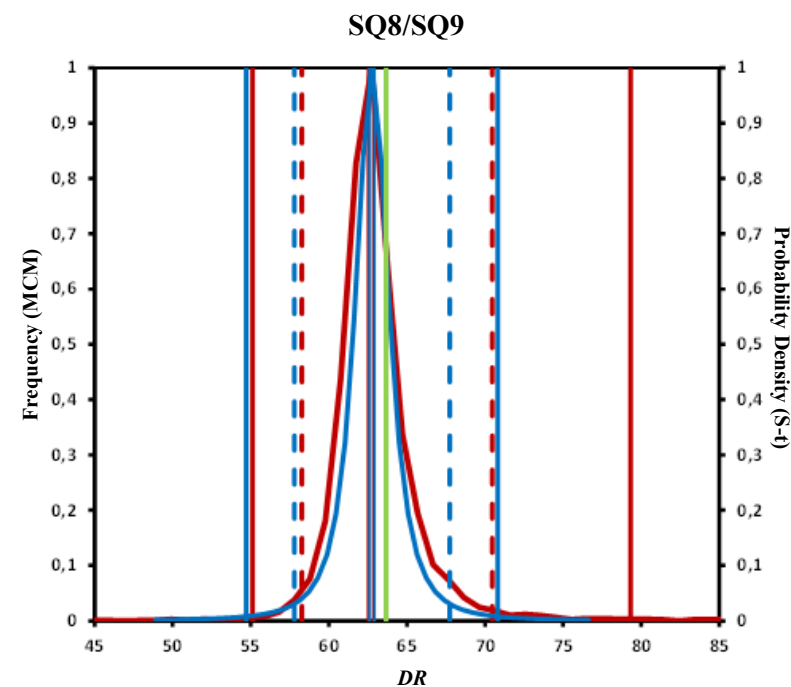
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.52. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



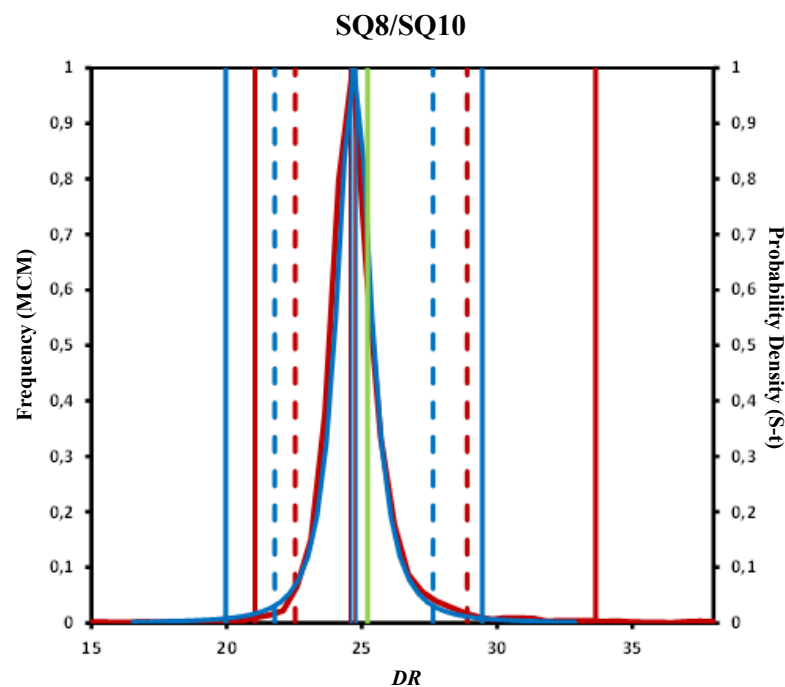
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.53. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



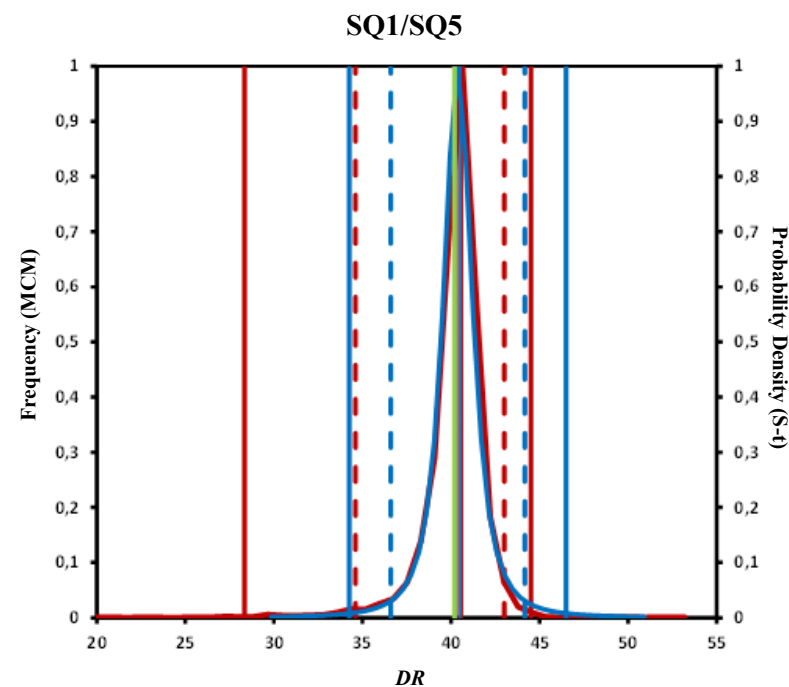
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.54. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



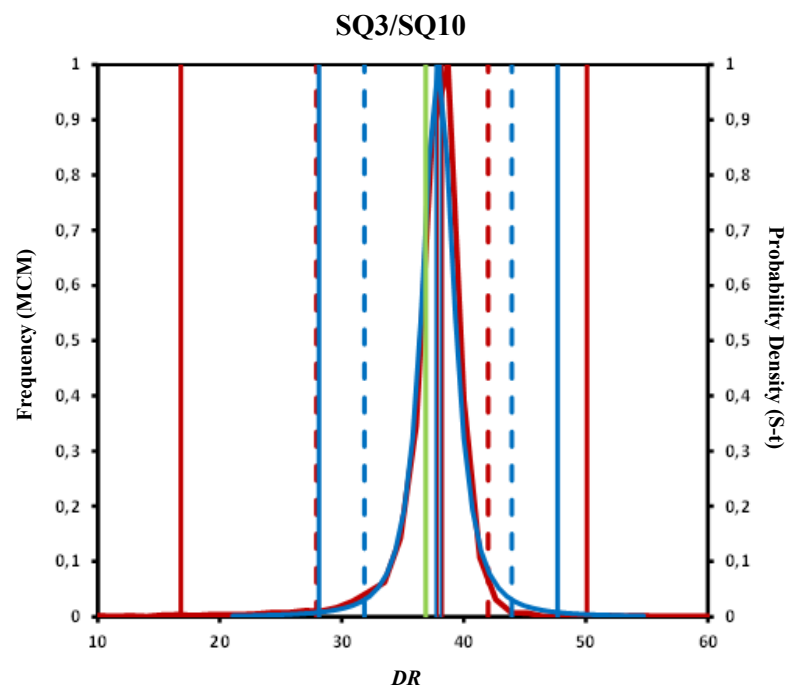
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.55. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



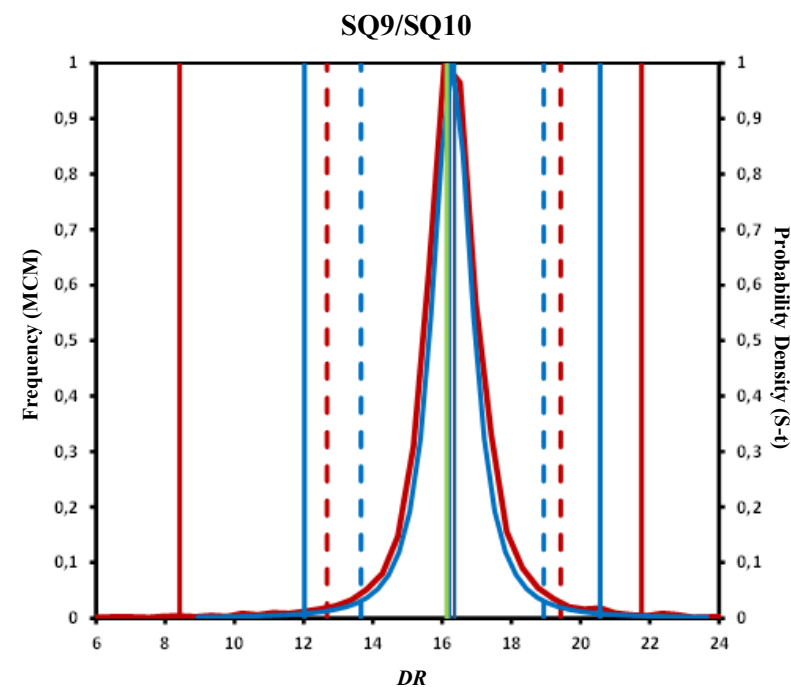
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.56. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



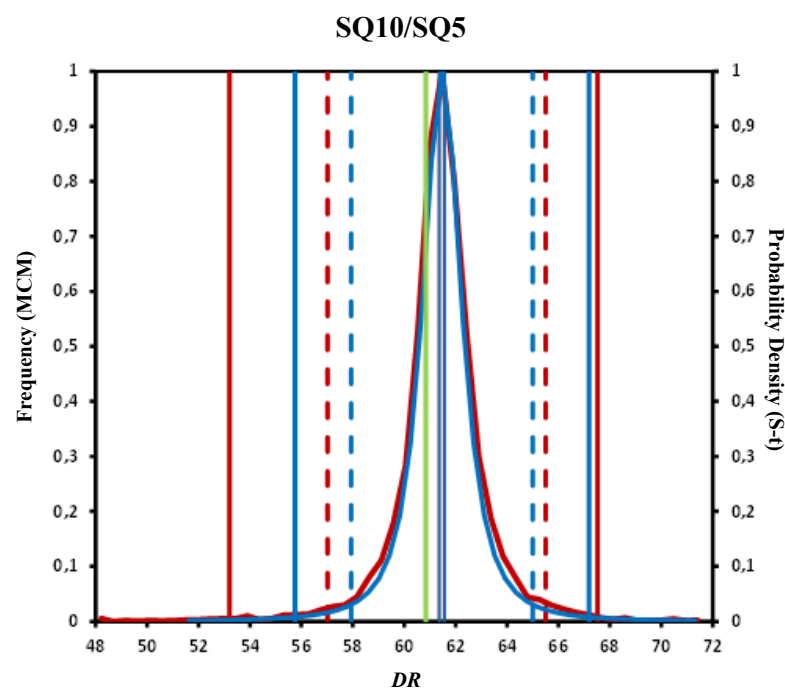
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.57. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



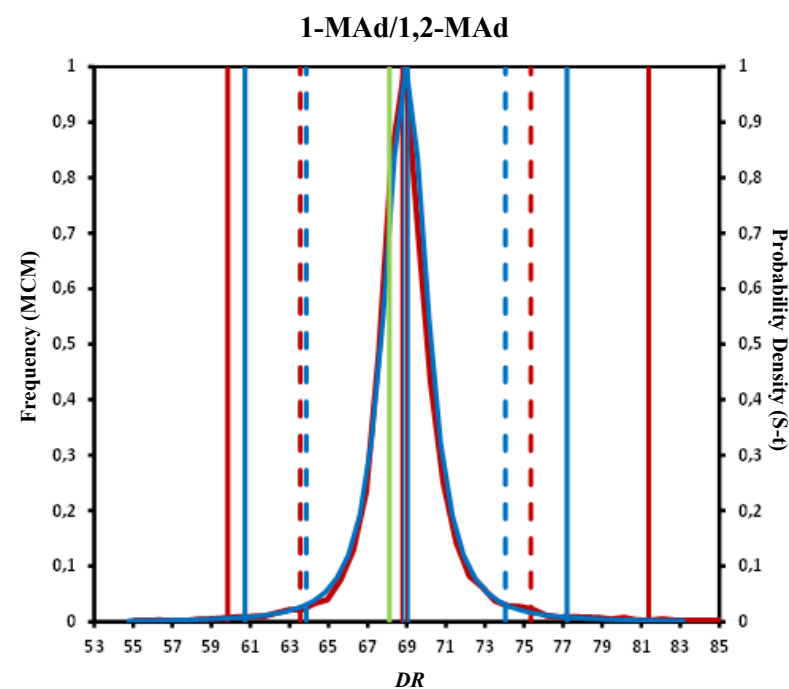
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.58. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.59. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.60. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.

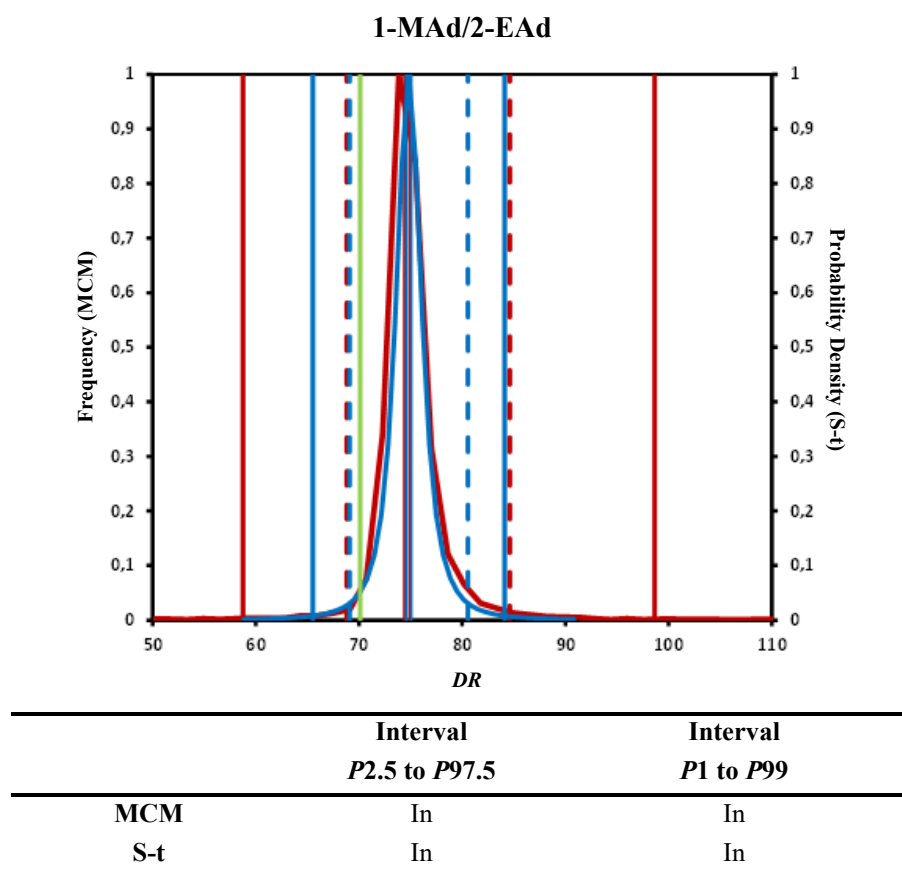


Figure A.61. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.

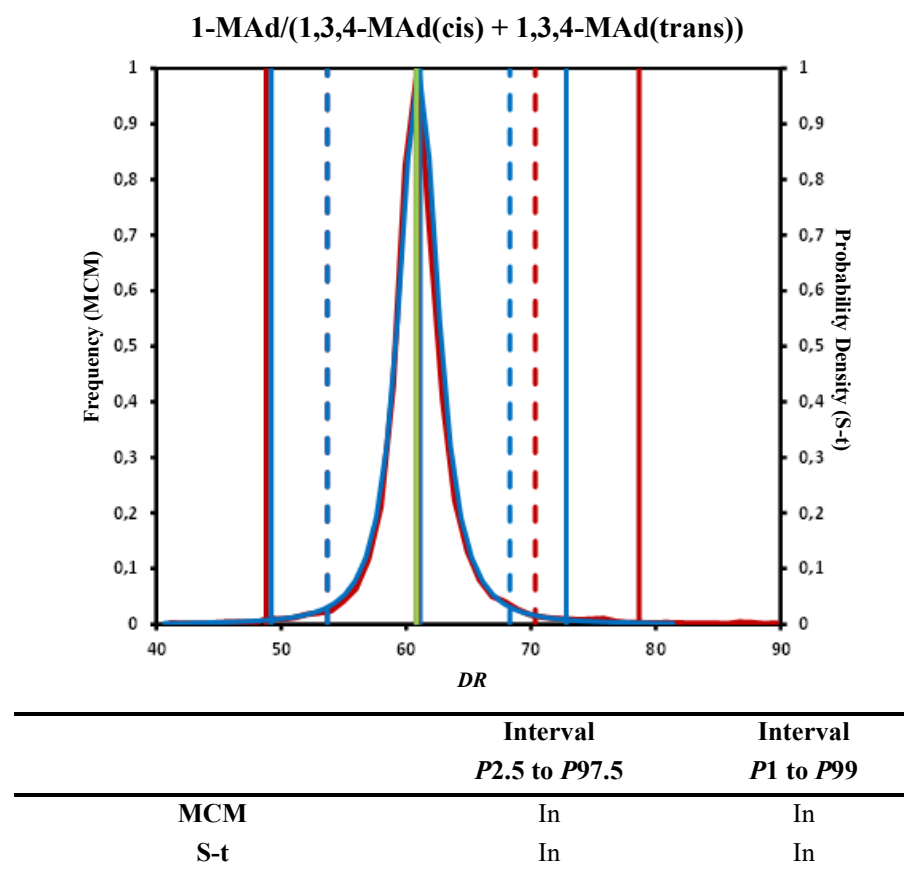
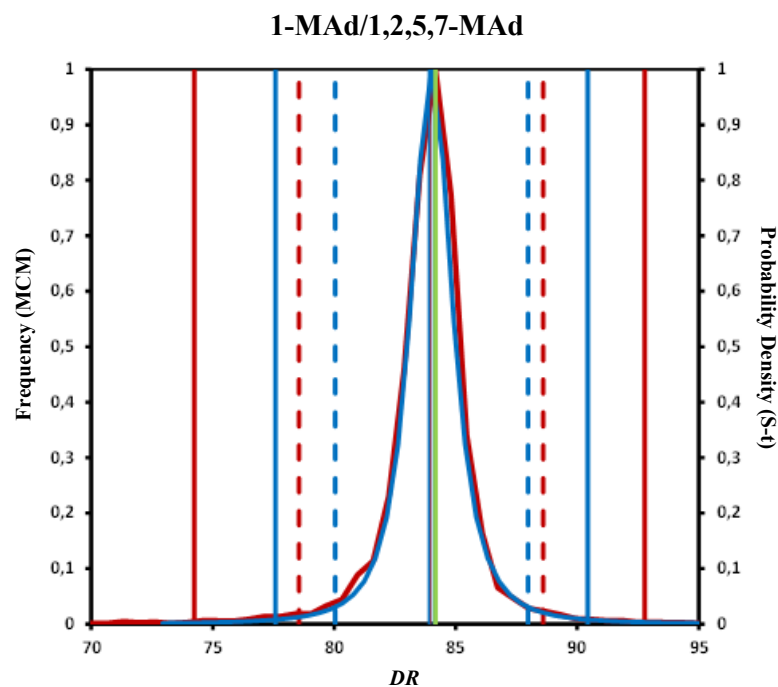
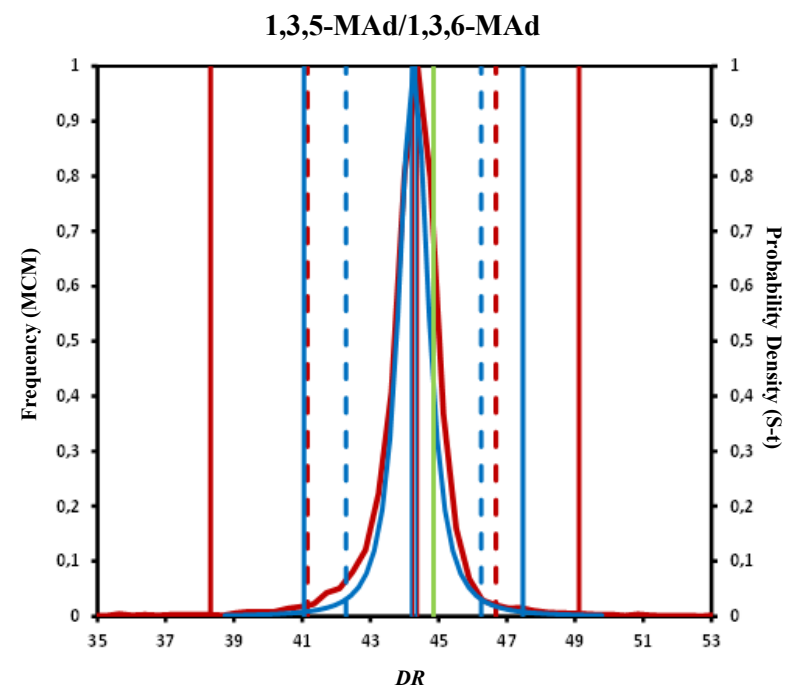


Figure A.62. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



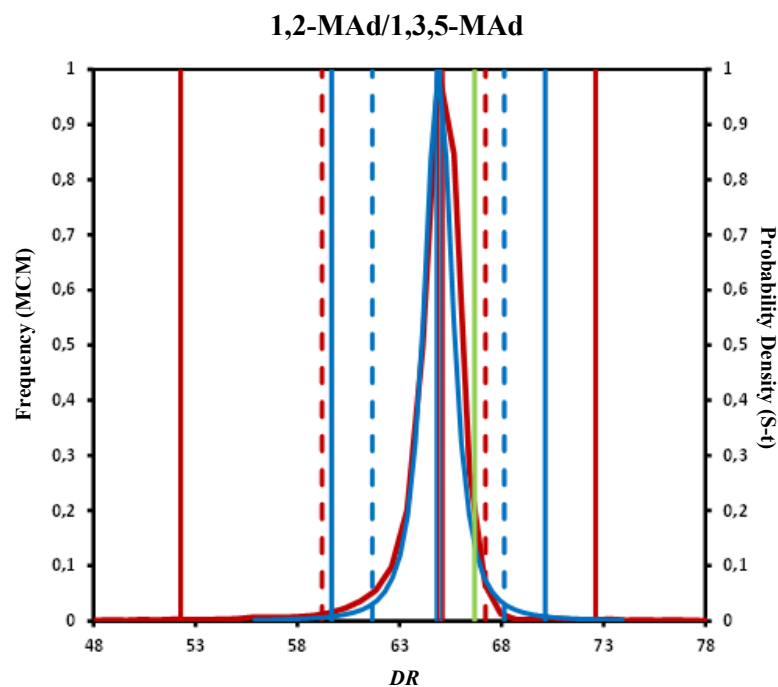
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.63. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



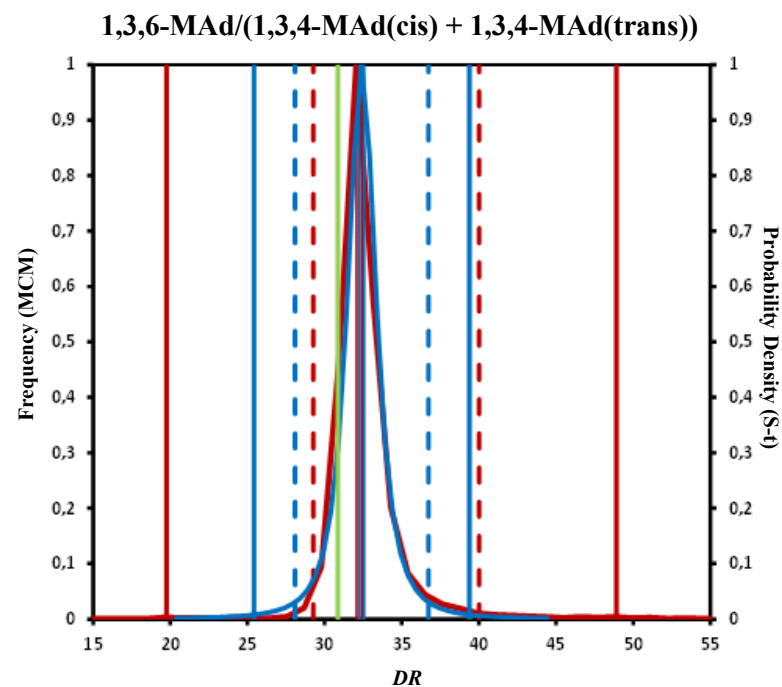
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.64. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



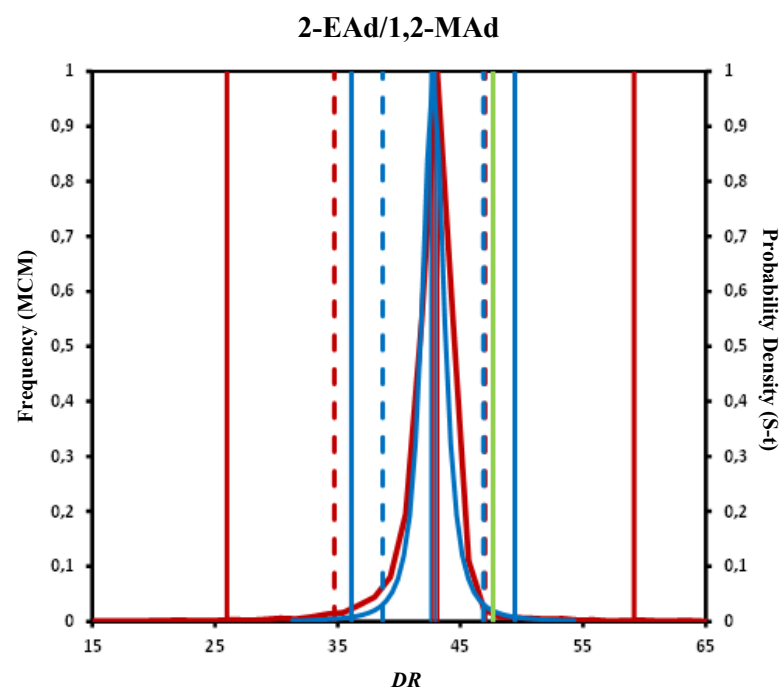
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.65. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



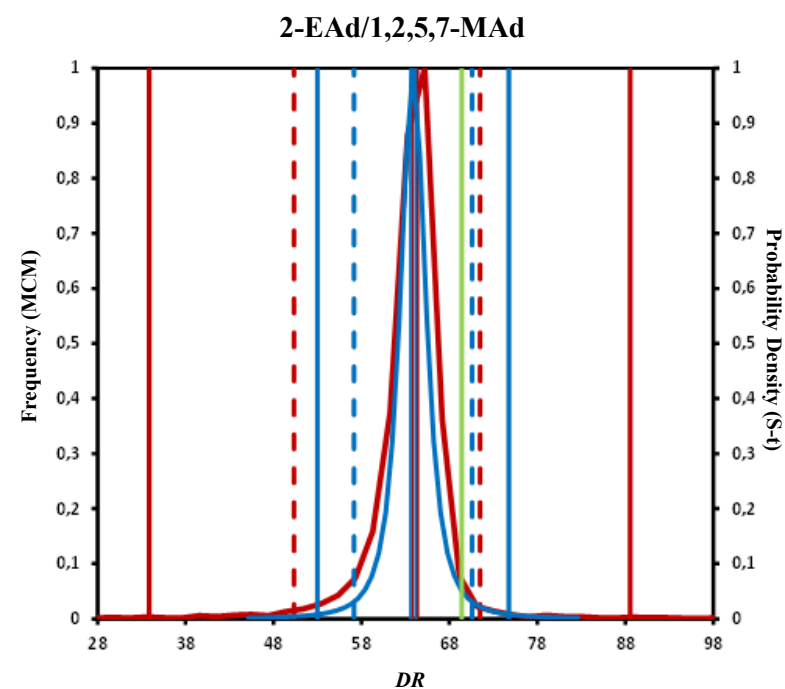
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.66. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



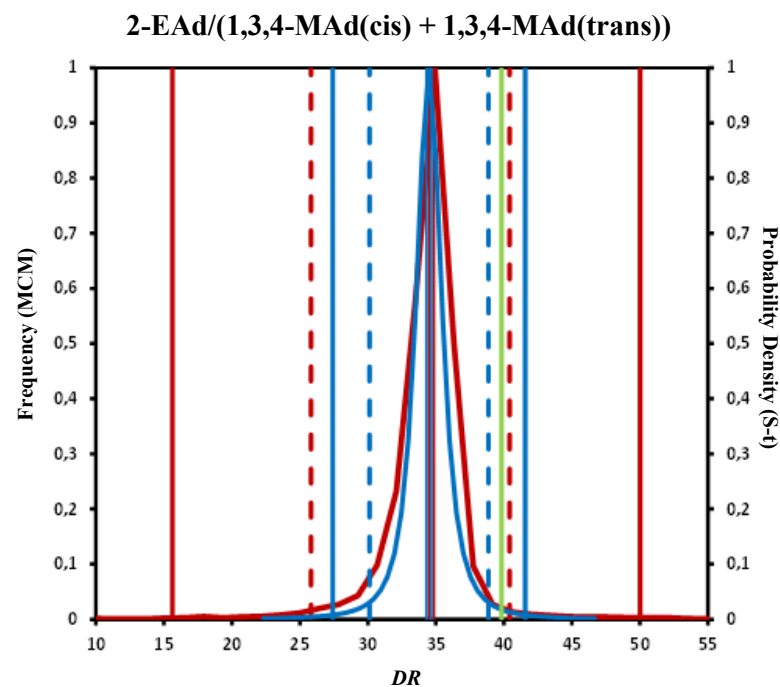
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	Out	In
S-t	Out	In

Figure A.67. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



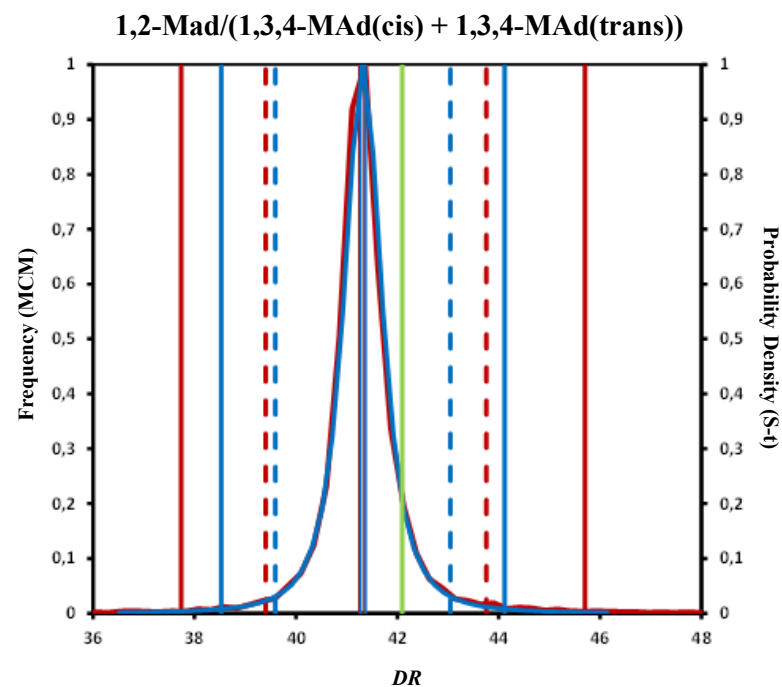
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.68. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



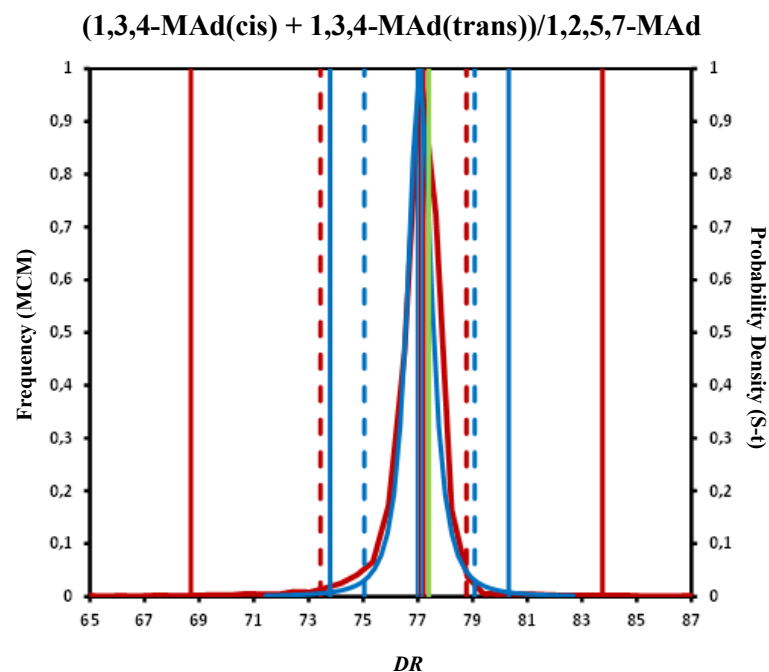
	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	Out	In

Figure A.69. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.70. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (DR) by the Monte Carlo Method (MCM) (red curve) and Student's t distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - - $P2.5$ and $P97.5$ and — $P1$ and $P99$. The green vertical line represents the DR value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's DR relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.



	Interval <i>P2.5 to P97.5</i>	Interval <i>P1 to P99</i>
MCM	In	In
S-t	In	In

Figure A.71. Normalised simulated frequency and modelled probability density function of the diagnostic ratio (*DR*) by the Monte Carlo Method (MCM) (red curve) and Student's *t* distribution (S-t) (blue curve), respectively. Red and blue vertical lines represent the χ^{th} percentiles of both models ($P\chi^{\text{th}}$): - - *P2.5* and *P97.5* and — *P1* and *P99*. The green vertical line represents the *DR* value from a GC-MS injection independent of the model (sample analysis: MixCrude_Inj07). The table below presents the positioning of sample's *DR* relative to studied limits: inclusion (In) or exclusion (Out) within 95% and 98% confidence limits from MCM or S-t models.

A.3. Spreadsheets to simulate diagnostic ratios using the Monte Carlo Method and represent the probability distributions of the data simulated and modelled by Student's t statistics

Available to download using this [weblink](#) 

File: Single&Multi_DR_Modelling.xlsm

A.4. Data comparison obtained by the developed tool and the NIST software

Available to download using this [weblink](#) 

File: Data_comparison_with_NIST_software.xlsx

Annex B

Supplementary material of Chapter 3

Content:

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B.1. Experimental details

The experimental details present the operational conditions used in the GC-MS analysis and the list of diagnostic ratios studied.

▪ GC-MS conditions

One microliter of MixCrude solution was injected in on-column mode, by an ALS syringe of 10 μ L tapered, fixed needle, 23-26s/42/cone (Agilent Technologies, Santa Clara, USA) with a fast plunger and no pre- and post-injection dwell, with the injector operated 3 °C above oven temperature. The carrier gas was helium (purity $\geq$ 99.999%) at a constant flow of 1.1 mL/min. One meter of deactivated fused silica capillary pre-column, with a 0.53 mm internal diameter (Agilent Technologies, Santa Clara, USA), was connected between the injector and a 60 m DB-5ms capillary column (non-polar phenyl arylene polymer capillary column virtually equivalent to (5%-phenyl)-methylpolysiloxane, 0.25 mm internal diameter, 0.25 μ m film thickness) (Agilent Technologies, Santa Clara, USA). The oven program started at an initial temperature of 42 °C for 1.3 min, rose to a final temperature of 320 °C at a rate of 5.5 °C/min and finished remaining at the final temperature of 320 °C for 25 min.

The quadrupole mass spectrometer detector was operated using 70 eV electron impact, with ion source, mass analyser and transfer line set to 230 °C, 150 °C and 320 °C, respectively. The analytical data were collected with 6.5 min of solvent delay, in the selected ion monitoring mode (SIM), with a dwell time of 30 ms for each ion fragment according to EN 15522-2. **Table B.1** shows the ion fragments used to quantify the chromatographic peaks needed to calculate the *DR* of the present study.

Table B.1. Compound classes and ion fragments used for peak quantification.

Class of compounds or compound	Fragment (<i>m/z</i>)
<i>n</i> -Alkanes	85; 169
Branched alkanes	169; 225
Isoprenoids	85; 113
Alkylcycloalkanes	83
Decalin, C1-, C2- and C3-decalins	138; 152; 166; 180
Sesquiterpanes	123; 179; 193
Adamantanes	135; 149; 163; 177
Diamantane and 4-Methyl-diamantane	187; 188
Tetralin and 2-Methyltetralin	104
Biphenyl	154
C3-de peak (unknown compound designation according to EN 15522-2)	180
Alkylbenzenes	92
Alkyltoluenes	106
C2-Benzothiophenes	162
Naphthalene, C1-, C2- and C3-Naphthalenes	128; 142; 156; 170
Acenaphthylene	152
C1- and C2-Fluorenes	180; 194
C1-, C2-, C3- and C4-Phenanthrenes/Anthracenes	192; 206; 220; 234
Octahydroanthracene/phenanthrene	186
C1-, C2- and C3-Dibenzothiophenes	198; 212; 226
C1- and C2-Fluoranthenes/Pyrenes	216; 230
1-Methyl-7-isopropylphenanthrene (Retene)	219
C1-Chrysenes	242
Benzo(a)pyrene and Benzo(e)pyrene	252
Fatty acid methyl esters	74
Tricyclic terpane	191; 290
Hopanes	191
Diasteranes and Steranes	217; 218
Triaromatic steranes	231

Table B.2. List of diagnostic ratios and abbreviations of compounds whose signals are considered in the study (normative ratios for crude oil (MixCrude) and light fuel (Round Robin test samples) according to EN 15522-2 standard).

Code	Ratio components	Abbreviation	MixCrude	RR samples
DR01	1-Methyladamantane/1,2-Dimethyladamantane	1-M-Adam/1,2-DM-Adam	○	● (*)
DR02	1-Methyladamantane/2-Ethyl-adamantane	1-M-Adam/2-E-Adam	○	● (*)
DR03	2,6-Dimethylundecane/2-Methyl-1,2,3,4-tetrahydronaphthalene	i-C13/2-M-tetralin	○	● (*)
DR04	<i>cis</i> -1,3,4-Trimethyladamantane/2-Ethyl-adamantane	c-1,3,4-TM-Adam/2-E-Adam	○	● (*)
DR05	Hexylbenzene/Heptylbenzene	C6-/C7-Benz	○	○ (*)
DR06	2-Ethyl-adamantane/2,6,10-Trimethylundecane	2-E-Adam/i-C14	○	● (*)
DR07	Sesquiterpane C ₁₄ H ₂₆ ⁽¹⁾ /Sesquiterpane C ₁₄ H ₂₆ ⁽¹⁾	BS1/BS2	○	● (*)
DR08	Unknown compound designation ⁽²⁾ /Sesquiterpane C ₁₄ H ₂₆ ⁽¹⁾	C3-de peak/BS2	○	● (*)
DR09	Biphenyl/2-Ethyl-naphthalene	B/2-E-N	○	● (*)
DR10	2-Ethyl-naphthalene/2,6+2,7-Dimethylnaphthalene	2-E-N/2,6+2,7-DM-N	○	● (*)
DR11	Sesquiterpane C ₁₅ H ₂₈ ⁽¹⁾ /8β(H)-Drimane ⁽¹⁾	BS4/BS5	○	● (*)
DR12	3 rd eluted branched alkane with <i>m/z</i> 169 ⁽³⁾ /Pentadecane	Br-alk-169-3/n-C15	○	● (*)
DR13	8β(H)-Drimane ⁽¹⁾ /Sesquiterpane C ₁₅ H ₂₈ ⁽¹⁾	BS5/BS6	○	● (*)
DR14	Sesquiterpane C ₁₆ H ₂₀ ⁽¹⁾ /Sesquiterpane C ₁₆ H ₂₀ ⁽¹⁾	BS8/BS9	○	● (*)
DR15	<i>meta</i> -Octyltoluene/ <i>ortho</i> -Octyltoluene	m-/o-C8-Tol	○	● (*)
DR16	8β(H)-Homodrimane ⁽¹⁾ /Norpristane	BS10/Norpri	○	● (*)
DR17	Norpristane/ <i>meta</i> -Nonyltoluene	Norpri/m-C9-Tol	○	● (*)
DR18	Decylbenzene/Undecylcyclohexane	C10-Benz/n-C11-CyC6	○	○ (*)
DR19	Heptadecane/Pristane	n-C17/Pri	● (*)	● (*)
DR20	Pristane/Phytane	Pri/Phy	● (*)	● (*)
DR21	Octadecane/Phytane	n-C18/Phy	● (*)	● (*)
DR22	4-Methyldibenzothiophene/1-Methyldibenzothiophene	4-M-Dbt/1-M-Dbt	● (*)	○ (*)
DR23	3 rd eluted branched alkane with <i>m/z</i> 225 ⁽³⁾ /Nonadecane	Br-alk-225-3/n-C19	● (*)	○

● Diagnostic ratio determined.

○ Diagnostic ratio not determined.

(*) Normative ratio for oil type.

(1) The label identifies the elution order of sesquiterpanes, *e.g.*, BS1 and BS2 are the first and the second sesquiterpanes to elute.

(2) Compound with quantification *m/z* 180 and the same retention time as BS2, eluting outside the elution range of C3-Decalins.

(3) Compound name unknown - differentiation among other branched alkane peaks based on quantification ion (*m/z* 169 or 225) and elution order number.

Table B.2 (cont.).

Code	Ratio components	Abbreviation	MixCrude	RR samples
DR24	2-Methylphenanthrene/1-Methylphenanthrene	2-M-Phe/1-M-Phe	● (*)	○ (*)
DR25	Hexadecanoic acid methyl ester/Octadecanoic acid methyl ester	FAME C16:0/C18:0	○	○ (*)
DR26	Dimethyldibenzothiophenes/Dimethylphenanthrenes&anthracenes	C2-dbt_s/C2-phe_s	● (*)	○
DR27	2-Methylfluoranthene/4-Methylpyrene	2-M-Fl/4-M-Py	● (*)	○
DR28	Pentadecylbenzene/Heptadecylbenzene	C15-/C17-Benz	○	○
DR29	Benzo(a)fluorene/4-Methylpyrene	BaF/4-M-Py	● (*)	○
DR30	Retene/24-Ethyl-5 α (H),14 β (H),17 β (H),20(R+S)-cholestane	Retene/29bb	● (*)	○
DR31	2-Methylpyrene/4-Methylpyrene	2-M-Py/4-M-Py	● (*)	○
DR32	1-Methylpyrene/4-Methylpyrene	1-M-Py/4-M-Py	● (*)	○
DR33	C23-Tricyclic terpane/C24-Tricyclic terpane	C23Tr/C24Tr	○	○
DR34	5 α (H),14 β (H),17 β (H),20(R+S)-Cholestane/24-Ethyl-5 α (H),14 β (H),17 β (H),20(R+S)-cholestane	27bb/29bb	● (*)	○
DR35	18 α (H)-22,29,30-Trisnorhopane/17 α (H),21 β (H)-Hopane (hopane)	27Ts/30ab	● (*)	○
DR36	C26,20S-Triaromatic sterane/C26,20R- & C27,20S-Triaromatic steranes	SC26/RC26+SC27TA	● (*)	○
DR37	17 α (H)-22,29,30-Trisnorhopane/17 α (H),21 β (H)-Hopane (hopane)	27Tm/30ab	● (*)	○
DR38	17 α (H),21 β (H)-28,30-Bisnorhopane/17 α (H),21 β (H)-Hopane (hopane)	28ab/30ab	○ (*)	○
DR39	C28,20S-Triaromatic sterane/C26,20R- & C27,20S-Triaromatic steranes	SC28/RC26+SC27TA	● (*)	○
DR40	17 α (H),21 β (H)-30-Norhopane/17 α (H),21 β (H)-Hopane (hopane)	29ab/30ab	● (*)	○
DR41	18 α (H)-Oleanane /17 α (H),21 β (H)-Hopane (hopane)	30O/30ab	● (*)	○
DR42	C28,20R-Triaromatic sterane/C26,20R- & C27,20S-Triaromatic steranes	RC28/RC26+SC27TA	● (*)	○
DR43	17 α (H),21 β (H),22(S)-Homohopane/17 α (H),21 β (H)-Hopane (hopane)	31abS/30ab	● (*)	○
DR44	Gammacerane/17 α (H),21 β (H)-Hopane (hopane)	30G/30ab	● (*)	○
DR45	Decalin/1-Methyladamantane	De/1-M-Adam	○	●
DR46	1-Methyladamantane/2-Methyladamantane	1-M-Adam/2-M-Adam	○	●
DR47	1,3,5-Trimethyladamantane/ <i>trans</i> -1,4-Dimethyladamantane	1,3,5-TM-Adam/tr-1,4-DM-Adam	○	●
DR48	1,3,5-Trimethyladamantane/1,3,6-Trimethyladamantane	1,3,5-TM-Adam/1,3,6-TM-Adam	○	●
DR49	C1-Decalins/C2-Decalins	C1-de_s/C2-de_s	○	●

● Diagnostic ratio determined.

○ Diagnostic ratio not determined.

(*) Normative ratio for oil type.

Table B.2 (cont.).

Code	Ratio components	Abbreviation	MixCrude	RR samples
DR50	1,2,3,4-Tetrahydronaphthalene/2-Methyl-1,2,3,4-tetrahydronaphthalene	Tetralin/2-M-Tetralin	○	○
DR51	1,2,5,7-Tetramethyladamantane/2-Ethyl-adamantane	1,2,5,7-TeM-Adam/2-E-Adam	○	●
DR52	1,2,5,7-Tetramethyladamantane/8β(H)-Homodrimane ⁽¹⁾	1,2,5,7-TeM-Adam/BS10	○	●
DR53	<i>meta</i> -Hexyltoluene/8β(H)-Homodrimane ⁽¹⁾	m-C6-Tol/BS10	○	●
DR54	<i>meta</i> -Hexyltoluene/ <i>ortho</i> -Hexyltoluene	m-/o-C6-Tol	○	●
DR55	Heptylbenzene/Decylbenzene	C7-/C10-Benz	○	○
DR56	Sesquiterpane C ₁₅ H ₂₈ ⁽¹⁾ /8β(H)-Drimane ⁽¹⁾	BS3/BS5	○	●
DR57	1,6-Dimethylnaphthalene/1,3+1,7-Dimethylnaphthalene	1,6-DM-N/1,3+1,7-DM-N	○	●
DR58	Acenaphthylene/1,2-Dimethylnaphthalene	ANY/1,2-DM-N	○	○
DR59	Diamantane/4-Methyldiamantane	Diam/4-M-Diam	○	○
DR60	Dodecanoic acid methyl ester/Hexadecanoic acid methyl ester	FAME C12:0/C16:0	○	○
DR61	1,3,7-Trimethylnaphthalene/1,3,6-Trimethylnaphthalene	1,3,7-TM-N/1,3,6-TM-N	○	●
DR62	Sesquiterpane C ₁₆ H ₂₀ ⁽¹⁾ /8β(H)-Homodrimane ⁽¹⁾	BS8/BS10	○	●
DR63	1,2,3,4,5,6,7,8-Octahydro-anthracene/1,2,3,4,5,6,7,8-Octahydrophenanthrene	8H-A/8H-Phe	○	○
DR64	1-Methylfluorene/1,2,3,4,5,6,7,8-Octahydrophenanthrene	1-M-F/8H-Phe	○	○
DR65	Tetradecanoic acid methyl ester/Hexadecanoic acid methyl ester	FAME C14:0/C16:0	○	○
DR66	<i>cis</i> -9-Hexadecenoic acid methyl ester/Hexadecanoic acid methyl ester	FAME C16:1/C16:0	○	○
DR67	1-Ethylphenanthrene/1,7-Dimethylphenanthrene	1-E-Phe/1,7-DM-Phe	○	○
DR68	Trimethyldibenzothiophenes/Trimethylphenanthrenes&anthracenes	C3-dbt_s/C3-phe_s	○	○
DR69	<i>cis</i> -9,12-Octadecadienoic acid methyl ester/Octadecanoic acid methyl ester	FAME C18:2/C18:0	○	○
DR70	<i>cis</i> -9-Octadecenoic acid methyl ester+9,12,15-Octadecatrienoic acid/Octadecanoic acid methyl ester	FAME C18:1+C18:3/C18:0	○	○
DR71	C21-Tricyclic terpane/C23-Tricyclic terpane	C21Tr/C23Tr	○	○
DR72	C23-Tricyclic terpane/Phytanyl-toluene	C23Tr/phy-tol	○	○
DR73	Eicosanoic acid methyl ester/Octadecanoic acid methyl ester	FAME C20:0/C18:0	○	○
DR74	C20-Triaromatic sterane/C21-Triaromatic sterane	C20TA/C21TA	○	○

● Diagnostic ratio determined.

○ Diagnostic ratio not determined.

(1) The label identifies the elution order of sesquiterpanes, e.g., BS1 and BS2 are the first and the second sesquiterpanes to elute.

Table B.2 (cont.).

Code	Ratio components	Abbreviation	MixCrude	RR samples
<i>DR75</i>	C21-Triaromatic sterane/C26,20R- & C27,20S-Triaromatic steranes	C21TA/RC26+SC27 TA	○	○
<i>DR76</i>	C28-Tricyclic terpane (22S)/17 α (H),21 β (H)-Hopane (hopane)	C28(22S)/30ab	○	○
<i>DR77</i>	Benzo(a)pyrene/Benzo(e)pyrene	BaPy/BePy	○	○
<i>DR78</i>	24-Ethyl-5 α (H),14 α (H),17 α (H),20S-cholestane/24-Ethyl-5 α (H),14 α (H),17 α (H),20R-cholestane	29aaS/29aaR	○	○
○ Diagnostic ratio not determined.				

B.2. Detailed results

Table B.3. Confidence limits of DR_x defined by the MCM and S-t methods considering 95% and 98% confidence levels, and by the SC method (SC_{LL} and SC_{UL}) for ratio formats $A/(A+B)$ and A/B , different replicate injections of sample x ($n_x = 3, 5, 8$) and single analysis of sample y .

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR19	3	0.613 - 0.652	0.599 - 0.662	0.616 - 0.653	0.604 - 0.664	0.551 - 0.730	1.59 - 1.87	1.49 - 1.95	1.60 - 1.87	1.51 - 1.96	1.51 - 2.00
	5	0.619 - 0.645	0.615 - 0.648	0.619 - 0.645	0.615 - 0.650	0.550 - 0.728	1.62 - 1.82	1.60 - 1.84	1.62 - 1.82	1.59 - 1.85	1.50 - 1.98
	8	0.622 - 0.644	0.619 - 0.647	0.622 - 0.645	0.619 - 0.648	0.550 - 0.729	1.64 - 1.81	1.62 - 1.83	1.64 - 1.81	1.62 - 1.84	1.50 - 1.99
DR20	3	0.581 - 0.606	0.575 - 0.615	0.581 - 0.604	0.574 - 0.611	0.515 - 0.681	1.39 - 1.54	1.36 - 1.60	1.38 - 1.52	1.34 - 1.56	1.26 - 1.67
	5	0.587 - 0.600	0.585 - 0.602	0.587 - 0.600	0.584 - 0.602	0.516 - 0.683	1.42 - 1.50	1.41 - 1.51	1.42 - 1.50	1.41 - 1.51	1.27 - 1.68
	8	0.579 - 0.601	0.576 - 0.604	0.579 - 0.601	0.576 - 0.604	0.513 - 0.679	1.37 - 1.51	1.36 - 1.52	1.37 - 1.50	1.36 - 1.52	1.25 - 1.66
DR21	3	0.675 - 0.736	0.657 - 0.755	0.676 - 0.734	0.658 - 0.752	0.613 - 0.811	2.07 - 2.79	1.92 - 3.08	2.06 - 2.72	1.85 - 2.92	2.08 - 2.75
	5	0.687 - 0.719	0.682 - 0.723	0.687 - 0.719	0.682 - 0.724	0.611 - 0.809	2.20 - 2.56	2.15 - 2.61	2.19 - 2.55	2.13 - 2.61	2.06 - 2.73
	8	0.690 - 0.712	0.687 - 0.715	0.690 - 0.712	0.687 - 0.715	0.610 - 0.807	2.23 - 2.48	2.20 - 2.50	2.22 - 2.48	2.19 - 2.51	2.04 - 2.70
DR22	3	0.618 - 0.681	0.602 - 0.703	0.618 - 0.677	0.600 - 0.695	0.563 - 0.745	1.61 - 2.13	1.50 - 2.34	1.60 - 2.07	1.46 - 2.22	1.60 - 2.12
	5	0.625 - 0.672	0.619 - 0.680	0.624 - 0.671	0.616 - 0.679	0.563 - 0.745	1.67 - 2.05	1.62 - 2.13	1.65 - 2.02	1.59 - 2.09	1.60 - 2.12
	8	0.630 - 0.662	0.626 - 0.666	0.630 - 0.662	0.626 - 0.667	0.562 - 0.743	1.70 - 1.96	1.68 - 1.99	1.70 - 1.96	1.66 - 1.99	1.59 - 2.10
DR23	3	0.443 - 0.466	0.436 - 0.474	0.443 - 0.465	0.436 - 0.472	0.394 - 0.522	0.794 - 0.874	0.773 - 0.903	0.794 - 0.868	0.771 - 0.891	0.722 - 0.956
	5	0.435 - 0.470	0.429 - 0.475	0.436 - 0.471	0.430 - 0.477	0.394 - 0.522	0.770 - 0.888	0.752 - 0.905	0.773 - 0.888	0.752 - 0.908	0.722 - 0.955
	8	0.434 - 0.472	0.429 - 0.476	0.435 - 0.473	0.429 - 0.478	0.394 - 0.522	0.765 - 0.895	0.750 - 0.908	0.767 - 0.896	0.749 - 0.913	0.722 - 0.956
DR24	3	0.470 - 0.494	0.464 - 0.502	0.471 - 0.493	0.464 - 0.500	0.419 - 0.554	0.888 - 0.977	0.864 - 1.01	0.889 - 0.972	0.863 - 0.997	0.808 - 1.07
	5	0.473 - 0.496	0.470 - 0.500	0.473 - 0.496	0.469 - 0.500	0.421 - 0.558	0.898 - 0.985	0.886 - 0.999	0.897 - 0.984	0.882 - 0.999	0.817 - 1.08
	8	0.472 - 0.495	0.469 - 0.498	0.472 - 0.495	0.469 - 0.498	0.420 - 0.556	0.893 - 0.980	0.885 - 0.992	0.892 - 0.978	0.880 - 0.989	0.812 - 1.08
DR26	3	0.407 - 0.442	0.394 - 0.451	0.409 - 0.442	0.399 - 0.452	0.370 - 0.489	0.685 - 0.792	0.649 - 0.821	0.690 - 0.790	0.659 - 0.821	0.643 - 0.851
	5	0.415 - 0.435	0.412 - 0.437	0.415 - 0.434	0.412 - 0.438	0.369 - 0.489	0.709 - 0.768	0.701 - 0.778	0.710 - 0.767	0.699 - 0.778	0.642 - 0.850
	8	0.418 - 0.433	0.416 - 0.435	0.417 - 0.433	0.415 - 0.435	0.369 - 0.489	0.717 - 0.763	0.713 - 0.769	0.716 - 0.762	0.710 - 0.769	0.643 - 0.851
DR27	3	0.214 - 0.228	0.210 - 0.233	0.214 - 0.227	0.210 - 0.231	0.192 - 0.254	0.272 - 0.295	0.266 - 0.303	0.273 - 0.294	0.266 - 0.300	0.246 - 0.326
	5	0.199 - 0.234	0.193 - 0.239	0.199 - 0.234	0.193 - 0.241	0.188 - 0.249	0.249 - 0.306	0.240 - 0.314	0.248 - 0.305	0.238 - 0.315	0.241 - 0.319
	8	0.202 - 0.226	0.200 - 0.228	0.203 - 0.226	0.199 - 0.229	0.186 - 0.247	0.254 - 0.291	0.249 - 0.295	0.254 - 0.292	0.249 - 0.297	0.237 - 0.314
DR29	3	0.586 - 0.617	0.576 - 0.626	0.586 - 0.616	0.577 - 0.626	0.523 - 0.692	1.41 - 1.61	1.36 - 1.68	1.42 - 1.60	1.36 - 1.66	1.31 - 1.74
	5	0.590 - 0.610	0.587 - 0.613	0.590 - 0.610	0.586 - 0.614	0.522 - 0.690	1.44 - 1.56	1.42 - 1.58	1.44 - 1.56	1.42 - 1.59	1.30 - 1.73
	8	0.583 - 0.612	0.580 - 0.615	0.584 - 0.613	0.580 - 0.617	0.520 - 0.689	1.40 - 1.58	1.38 - 1.60	1.40 - 1.58	1.38 - 1.61	1.30 - 1.72

Table B.3 (cont.).

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$SC_{LL} - SC_{UL}$	$P1 - P99$	$P2.5 - P97.5$	$P2.5 - P97.5$	$SC_{LL} - SC_{UL}$
DR30	3	0.373 - 0.420	0.360 - 0.435	0.373 - 0.418	0.359 - 0.431	0.344 - 0.455	0.593 - 0.723	0.560 - 0.768	0.594 - 0.715	0.556 - 0.752	0.569 - 0.753
	5	0.362 - 0.453	0.349 - 0.468	0.361 - 0.452	0.345 - 0.468	0.353 - 0.468	0.566 - 0.827	0.534 - 0.875	0.554 - 0.818	0.508 - 0.864	0.596 - 0.789
	8	0.383 - 0.441	0.377 - 0.448	0.382 - 0.441	0.374 - 0.449	0.358 - 0.473	0.621 - 0.789	0.605 - 0.811	0.615 - 0.784	0.592 - 0.807	0.608 - 0.805
DR31	3	0.245 - 0.266	0.240 - 0.274	0.245 - 0.264	0.238 - 0.271	0.221 - 0.293	0.325 - 0.362	0.317 - 0.377	0.323 - 0.359	0.312 - 0.370	0.297 - 0.393
	5	0.244 - 0.271	0.240 - 0.275	0.245 - 0.271	0.240 - 0.275	0.224 - 0.297	0.323 - 0.372	0.316 - 0.379	0.323 - 0.371	0.315 - 0.379	0.302 - 0.400
	8	0.244 - 0.271	0.241 - 0.274	0.244 - 0.272	0.240 - 0.276	0.224 - 0.297	0.323 - 0.373	0.318 - 0.378	0.323 - 0.373	0.316 - 0.379	0.302 - 0.400
DR32	3	0.375 - 0.434	0.362 - 0.457	0.374 - 0.429	0.356 - 0.446	0.349 - 0.462	0.599 - 0.764	0.565 - 0.833	0.593 - 0.748	0.545 - 0.796	0.583 - 0.772
	5	0.383 - 0.425	0.377 - 0.431	0.383 - 0.425	0.376 - 0.432	0.351 - 0.465	0.620 - 0.739	0.604 - 0.759	0.619 - 0.736	0.598 - 0.757	0.589 - 0.780
	8	0.386 - 0.417	0.383 - 0.421	0.387 - 0.418	0.383 - 0.422	0.350 - 0.463	0.630 - 0.716	0.620 - 0.726	0.629 - 0.717	0.618 - 0.729	0.585 - 0.774
DR34	3	0.448 - 0.531	0.421 - 0.556	0.451 - 0.530	0.427 - 0.555	0.426 - 0.565	0.807 - 1.13	0.718 - 1.24	0.812 - 1.12	0.719 - 1.21	0.838 - 1.11
	5	0.467 - 0.526	0.459 - 0.535	0.466 - 0.525	0.456 - 0.535	0.430 - 0.570	0.877 - 1.11	0.849 - 1.15	0.866 - 1.10	0.826 - 1.14	0.853 - 1.13
	8	0.473 - 0.519	0.468 - 0.524	0.473 - 0.519	0.467 - 0.525	0.431 - 0.571	0.898 - 1.08	0.880 - 1.10	0.894 - 1.07	0.870 - 1.10	0.856 - 1.13
DR35	3	0.115 - 0.141	0.105 - 0.146	0.118 - 0.142	0.110 - 0.150	0.113 - 0.150	0.130 - 0.164	0.116 - 0.171	0.133 - 0.166	0.123 - 0.176	0.130 - 0.172
	5	0.122 - 0.140	0.118 - 0.143	0.122 - 0.141	0.119 - 0.144	0.114 - 0.151	0.138 - 0.163	0.134 - 0.166	0.139 - 0.164	0.134 - 0.168	0.131 - 0.174
	8	0.127 - 0.140	0.125 - 0.142	0.126 - 0.140	0.125 - 0.142	0.116 - 0.153	0.145 - 0.163	0.143 - 0.165	0.145 - 0.163	0.142 - 0.165	0.134 - 0.177
DR36	3	0.214 - 0.272	0.200 - 0.295	0.211 - 0.267	0.194 - 0.285	0.208 - 0.275	0.272 - 0.374	0.251 - 0.418	0.266 - 0.363	0.236 - 0.394	0.274 - 0.362
	5	0.225 - 0.262	0.220 - 0.268	0.225 - 0.261	0.218 - 0.267	0.211 - 0.279	0.290 - 0.355	0.282 - 0.366	0.289 - 0.352	0.278 - 0.363	0.279 - 0.369
	8	0.229 - 0.255	0.226 - 0.258	0.229 - 0.255	0.225 - 0.258	0.210 - 0.278	0.297 - 0.342	0.292 - 0.347	0.296 - 0.342	0.290 - 0.348	0.277 - 0.367
DR37	3	0.166 - 0.183	0.162 - 0.190	0.165 - 0.182	0.160 - 0.187	0.151 - 0.200	0.199 - 0.225	0.193 - 0.235	0.198 - 0.222	0.190 - 0.230	0.182 - 0.242
	5	0.169 - 0.178	0.168 - 0.179	0.169 - 0.178	0.167 - 0.179	0.151 - 0.199	0.203 - 0.216	0.202 - 0.219	0.203 - 0.216	0.201 - 0.218	0.182 - 0.241
	8	0.166 - 0.179	0.165 - 0.181	0.166 - 0.179	0.164 - 0.181	0.150 - 0.198	0.199 - 0.218	0.197 - 0.221	0.198 - 0.218	0.196 - 0.220	0.181 - 0.239
DR39	3	0.338 - 0.416	0.321 - 0.446	0.336 - 0.411	0.313 - 0.434	0.324 - 0.430	0.512 - 0.713	0.471 - 0.800	0.500 - 0.692	0.440 - 0.751	0.518 - 0.686
	5	0.356 - 0.394	0.351 - 0.401	0.355 - 0.393	0.348 - 0.400	0.325 - 0.430	0.553 - 0.650	0.541 - 0.668	0.549 - 0.647	0.532 - 0.664	0.520 - 0.688
	8	0.363 - 0.386	0.361 - 0.388	0.363 - 0.386	0.360 - 0.389	0.325 - 0.431	0.570 - 0.628	0.564 - 0.635	0.569 - 0.627	0.561 - 0.635	0.520 - 0.688
DR40	3	0.348 - 0.374	0.342 - 0.384	0.347 - 0.372	0.340 - 0.380	0.313 - 0.414	0.534 - 0.599	0.520 - 0.625	0.532 - 0.593	0.513 - 0.611	0.489 - 0.647
	5	0.343 - 0.389	0.336 - 0.397	0.343 - 0.389	0.335 - 0.397	0.318 - 0.421	0.521 - 0.637	0.506 - 0.656	0.520 - 0.634	0.500 - 0.654	0.501 - 0.664
	8	0.351 - 0.382	0.348 - 0.386	0.350 - 0.382	0.346 - 0.386	0.318 - 0.421	0.540 - 0.618	0.533 - 0.628	0.538 - 0.617	0.528 - 0.627	0.502 - 0.664
DR41	3	0.279 - 0.302	0.271 - 0.309	0.280 - 0.302	0.273 - 0.309	0.253 - 0.335	0.387 - 0.434	0.373 - 0.447	0.388 - 0.432	0.375 - 0.446	0.357 - 0.472
	5	0.283 - 0.298	0.280 - 0.300	0.283 - 0.298	0.280 - 0.300	0.252 - 0.334	0.394 - 0.424	0.390 - 0.428	0.394 - 0.423	0.389 - 0.429	0.355 - 0.470
	8	0.282 - 0.300	0.280 - 0.302	0.282 - 0.300	0.279 - 0.302	0.253 - 0.334	0.393 - 0.428	0.389 - 0.433	0.392 - 0.428	0.387 - 0.432	0.356 - 0.471
DR42	3	0.311 - 0.378	0.292 - 0.401	0.311 - 0.375	0.291 - 0.395	0.298 - 0.395	0.452 - 0.609	0.415 - 0.671	0.449 - 0.596	0.403 - 0.642	0.454 - 0.601
	5	0.328 - 0.359	0.324 - 0.364	0.328 - 0.359	0.322 - 0.364	0.298 - 0.395	0.488 - 0.561	0.479 - 0.574	0.487 - 0.558	0.474 - 0.571	0.454 - 0.601
	8	0.332 - 0.354	0.329 - 0.357	0.332 - 0.354	0.329 - 0.357	0.298 - 0.395	0.496 - 0.549	0.491 - 0.554	0.496 - 0.548	0.490 - 0.555	0.454 - 0.601

Table B.3 (cont.).

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		MCM		SC
		$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR43	3	0.215 - 0.251	0.201 - 0.258	0.219 - 0.253	0.209 - 0.263	0.205 - 0.271	0.274 - 0.335	0.249 - 0.347	0.280 - 0.337	0.262 - 0.355	0.268 - 0.355
	5	0.219 - 0.252	0.214 - 0.256	0.221 - 0.253	0.215 - 0.258	0.206 - 0.272	0.281 - 0.336	0.272 - 0.344	0.282 - 0.338	0.273 - 0.348	0.269 - 0.357
	8	0.227 - 0.247	0.224 - 0.249	0.227 - 0.247	0.224 - 0.250	0.206 - 0.273	0.293 - 0.327	0.289 - 0.331	0.293 - 0.328	0.288 - 0.333	0.270 - 0.357
DR44	3	0.139 - 0.153	0.135 - 0.159	0.138 - 0.152	0.134 - 0.156	0.126 - 0.167	0.161 - 0.181	0.157 - 0.189	0.160 - 0.179	0.155 - 0.185	0.148 - 0.195
	5	0.141 - 0.152	0.139 - 0.154	0.141 - 0.152	0.139 - 0.154	0.127 - 0.168	0.164 - 0.179	0.162 - 0.182	0.164 - 0.179	0.161 - 0.181	0.149 - 0.197
	8	0.139 - 0.153	0.137 - 0.155	0.138 - 0.153	0.136 - 0.155	0.127 - 0.168	0.161 - 0.181	0.159 - 0.184	0.161 - 0.181	0.158 - 0.183	0.148 - 0.196

Table B.4. Confidence limits of differences between DR means ($\overline{DR}_{x;i} - \overline{DR}_{y;i}$) defined by the MCM and S-t methods considering 95% and 98% confidence levels, and by the SC method (SC_{LL} and SC_{UL}) for ratio formats $A/(A+B)$ and A/B , different replicate injections of sample x ($n_x = 3, 5, 8$) and duplicate injections of sample y .

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR19	3	-0.0804 - 0.0679	-0.195 - 0.179	-0.0127 - 0.00628	-0.0168 - 0.0103	-0.0890 - 0.0890	-0.546 - 0.512	-1.31 - 1.27	-0.0954 - 0.0473	-0.126 - 0.0777	-0.244 - 0.244
	5	-0.119 - 0.110	-0.287 - 0.276	-0.0125 - 0.00229	-0.0151 - 0.00487	-0.0889 - 0.0889	-1.00 - 0.932	-2.57 - 2.41	-0.0933 - 0.0173	-0.113 - 0.0366	-0.244 - 0.244
	8	-0.151 - 0.137	-0.359 - 0.362	-0.0125 - 0.00193	-0.0155 - 0.00500	-0.0889 - 0.0889	-1.09 - 1.03	-2.66 - 2.61	-0.0932 - 0.0149	-0.116 - 0.0379	-0.243 - 0.243
DR20	3	-0.0523 - 0.0691	-0.14 - 0.165	-0.0427 - 0.0557	-0.117 - 0.130	-0.0825 - 0.0825	-0.315 - 0.396	-0.817 - 0.912	-0.250 - 0.327	-0.683 - 0.760	-0.201 - 0.201
	5	-0.0959 - 0.113	-0.234 - 0.275	-0.0395 - 0.0546	-0.110 - 0.125	-0.0825 - 0.0825	-0.570 - 0.706	-1.44 - 1.70	-0.230 - 0.320	-0.644 - 0.734	-0.201 - 0.201
	8	-0.188 - 0.203	-0.495 - 0.505	-0.0424 - 0.0534	-0.115 - 0.126	-0.0824 - 0.0824	-1.08 - 1.17	-2.78 - 2.88	-0.248 - 0.313	-0.669 - 0.734	-0.200 - 0.200
DR21	3	-0.167 - 0.174	-0.432 - 0.421	-0.01000 - 0.0182	-0.0160 - 0.0242	-0.0984 - 0.0984	-1.89 - 1.98	-4.83 - 4.89	-0.113 - 0.207	-0.181 - 0.275	-0.331 - 0.331
	5	-0.207 - 0.207	-0.553 - 0.496	-0.00670 - 0.0116	-0.00991 - 0.0148	-0.0983 - 0.0983	-2.38 - 2.49	-6.05 - 6.16	-0.0750 - 0.132	-0.111 - 0.168	-0.330 - 0.330
	8	-0.246 - 0.244	-0.622 - 0.628	-0.00710 - 0.0101	-0.0108 - 0.0138	-0.0982 - 0.0982	-2.63 - 2.66	-6.65 - 6.65	-0.0793 - 0.115	-0.121 - 0.156	-0.329 - 0.329
DR22	3	-0.126 - 0.125	-0.305 - 0.328	-0.0164 - 0.0132	-0.0227 - 0.0195	-0.0908 - 0.0908	-1.07 - 1.04	-2.56 - 2.67	-0.131 - 0.106	-0.181 - 0.157	-0.258 - 0.258
	5	-0.199 - 0.194	-0.493 - 0.490	-0.0131 - 0.00982	-0.0167 - 0.0134	-0.0908 - 0.0908	-1.75 - 1.68	-4.48 - 4.38	-0.105 - 0.0802	-0.133 - 0.109	-0.258 - 0.258
	8	-0.295 - 0.293	-0.735 - 0.729	-0.0141 - 0.00789	-0.0187 - 0.0126	-0.0907 - 0.0907	-2.21 - 2.20	-5.63 - 5.53	-0.113 - 0.0646	-0.150 - 0.102	-0.257 - 0.257
DR23	3	-0.0935 - 0.0696	-0.231 - 0.191	-0.0619 - 0.0457	-0.143 - 0.127	-0.0641 - 0.0641	-0.323 - 0.271	-0.768 - 0.716	-0.213 - 0.157	-0.491 - 0.436	-0.118 - 0.118
	5	-0.184 - 0.169	-0.427 - 0.428	-0.0292 - 0.0124	-0.0421 - 0.0253	-0.0641 - 0.0641	-0.660 - 0.614	-1.67 - 1.58	-0.0996 - 0.0428	-0.144 - 0.0868	-0.118 - 0.118
	8	-0.305 - 0.287	-0.744 - 0.733	-0.0294 - 0.0101	-0.0417 - 0.0223	-0.0640 - 0.0640	-1.17 - 1.06	-2.95 - 2.74	-0.100 - 0.0349	-0.142 - 0.0768	-0.118 - 0.118
DR24	3	-0.0812 - 0.0902	-0.214 - 0.223	-0.0570 - 0.0640	-0.148 - 0.155	-0.0672 - 0.0672	-0.304 - 0.316	-0.767 - 0.766	-0.210 - 0.236	-0.545 - 0.571	-0.129 - 0.129
	5	-0.162 - 0.173	-0.404 - 0.435	-0.0559 - 0.0683	-0.149 - 0.162	-0.0674 - 0.0674	-0.617 - 0.659	-1.56 - 1.58	-0.206 - 0.252	-0.551 - 0.596	-0.130 - 0.130
	8	-0.194 - 0.208	-0.521 - 0.502	-0.0538 - 0.0650	-0.143 - 0.154	-0.0674 - 0.0674	-0.741 - 0.810	-1.94 - 1.93	-0.198 - 0.239	-0.527 - 0.569	-0.130 - 0.130
DR26	3	-0.0815 - 0.0902	-0.212 - 0.233	-0.00794 - 0.0116	-0.0140 - 0.0176	-0.0594 - 0.0594	-0.248 - 0.252	-0.624 - 0.610	-0.0240 - 0.0351	-0.0423 - 0.0534	-0.103 - 0.103
	5	-0.127 - 0.135	-0.323 - 0.337	-0.00285 - 0.00542	-0.00412 - 0.00670	-0.0594 - 0.0594	-0.419 - 0.416	-1.05 - 1.03	-0.00857 - 0.0164	-0.0124 - 0.0203	-0.103 - 0.103
	8	-0.144 - 0.145	-0.374 - 0.363	-0.00100 - 0.00453	-0.00170 - 0.00523	-0.0594 - 0.0594	-0.463 - 0.474	-1.15 - 1.17	-0.00298 - 0.0137	-0.00512 - 0.0159	-0.103 - 0.103
DR27	3	-0.0656 - 0.0750	-0.17 - 0.183	-0.0547 - 0.0587	-0.140 - 0.144	-0.0308 - 0.0308	-0.114 - 0.117	-0.283 - 0.282	-0.0896 - 0.0962	-0.229 - 0.236	-0.0394 - 0.0394
	5	-0.138 - 0.133	-0.354 - 0.326	-0.0244 - 0.0205	-0.0382 - 0.0344	-0.0305 - 0.0305	-0.229 - 0.235	-0.564 - 0.584	-0.0397 - 0.0335	-0.0624 - 0.0562	-0.0390 - 0.0390
	8	-0.182 - 0.177	-0.441 - 0.456	-0.0643 - 0.0573	-0.156 - 0.149	-0.0304 - 0.0304	-0.279 - 0.269	-0.696 - 0.682	-0.105 - 0.0937	-0.255 - 0.243	-0.0388 - 0.0388
DR29	3	-0.0764 - 0.0738	-0.184 - 0.189	-0.0101 - 0.00670	-0.0137 - 0.0103	-0.0843 - 0.0843	-0.500 - 0.507	-1.26 - 1.21	-0.0636 - 0.0423	-0.0862 - 0.0649	-0.212 - 0.212
	5	-0.143 - 0.140	-0.361 - 0.349	-0.0106 - 0.00441	-0.0138 - 0.00761	-0.0842 - 0.0842	-0.915 - 0.904	-2.27 - 2.20	-0.0668 - 0.0279	-0.0870 - 0.0481	-0.211 - 0.211
	8	-0.293 - 0.278	-0.74 - 0.741	-0.0120 - 0.00222	-0.0142 - 0.00441	-0.0841 - 0.0841	-1.74 - 1.74	-4.23 - 4.41	-0.0740 - 0.0138	-0.0876 - 0.0274	-0.211 - 0.211
DR30	3	-0.128 - 0.102	-0.297 - 0.283	-0.0306 - 0.00600	-0.0358 - 0.00076	-0.0566 - 0.0566	-0.364 - 0.256	-0.812 - 0.701	-0.0859 - 0.0172	-0.101 - 0.00249	-0.0952 - 0.0952
	5	-0.323 - 0.305	-0.786 - 0.76	-0.0272 - 0.0128	-0.0333 - 0.0190	-0.0574 - 0.0574	-0.984 - 0.958	-2.40 - 2.31	-0.0773 - 0.0380	-0.0951 - 0.0558	-0.0974 - 0.0974
	8	-0.395 - 0.389	-0.986 - 1.02	-0.0166 - 0.00856	-0.0199 - 0.0119	-0.0576 - 0.0576	-1.14 - 1.13	-2.94 - 2.90	-0.0470 - 0.0253	-0.0567 - 0.0350	-0.0980 - 0.0980
DR31	3	-0.0683 - 0.0565	-0.162 - 0.138	-0.0175 - 0.00837	-0.0255 - 0.0164	-0.0359 - 0.0359	-0.117 - 0.104	-0.284 - 0.255	-0.0777 - 0.0612	-0.182 - 0.166	-0.0484 - 0.0484
	5	-0.179 - 0.181	-0.435 - 0.470	-0.0161 - 0.0134	-0.0252 - 0.0225	-0.0362 - 0.0362	-0.333 - 0.325	-0.836 - 0.851	-0.0292 - 0.0244	-0.0458 - 0.0410	-0.0488 - 0.0488
	8	-0.280 - 0.282	-0.73 - 0.707	-0.0161 - 0.0128	-0.0251 - 0.0217	-0.0362 - 0.0362	-0.526 - 0.546	-1.30 - 1.33	-0.0292 - 0.0232	-0.0455 - 0.0394	-0.0487 - 0.0487

Table B.4 (cont.).

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR32	3	-0.120 - 0.115	-0.282 - 0.295	-0.0166 - 0.0118	-0.0226 - 0.0178	-0.0564 - 0.0564	-0.344 - 0.327	-0.816 - 0.851	-0.0462 - 0.0330	-0.0631 - 0.0499	-0.0943 - 0.0943
	5	-0.288 - 0.283	-0.702 - 0.726	-0.0114 - 0.0116	-0.0154 - 0.0156	-0.0565 - 0.0565	-0.820 - 0.859	-2.03 - 2.15	-0.0320 - 0.0329	-0.0433 - 0.0442	-0.0948 - 0.0948
	8	-0.367 - 0.368	-0.937 - 0.930	-0.0121 - 0.00946	-0.0168 - 0.0141	-0.0564 - 0.0564	-1.02 - 1.06	-2.46 - 2.72	-0.0340 - 0.0268	-0.0470 - 0.0398	-0.0946 - 0.0946
DR34	3	-0.197 - 0.177	-0.49 - 0.471	-0.0357 - 0.0100	-0.0499 - 0.0242	-0.0696 - 0.0696	-0.798 - 0.675	-1.88 - 1.73	-0.138 - 0.0372	-0.192 - 0.0913	-0.138 - 0.138
	5	-0.279 - 0.257	-0.7 - 0.659	-0.0214 - 0.00489	-0.0260 - 0.00950	-0.0699 - 0.0699	-1.16 - 1.12	-2.80 - 2.74	-0.0840 - 0.0194	-0.102 - 0.0375	-0.140 - 0.140
	8	-0.343 - 0.314	-0.859 - 0.782	-0.0166 - 0.00113	-0.0187 - 0.00094	-0.0699 - 0.0699	-1.42 - 1.31	-3.62 - 3.33	-0.0651 - 0.00443	-0.0732 - 0.00370	-0.140 - 0.140
DR35	3	-0.0186 - 0.00687	-0.0336 - 0.0183	-0.0119 - 0.00226	-0.0163 - 0.00664	-0.0185 - 0.0185	-0.0245 - 0.00912	-0.0437 - 0.0243	-0.0157 - 0.00295	-0.0215 - 0.00872	-0.0214 - 0.0214
	5	-0.0762 - 0.0672	-0.186 - 0.179	-0.00768 - 0.00070	-0.00915 - 0.00217	-0.0186 - 0.0186	-0.0993 - 0.0901	-0.245 - 0.220	-0.0102 - 0.00093	-0.0121 - 0.00287	-0.0215 - 0.0215
	8	-0.144 - 0.139	-0.352 - 0.351	-0.00553 - 0.00051	-0.00634 - 0.00132	-0.0187 - 0.0187	-0.202 - 0.196	-0.491 - 0.518	-0.00734 - 0.00069	-0.00842 - 0.00177	-0.0216 - 0.0216
DR36	3	-0.147 - 0.137	-0.355 - 0.347	-0.0252 - 0.00610	-0.0318 - 0.0128	-0.0342 - 0.0342	-0.239 - 0.226	-0.567 - 0.575	-0.0440 - 0.0107	-0.0557 - 0.0224	-0.0452 - 0.0452
	5	-0.252 - 0.226	-0.622 - 0.573	-0.0198 - 0.00750	-0.0257 - 0.0133	-0.0344 - 0.0344	-0.432 - 0.421	-1.07 - 1.04	-0.0348 - 0.0132	-0.0450 - 0.0234	-0.0456 - 0.0456
	8	-0.264 - 0.253	-0.67 - 0.644	-0.0230 - 0.00895	-0.0329 - 0.0188	-0.0344 - 0.0344	-0.477 - 0.462	-1.22 - 1.19	-0.0405 - 0.0159	-0.0580 - 0.0333	-0.0455 - 0.0455
DR37	3	-0.0132 - 0.0179	-0.0338 - 0.0414	-0.00293 - 0.00541	-0.00471 - 0.00719	-0.0242 - 0.0242	-0.0210 - 0.0264	-0.0514 - 0.0609	-0.00429 - 0.00792	-0.00689 - 0.0105	-0.0293 - 0.0293
	5	-0.0525 - 0.0577	-0.134 - 0.139	-0.00179 - 0.00368	-0.00274 - 0.00464	-0.0242 - 0.0242	-0.0806 - 0.0843	-0.191 - 0.197	-0.00261 - 0.00539	-0.00401 - 0.00678	-0.0292 - 0.0292
	8	-0.135 - 0.139	-0.338 - 0.344	-0.00254 - 0.00347	-0.00334 - 0.00428	-0.0241 - 0.0241	-0.211 - 0.210	-0.529 - 0.522	-0.00369 - 0.00508	-0.00486 - 0.00625	-0.0292 - 0.0292
DR39	3	-0.0993 - 0.0931	-0.232 - 0.223	-0.0214 - 0.0132	-0.0288 - 0.0206	-0.0526 - 0.0526	-0.246 - 0.254	-0.574 - 0.623	-0.0547 - 0.0340	-0.0737 - 0.0530	-0.0841 - 0.0841
	5	-0.205 - 0.209	-0.52 - 0.508	-0.0128 - 0.00619	-0.0157 - 0.00913	-0.0526 - 0.0526	-0.559 - 0.521	-1.34 - 1.31	-0.0327 - 0.0160	-0.0403 - 0.0236	-0.0843 - 0.0843
	8	-0.316 - 0.323	-0.817 - 0.830	-0.0117 - 0.00641	-0.0156 - 0.0103	-0.0527 - 0.0527	-0.851 - 0.826	-2.12 - 2.05	-0.0300 - 0.0166	-0.0399 - 0.0265	-0.0844 - 0.0844
DR40	3	-0.0494 - 0.0408	-0.118 - 0.109	-0.0107 - 0.00132	-0.0133 - 0.00390	-0.0507 - 0.0507	-0.128 - 0.107	-0.292 - 0.278	-0.0263 - 0.00319	-0.0326 - 0.00949	-0.0795 - 0.0795
	5	-0.319 - 0.312	-0.793 - 0.754	-0.00944 - 0.0117	-0.0131 - 0.0154	-0.0511 - 0.0511	-0.764 - 0.774	-1.92 - 1.92	-0.0233 - 0.0293	-0.0325 - 0.0385	-0.0805 - 0.0805
	8	-0.315 - 0.318	-0.789 - 0.829	-0.00466 - 0.00709	-0.00617 - 0.00860	-0.0511 - 0.0511	-0.771 - 0.788	-1.90 - 1.98	-0.0115 - 0.0178	-0.0152 - 0.0215	-0.0805 - 0.0805
DR41	3	-0.0707 - 0.0771	-0.189 - 0.189	-0.0437 - 0.0478	-0.113 - 0.117	-0.0406 - 0.0406	-0.137 - 0.145	-0.334 - 0.350	-0.0865 - 0.0946	-0.223 - 0.231	-0.0571 - 0.0571
	5	-0.107 - 0.111	-0.272 - 0.271	-0.0429 - 0.0457	-0.110 - 0.112	-0.0405 - 0.0405	-0.211 - 0.224	-0.532 - 0.555	-0.0849 - 0.0903	-0.217 - 0.222	-0.0571 - 0.0571
	8	-0.155 - 0.163	-0.402 - 0.419	-0.0420 - 0.0464	-0.108 - 0.113	-0.0406 - 0.0406	-0.328 - 0.340	-0.818 - 0.891	-0.0831 - 0.0919	-0.215 - 0.223	-0.0572 - 0.0572
DR42	3	-0.167 - 0.162	-0.409 - 0.399	-0.0204 - 0.00910	-0.0267 - 0.0154	-0.0484 - 0.0484	-0.376 - 0.376	-0.884 - 0.947	-0.0471 - 0.0210	-0.0617 - 0.0355	-0.0741 - 0.0741
	5	-0.203 - 0.202	-0.519 - 0.505	-0.0135 - 0.00215	-0.0160 - 0.00458	-0.0484 - 0.0484	-0.474 - 0.445	-1.16 - 1.11	-0.0329 - 0.00646	-0.0398 - 0.0133	-0.0741 - 0.0741
	8	-0.234 - 0.218	-0.601 - 0.547	-0.0134 - 0.00232	-0.0167 - 0.00566	-0.0484 - 0.0484	-0.534 - 0.509	-1.34 - 1.31	-0.0311 - 0.00545	-0.0389 - 0.0133	-0.0741 - 0.0741
DR43	3	-0.0650 - 0.0609	-0.164 - 0.148	-0.0165 - 0.0203	-0.0279 - 0.0317	-0.0329 - 0.0329	-0.104 - 0.108	-0.263 - 0.257	-0.0282 - 0.0346	-0.0477 - 0.0541	-0.0430 - 0.0430
	5	-0.134 - 0.136	-0.332 - 0.340	-0.0165 - 0.0219	-0.0284 - 0.0338	-0.0329 - 0.0329	-0.246 - 0.249	-0.630 - 0.600	-0.0282 - 0.0375	-0.0485 - 0.0579	-0.0431 - 0.0431
	8	-0.174 - 0.181	-0.44 - 0.462	-0.0486 - 0.0532	-0.125 - 0.130	-0.0329 - 0.0329	-0.302 - 0.307	-0.777 - 0.777	-0.0829 - 0.0908	-0.214 - 0.222	-0.0430 - 0.0430
DR44	3	-0.0313 - 0.0316	-0.0808 - 0.0796	-0.00320 - 0.00460	-0.00486 - 0.00626	-0.0203 - 0.0203	-0.0383 - 0.0421	-0.0962 - 0.101	-0.00437 - 0.00628	-0.00665 - 0.00856	-0.0237 - 0.0237
	5	-0.0878 - 0.0890	-0.221 - 0.225	-0.00151 - 0.00508	-0.00266 - 0.00623	-0.0204 - 0.0204	-0.127 - 0.126	-0.306 - 0.302	-0.00207 - 0.00696	-0.00364 - 0.00854	-0.0238 - 0.0238
	8	-0.155 - 0.171	-0.402 - 0.439	-0.00205 - 0.00494	-0.00313 - 0.00602	-0.0203 - 0.0203	-0.198 - 0.221	-0.504 - 0.561	-0.00280 - 0.00677	-0.00427 - 0.00825	-0.0238 - 0.0238

Table B.5. Confidence limits of differences between DR means ($\overline{DR}_{x;i} - \overline{DR}_{y;i}$) defined by the MCM and S-t methods considering 95% and 98% confidence levels, and by the SC method (SC_{LL} and SC_{UL}) for ratio formats $A/(A+B)$ and A/B , different replicate injections of sample x ($n_x = 3, 5, 8$) and triplicate injections of sample y .

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR19	3	-0.0155 - 0.00904	-0.0232 - 0.0158	-0.0115 - 0.00542	-0.0152 - 0.00904	-0.0890 - 0.0890	-0.114 - 0.0711	-0.165 - 0.120	-0.0864 - 0.0406	-0.113 - 0.0677	-0.244 - 0.244
	5	-0.0122 - 0.00264	-0.0145 - 0.00589	-0.0109 - 0.00096	-0.0127 - 0.00279	-0.0889 - 0.0889	-0.0908 - 0.0199	-0.109 - 0.0425	-0.0808 - 0.00715	-0.0944 - 0.0207	-0.243 - 0.243
	8	-0.0114 - 0.00029	-0.0133 - 0.00301	-0.0101 - 0.00149	-0.0112 - 0.00039	-0.0888 - 0.0888	-0.0848 - 0.00208	-0.0983 - 0.0227	-0.0751 - 0.0110	-0.0833 - 0.00283	-0.243 - 0.243
DR20	3	-0.00609 - 0.0183	-0.0136 - 0.0244	-0.00071 - 0.0136	-0.00320 - 0.0160	-0.0825 - 0.0825	-0.0377 - 0.109	-0.0845 - 0.144	-0.00400 - 0.0800	-0.0187 - 0.0947	-0.201 - 0.201
	5	-0.00322 - 0.0166	-0.0104 - 0.0210	0.00010 - 0.0148	-0.00304 - 0.0179	-0.0825 - 0.0825	-0.0188 - 0.0968	-0.0607 - 0.120	0.00107 - 0.0873	-0.0173 - 0.106	-0.201 - 0.201
	8	-0.00406 - 0.0151	-0.0108 - 0.0193	-0.00143 - 0.0137	-0.00465 - 0.0169	-0.0825 - 0.0825	-0.0243 - 0.0874	-0.0668 - 0.111	-0.00240 - 0.0750	-0.0159 - 0.0885	-0.201 - 0.201
DR21	3	-0.0151 - 0.0231	-0.0259 - 0.0334	-0.0133 - 0.0219	-0.0241 - 0.0327	-0.0984 - 0.0984	-0.163 - 0.274	-0.280 - 0.416	-0.151 - 0.250	-0.274 - 0.374	-0.331 - 0.331
	5	-0.00692 - 0.0116	-0.0109 - 0.0145	-0.00459 - 0.00995	-0.00683 - 0.0122	-0.0982 - 0.0982	-0.0771 - 0.131	-0.123 - 0.163	-0.0515 - 0.114	-0.0770 - 0.139	-0.330 - 0.330
	8	-0.00534 - 0.00883	-0.0089 - 0.0111	-0.00325 - 0.00732	-0.00460 - 0.00868	-0.0982 - 0.0982	-0.0597 - 0.0996	-0.102 - 0.126	-0.0362 - 0.0834	-0.0515 - 0.0987	-0.329 - 0.329
DR22	3	-0.0225 - 0.0288	-0.0344 - 0.0471	-0.0130 - 0.0160	-0.0180 - 0.0210	-0.0906 - 0.0906	-0.176 - 0.235	-0.270 - 0.380	-0.103 - 0.127	-0.143 - 0.168	-0.256 - 0.256
	5	-0.0164 - 0.0210	-0.0238 - 0.0320	-0.0109 - 0.0138	-0.0144 - 0.0173	-0.0906 - 0.0906	-0.135 - 0.171	-0.195 - 0.248	-0.0865 - 0.111	-0.115 - 0.139	-0.257 - 0.257
	8	-0.0145 - 0.0189	-0.0221 - 0.0297	-0.0101 - 0.0119	-0.0135 - 0.0153	-0.0905 - 0.0905	-0.121 - 0.144	-0.187 - 0.220	-0.0804 - 0.0955	-0.108 - 0.123	-0.256 - 0.256
DR23	3	-0.0199 - 0.00832	-0.0258 - 0.0191	-0.0164 - 0.00205	-0.0203 - 0.00598	-0.0640 - 0.0640	-0.0688 - 0.0286	-0.0900 - 0.0659	-0.0559 - 0.00723	-0.0694 - 0.0207	-0.118 - 0.118
	5	-0.0206 - 0.00763	-0.0258 - 0.0172	-0.0165 - 0.00171	-0.0191 - 0.00430	-0.0640 - 0.0640	-0.0697 - 0.0257	-0.0877 - 0.0550	-0.0560 - 0.00591	-0.0648 - 0.0147	-0.118 - 0.118
	8	-0.0218 - 0.00454	-0.0266 - 0.0135	-0.0182 - 0.00118	-0.0206 - 0.00124	-0.0639 - 0.0639	-0.0739 - 0.0146	-0.0903 - 0.0432	-0.0615 - 0.00370	-0.0697 - 0.00451	-0.117 - 0.117
DR24	3	-0.0141 - 0.0165	-0.0250 - 0.0232	-0.00766 - 0.0126	-0.0120 - 0.0169	-0.0673 - 0.0673	-0.0542 - 0.0612	-0.0990 - 0.0862	-0.0283 - 0.0464	-0.0442 - 0.0624	-0.130 - 0.130
	5	-0.0101 - 0.0181	-0.0207 - 0.0236	-0.00422 - 0.0145	-0.00748 - 0.0177	-0.0675 - 0.0675	-0.0377 - 0.0658	-0.0770 - 0.0858	-0.0155 - 0.0537	-0.0276 - 0.0658	-0.130 - 0.130
	8	-0.0101 - 0.0173	-0.0203 - 0.0230	-0.00499 - 0.0148	-0.00921 - 0.0190	-0.0675 - 0.0675	-0.0370 - 0.0627	-0.0760 - 0.0822	-0.0183 - 0.0546	-0.0338 - 0.0702	-0.130 - 0.130
DR26	3	-0.00893 - 0.0119	-0.0154 - 0.0176	-0.00775 - 0.0115	-0.0137 - 0.0174	-0.0594 - 0.0594	-0.0264 - 0.0359	-0.0456 - 0.0537	-0.0235 - 0.0349	-0.0415 - 0.0529	-0.103 - 0.103
	5	-0.00335 - 0.00585	-0.00491 - 0.00718	-0.00300 - 0.00569	-0.00452 - 0.00721	-0.0594 - 0.0594	-0.00991 - 0.0179	-0.0145 - 0.0221	-0.00905 - 0.0172	-0.0136 - 0.0218	-0.103 - 0.103
	8	-0.00127 - 0.00532	-0.00227 - 0.00614	-0.00090 - 0.00509	-0.00170 - 0.00590	-0.0594 - 0.0594	-0.00374 - 0.0162	-0.00653 - 0.0185	-0.00269 - 0.0154	-0.00512 - 0.0179	-0.103 - 0.103
DR27	3	-0.0139 - 0.0223	-0.0258 - 0.0321	-0.0124 - 0.0224	-0.0231 - 0.0332	-0.0305 - 0.0305	-0.0230 - 0.0362	-0.0447 - 0.0521	-0.0202 - 0.0366	-0.0377 - 0.0541	-0.0391 - 0.0391
	5	-0.0187 - 0.0194	-0.0304 - 0.0290	-0.0124 - 0.0146	-0.0171 - 0.0193	-0.0303 - 0.0303	-0.0303 - 0.0309	-0.0509 - 0.0444	-0.0201 - 0.0238	-0.0278 - 0.0314	-0.0386 - 0.0386
	8	-0.0185 - 0.0179	-0.0300 - 0.0266	-0.0138 - 0.0145	-0.0199 - 0.0205	-0.0302 - 0.0302	-0.0308 - 0.0285	-0.0511 - 0.0418	-0.0225 - 0.0235	-0.0323 - 0.0334	-0.0385 - 0.0385
DR29	3	-0.0130 - 0.0138	-0.0199 - 0.0221	-0.00775 - 0.00754	-0.0104 - 0.0102	-0.0842 - 0.0842	-0.0817 - 0.0871	-0.123 - 0.140	-0.0487 - 0.0474	-0.0654 - 0.0641	-0.211 - 0.211
	5	-0.0107 - 0.00848	-0.0150 - 0.0145	-0.00791 - 0.00488	-0.00988 - 0.00685	-0.0841 - 0.0841	-0.0683 - 0.0542	-0.0970 - 0.0883	-0.0496 - 0.0307	-0.0620 - 0.0431	-0.211 - 0.211
	8	-0.0133 - 0.00776	-0.0173 - 0.0133	-0.0105 - 0.00393	-0.0123 - 0.00577	-0.0840 - 0.0840	-0.0832 - 0.0470	-0.109 - 0.0804	-0.0657 - 0.0255	-0.0779 - 0.0377	-0.210 - 0.210
DR30	3	-0.0341 - 0.00226	-0.0437 - 0.00677	-0.0284 - 0.00699	-0.0329 - 0.00243	-0.0566 - 0.0566	-0.0950 - 0.00637	-0.120 - 0.0198	-0.0793 - 0.0202	-0.0919 - 0.00762	-0.0951 - 0.0951
	5	-0.0287 - 0.0147	-0.0364 - 0.0216	-0.0275 - 0.0143	-0.0348 - 0.0216	-0.0574 - 0.0574	-0.0803 - 0.0444	-0.101 - 0.0646	-0.0782 - 0.0424	-0.0993 - 0.0635	-0.0973 - 0.0973
	8	-0.0189 - 0.0110	-0.0236 - 0.0145	-0.0171 - 0.00965	-0.0206 - 0.0132	-0.0576 - 0.0576	-0.0543 - 0.0319	-0.0684 - 0.0427	-0.0483 - 0.0285	-0.0585 - 0.0388	-0.0979 - 0.0979
DR31	3	-0.0164 - 0.00677	-0.0212 - 0.0152	-0.0137 - 0.00188	-0.0170 - 0.00520	-0.0360 - 0.0360	-0.0295 - 0.0119	-0.0387 - 0.0273	-0.0248 - 0.00343	-0.0308 - 0.00945	-0.0485 - 0.0485
	5	-0.0128 - 0.00885	-0.0172 - 0.0152	-0.0102 - 0.00490	-0.0126 - 0.00724	-0.0363 - 0.0363	-0.0235 - 0.0158	-0.0310 - 0.0274	-0.0186 - 0.00894	-0.0228 - 0.0132	-0.0490 - 0.0490
	8	-0.0136 - 0.00698	-0.0174 - 0.0135	-0.0110 - 0.00338	-0.0131 - 0.00542	-0.0362 - 0.0362	-0.0245 - 0.0128	-0.0316 - 0.0239	-0.0199 - 0.00615	-0.0237 - 0.00986	-0.0488 - 0.0488

Table B.5 (cont.).

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR32	3	-0.0192 - 0.0198	-0.0283 - 0.0337	-0.0145 - 0.0117	-0.0201 - 0.0172	-0.0563 - 0.0563	-0.0531 - 0.0562	-0.0755 - 0.0974	-0.0403 - 0.0327	-0.0559 - 0.0482	-0.0942 - 0.0942
	5	-0.0110 - 0.0143	-0.0151 - 0.0201	-0.00813 - 0.0103	-0.0107 - 0.0129	-0.0565 - 0.0565	-0.0309 - 0.0402	-0.0416 - 0.0554	-0.0228 - 0.0292	-0.0302 - 0.0366	-0.0946 - 0.0946
	8	-0.0101 - 0.0109	-0.0136 - 0.0161	-0.00754 - 0.00731	-0.00944 - 0.00921	-0.0564 - 0.0564	-0.0282 - 0.0302	-0.0373 - 0.0439	-0.0210 - 0.0208	-0.0264 - 0.0261	-0.0944 - 0.0944
DR34	3	-0.0372 - 0.0118	-0.0519 - 0.0260	-0.0353 - 0.0107	-0.0495 - 0.0249	-0.0696 - 0.0696	-0.140 - 0.0480	-0.191 - 0.110	-0.136 - 0.0399	-0.191 - 0.0943	-0.138 - 0.138
	5	-0.0211 - 0.00575	-0.0249 - 0.00979	-0.0210 - 0.00554	-0.0256 - 0.0102	-0.0699 - 0.0699	-0.0818 - 0.0240	-0.0967 - 0.0419	-0.0821 - 0.0220	-0.100 - 0.0402	-0.140 - 0.140
	8	-0.0185 - -0.00023	-0.0208 - 0.00213	-0.0182 - -0.00047	-0.0207 - 0.00205	-0.0698 - 0.0698	-0.0722 - -0.00094	-0.0808 - 0.00850	-0.0713 - -0.00169	-0.0812 - 0.00821	-0.139 - 0.139
DR35	3	-0.0130 - 0.00361	-0.0187 - 0.00776	-0.00980 - 0.00146	-0.0122 - 0.00387	-0.0185 - 0.0185	-0.0168 - 0.00470	-0.0241 - 0.00987	-0.0130 - 0.00191	-0.0161 - 0.00509	-0.0213 - 0.0213
	5	-0.00807 - 0.00242	-0.0101 - 0.00434	-0.00706 - 0.00139	-0.00837 - 0.00269	-0.0186 - 0.0186	-0.0107 - 0.00316	-0.0131 - 0.00550	-0.00937 - 0.00185	-0.0111 - 0.00358	-0.0214 - 0.0214
	8	-0.00642 - 0.00262	-0.00790 - 0.00422	-0.00565 - 0.00178	-0.00660 - 0.00273	-0.0186 - 0.0186	-0.00854 - 0.00349	-0.0104 - 0.00556	-0.00750 - 0.00238	-0.00876 - 0.00364	-0.0215 - 0.0215
DR36	3	-0.0287 - 0.0126	-0.0408 - 0.0242	-0.0222 - 0.00574	-0.0281 - 0.0117	-0.0341 - 0.0341	-0.0494 - 0.0216	-0.0684 - 0.0431	-0.0387 - 0.0100	-0.0490 - 0.0204	-0.0451 - 0.0451
	5	-0.0184 - 0.00748	-0.0256 - 0.0124	-0.0139 - 0.00415	-0.0164 - 0.00671	-0.0343 - 0.0343	-0.0327 - 0.0131	-0.0460 - 0.0206	-0.0242 - 0.00728	-0.0287 - 0.0118	-0.0455 - 0.0455
	8	-0.0182 - 0.00424	-0.0254 - 0.00815	-0.0139 - 0.00155	-0.0161 - 0.00374	-0.0342 - 0.0342	-0.0319 - 0.00722	-0.0459 - 0.0140	-0.0243 - 0.00278	-0.0282 - 0.00663	-0.0453 - 0.0453
DR37	3	-0.00400 - 0.00731	-0.00716 - 0.0109	-0.00239 - 0.00535	-0.00405 - 0.00700	-0.0242 - 0.0242	-0.00580 - 0.0106	-0.00981 - 0.0158	-0.00351 - 0.00783	-0.00592 - 0.0102	-0.0292 - 0.0292
	5	-0.00181 - 0.00396	-0.00324 - 0.00498	-0.00091 - 0.00328	-0.00150 - 0.00387	-0.0242 - 0.0242	-0.00268 - 0.00574	-0.00477 - 0.00720	-0.00133 - 0.00480	-0.00220 - 0.00567	-0.0292 - 0.0292
	8	-0.00288 - 0.00443	-0.00413 - 0.00541	-0.00224 - 0.00398	-0.00307 - 0.00482	-0.0241 - 0.0241	-0.00421 - 0.00648	-0.00602 - 0.00788	-0.00325 - 0.00583	-0.00446 - 0.00704	-0.0292 - 0.0292
DR39	3	-0.0266 - 0.0211	-0.0386 - 0.0388	-0.0270 - 0.0177	-0.0408 - 0.0315	-0.0526 - 0.0526	-0.0654 - 0.0542	-0.0906 - 0.103	-0.0690 - 0.0456	-0.104 - 0.0811	-0.0842 - 0.0842
	5	-0.0137 - 0.00719	-0.0166 - 0.0120	-0.0124 - 0.00473	-0.0150 - 0.00738	-0.0526 - 0.0526	-0.0350 - 0.0189	-0.0425 - 0.0317	-0.0316 - 0.0123	-0.0384 - 0.0191	-0.0844 - 0.0844
	8	-0.0110 - 0.00429	-0.0132 - 0.00850	-0.00958 - 0.00203	-0.0111 - 0.00352	-0.0526 - 0.0526	-0.0281 - 0.0112	-0.0336 - 0.0219	-0.0245 - 0.00531	-0.0283 - 0.00912	-0.0844 - 0.0844
DR40	3	-0.0134 - 0.00704	-0.0190 - 0.0133	-0.00947 - 0.00264	-0.0116 - 0.00475	-0.0506 - 0.0506	-0.0331 - 0.0182	-0.0462 - 0.0341	-0.0232 - 0.00644	-0.0284 - 0.0116	-0.0793 - 0.0793
	5	-0.00994 - 0.0148	-0.0146 - 0.0192	-0.00774 - 0.0126	-0.0109 - 0.0157	-0.0510 - 0.0510	-0.0242 - 0.0369	-0.0347 - 0.0470	-0.0191 - 0.0315	-0.0269 - 0.0393	-0.0803 - 0.0803
	8	-0.00574 - 0.0121	-0.00906 - 0.0150	-0.00361 - 0.0101	-0.00537 - 0.0119	-0.0511 - 0.0511	-0.0143 - 0.0298	-0.0228 - 0.0376	-0.00885 - 0.0252	-0.0132 - 0.0296	-0.0804 - 0.0804
DR41	3	-0.0155 - 0.0138	-0.0253 - 0.0207	-0.00922 - 0.00976	-0.0133 - 0.0138	-0.0407 - 0.0407	-0.0310 - 0.0274	-0.0525 - 0.0404	-0.0183 - 0.0193	-0.0264 - 0.0274	-0.0574 - 0.0574
	5	-0.0136 - 0.0110	-0.0233 - 0.0170	-0.00945 - 0.00865	-0.0133 - 0.0125	-0.0407 - 0.0407	-0.0281 - 0.0218	-0.0459 - 0.0329	-0.0188 - 0.0171	-0.0264 - 0.0248	-0.0573 - 0.0573
	8	-0.0137 - 0.0117	-0.0225 - 0.0173	-0.00910 - 0.00916	-0.0130 - 0.0131	-0.0407 - 0.0407	-0.0272 - 0.0226	-0.0455 - 0.0334	-0.0181 - 0.0182	-0.0258 - 0.0259	-0.0574 - 0.0574
DR42	3	-0.0255 - 0.0145	-0.0376 - 0.0266	-0.0245 - 0.0134	-0.0362 - 0.0251	-0.0484 - 0.0484	-0.0595 - 0.0360	-0.0837 - 0.0661	-0.0566 - 0.0308	-0.0837 - 0.0579	-0.0741 - 0.0741
	5	-0.0145 - 0.00274	-0.0182 - 0.00541	-0.0126 - 0.00132	-0.0147 - 0.00346	-0.0484 - 0.0484	-0.0338 - 0.00633	-0.0417 - 0.0122	-0.0291 - 0.00299	-0.0340 - 0.00794	-0.0740 - 0.0740
	8	-0.0128 - -0.00025	-0.0157 - 0.00156	-0.0110 - -0.00144	-0.0122 - -0.00022	-0.0484 - 0.0484	-0.0296 - -0.00064	-0.0373 - 0.00342	-0.0255 - -0.00338	-0.0283 - -0.00055	-0.0740 - 0.0740
DR43	3	-0.0163 - 0.0173	-0.0252 - 0.0275	-0.00966 - 0.00998	-0.0131 - 0.0134	-0.0330 - 0.0330	-0.0279 - 0.0287	-0.0438 - 0.0452	-0.0165 - 0.0170	-0.0224 - 0.0229	-0.0432 - 0.0432
	5	-0.0120 - 0.0158	-0.0178 - 0.0247	-0.00868 - 0.0106	-0.0117 - 0.0136	-0.0331 - 0.0331	-0.0209 - 0.0270	-0.0302 - 0.0427	-0.0148 - 0.0183	-0.0200 - 0.0234	-0.0433 - 0.0433
	8	-0.0117 - 0.0137	-0.0168 - 0.0229	-0.00902 - 0.00933	-0.0122 - 0.0125	-0.0330 - 0.0330	-0.0200 - 0.0234	-0.0288 - 0.0387	-0.0154 - 0.0160	-0.0209 - 0.0215	-0.0432 - 0.0432
DR44	3	-0.0115 - 0.00936	-0.0172 - 0.0165	-0.00877 - 0.00601	-0.0119 - 0.00916	-0.0204 - 0.0204	-0.0163 - 0.0134	-0.0245 - 0.0232	-0.0121 - 0.00825	-0.0164 - 0.0126	-0.0239 - 0.0239
	5	-0.0102 - 0.00988	-0.0156 - 0.0160	-0.00762 - 0.00703	-0.0107 - 0.0102	-0.0205 - 0.0205	-0.0137 - 0.0130	-0.0212 - 0.0214	-0.0105 - 0.00966	-0.0148 - 0.0140	-0.0240 - 0.0240
	8	-0.0109 - 0.00860	-0.0163 - 0.0143	-0.00879 - 0.00615	-0.0120 - 0.00934	-0.0204 - 0.0204	-0.0147 - 0.0116	-0.0224 - 0.0197	-0.0121 - 0.00845	-0.0165 - 0.0128	-0.0239 - 0.0239

Table B.6. Confidence limits of differences between DR means ($\overline{DR}_{x;i} - \overline{DR}_{y;i}$) defined by the MCM and S-t methods considering 95% and 98% confidence levels, and by the SC method (SC_{LL} and SC_{UL}) for ratio formats $A/(A+B)$ and A/B and duplicate injections of sample x and sample y .

DR Code	$A/(A+B)$					A/B				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR19	-0.0163 - 0.0228	-0.0252 - 0.0366	-0.0160 - 0.0197	-0.0271 - 0.0308	-0.0888 - 0.0888	-0.124 - 0.164	-0.200 - 0.258	-0.119 - 0.146	-0.201 - 0.229	-0.243 - 0.243
DR20	-0.00693 - 0.0180	-0.0142 - 0.0251	-0.00549 - 0.0166	-0.0123 - 0.0234	-0.0826 - 0.0826	-0.0396 - 0.109	-0.0780 - 0.154	-0.0329 - 0.0993	-0.0738 - 0.140	-0.202 - 0.202
DR21	-0.0187 - 0.0273	-0.0316 - 0.0414	-0.0604 - 0.0683	-0.157 - 0.165	-0.0983 - 0.0983	-0.201 - 0.322	-0.335 - 0.504	-0.688 - 0.780	-1.79 - 1.88	-0.330 - 0.330
DR22	-0.0288 - 0.0270	-0.0454 - 0.0427	-0.0751 - 0.0734	-0.187 - 0.185	-0.0901 - 0.0901	-0.219 - 0.223	-0.330 - 0.360	-0.594 - 0.582	-1.48 - 1.47	-0.253 - 0.253
DR23	-0.0309 - 0.0343	-0.0525 - 0.0519	-0.0264 - 0.0318	-0.0444 - 0.0498	-0.0637 - 0.0637	-0.105 - 0.114	-0.181 - 0.171	-0.0882 - 0.106	-0.148 - 0.166	-0.117 - 0.117
DR24	-0.0125 - 0.0192	-0.0212 - 0.0300	-0.0406 - 0.0457	-0.105 - 0.111	-0.0677 - 0.0677	-0.0456 - 0.0737	-0.0734 - 0.116	-0.153 - 0.172	-0.397 - 0.417	-0.131 - 0.131
DR26	-0.0216 - 0.0172	-0.0334 - 0.0273	-0.0185 - 0.0157	-0.0292 - 0.0263	-0.0595 - 0.0595	-0.0641 - 0.0518	-0.0996 - 0.0823	-0.0562 - 0.0478	-0.0884 - 0.0799	-0.103 - 0.103
DR27	-0.0233 - 0.0276	-0.0399 - 0.0402	-0.0664 - 0.0737	-0.172 - 0.179	-0.0304 - 0.0304	-0.0383 - 0.0447	-0.0665 - 0.0640	-0.108 - 0.120	-0.280 - 0.292	-0.0388 - 0.0388
DR29	-0.0251 - 0.0344	-0.0438 - 0.0514	-0.0773 - 0.0883	-0.202 - 0.213	-0.0837 - 0.0837	-0.163 - 0.203	-0.302 - 0.294	-0.468 - 0.535	-1.22 - 1.29	-0.208 - 0.208
DR30	-0.0619 - 0.0285	-0.0926 - 0.0513	-0.138 - 0.109	-0.323 - 0.295	-0.0572 - 0.0572	-0.163 - 0.0880	-0.231 - 0.169	-0.388 - 0.307	-0.910 - 0.829	-0.0967 - 0.0967
DR31	-0.0325 - 0.0341	-0.0516 - 0.0526	-0.0285 - 0.0303	-0.0467 - 0.0485	-0.0359 - 0.0359	-0.0586 - 0.0610	-0.0947 - 0.0940	-0.0516 - 0.0547	-0.0845 - 0.0875	-0.0482 - 0.0482
DR32	-0.0325 - 0.0396	-0.0560 - 0.0582	-0.0921 - 0.102	-0.238 - 0.248	-0.0562 - 0.0562	-0.0860 - 0.116	-0.141 - 0.177	-0.259 - 0.287	-0.670 - 0.698	-0.0938 - 0.0938
DR34	-0.0447 - 0.0247	-0.0658 - 0.0436	-0.0408 - 0.0228	-0.0605 - 0.0425	-0.0693 - 0.0693	-0.169 - 0.102	-0.244 - 0.180	-0.158 - 0.0877	-0.234 - 0.164	-0.137 - 0.137
DR35	-0.0159 - 0.0107	-0.0237 - 0.0175	-0.0141 - 0.00964	-0.0215 - 0.0170	-0.0188 - 0.0188	-0.0208 - 0.0141	-0.0307 - 0.0239	-0.0189 - 0.0129	-0.0287 - 0.0227	-0.0217 - 0.0217
DR36	-0.0388 - 0.0253	-0.0579 - 0.0429	-0.0345 - 0.0228	-0.0523 - 0.0405	-0.0340 - 0.0340	-0.0662 - 0.0446	-0.0970 - 0.0764	-0.0603 - 0.0398	-0.0912 - 0.0707	-0.0449 - 0.0449
DR37	-0.0120 - 0.00770	-0.0185 - 0.0129	-0.0289 - 0.0255	-0.0698 - 0.0663	-0.0242 - 0.0242	-0.0175 - 0.0112	-0.0275 - 0.0186	-0.0424 - 0.0373	-0.102 - 0.0973	-0.0293 - 0.0293
DR39	-0.0165 - 0.00304	-0.0210 - 0.00996	-0.0161 - 0.00108	-0.0214 - 0.00639	-0.0522 - 0.0522	-0.0419 - 0.00770	-0.0530 - 0.0257	-0.0409 - 0.00274	-0.0545 - 0.0163	-0.0833 - 0.0833
DR40	-0.0358 - 0.0310	-0.0563 - 0.0490	-0.0322 - 0.0286	-0.0510 - 0.0474	-0.0510 - 0.0510	-0.0858 - 0.0792	-0.130 - 0.129	-0.0797 - 0.0713	-0.126 - 0.118	-0.0803 - 0.0803
DR41	-0.0178 - 0.00967	-0.0252 - 0.0173	-0.0402 - 0.0321	-0.0946 - 0.0865	-0.0409 - 0.0409	-0.0354 - 0.0189	-0.0508 - 0.0332	-0.0325 - 0.0163	-0.0476 - 0.0313	-0.0577 - 0.0577
DR42	-0.0336 - 0.0226	-0.05045 - 0.0393	-0.0314 - 0.0201	-0.0473 - 0.0360	-0.0481 - 0.0481	-0.0784 - 0.0523	-0.116 - 0.0900	-0.0727 - 0.0465	-0.110 - 0.0834	-0.0732 - 0.0732
DR43	-0.0137 - 0.0283	-0.0237 - 0.0424	-0.0127 - 0.0251	-0.0244 - 0.0368	-0.0332 - 0.0332	-0.0237 - 0.0489	-0.0410 - 0.0731	-0.0218 - 0.0432	-0.0420 - 0.0633	-0.0435 - 0.0435
DR44	-0.0150 - 0.0171	-0.0220 - 0.0282	-0.0146 - 0.0138	-0.0234 - 0.0225	-0.0205 - 0.0205	-0.0209 - 0.0231	-0.0309 - 0.0390	-0.0201 - 0.0189	-0.0321 - 0.0310	-0.0240 - 0.0240

Table B.7. Amplitudes of the confidence intervals of DR_x , normalised to the 50th percentile simulated by MCM (Δ^N), defined by the MCM and S-t methods considering 95% and 98% confidence levels, and SC method for ratio formats $A/(A+B)$ and A/B and different replicate injections of sample x ($n_x = 3, 5, 8$) and single analysis of sample y .

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		$\Delta^N 95$	$\Delta^N 98$	$\Delta^N 95$	$\Delta^N 98$	$\Delta^N SC$	$\Delta^N 95$	$\Delta^N 98$	$\Delta^N 95$	$\Delta^N 98$	$\Delta^N SC$
DR19	3	0.0615	0.0993	0.0583	0.0946	0.282	0.161	0.265	0.156	0.259	0.282
	5	0.0411	0.0522	0.0411	0.0553	0.281	0.116	0.139	0.116	0.151	0.279
	8	0.0347	0.0442	0.0363	0.0458	0.283	0.0984	0.122	0.0984	0.127	0.284
DR20	3	0.0422	0.0675	0.0388	0.0625	0.280	0.103	0.165	0.0964	0.151	0.282
	5	0.0219	0.0287	0.0219	0.0303	0.281	0.0548	0.0685	0.0548	0.0685	0.281
	8	0.0373	0.0475	0.0373	0.0475	0.281	0.0973	0.111	0.0904	0.111	0.285
DR21	3	0.0866	0.139	0.0823	0.133	0.281	0.302	0.486	0.277	0.448	0.281
	5	0.0455	0.0583	0.0455	0.0597	0.282	0.152	0.194	0.152	0.203	0.283
	8	0.0314	0.0399	0.0314	0.0399	0.281	0.106	0.128	0.111	0.136	0.281
DR22	3	0.0973	0.156	0.0911	0.147	0.281	0.283	0.457	0.256	0.414	0.283
	5	0.0726	0.0942	0.0726	0.0973	0.281	0.207	0.278	0.202	0.272	0.283
	8	0.0495	0.0619	0.0495	0.0635	0.280	0.142	0.170	0.142	0.181	0.279
DR23	3	0.0507	0.0837	0.0485	0.0793	0.282	0.0963	0.156	0.0891	0.144	0.282
	5	0.0772	0.101	0.0772	0.104	0.282	0.142	0.184	0.139	0.188	0.281
	8	0.0837	0.104	0.0837	0.108	0.282	0.156	0.190	0.155	0.197	0.281
DR24	3	0.0498	0.0789	0.0457	0.0747	0.280	0.0957	0.157	0.0892	0.144	0.282
	5	0.0475	0.0619	0.0475	0.0640	0.283	0.0925	0.120	0.0925	0.124	0.280
	8	0.0476	0.0600	0.0476	0.0600	0.282	0.0931	0.115	0.0920	0.117	0.287
DR26	3	0.0823	0.134	0.0776	0.125	0.280	0.145	0.232	0.135	0.219	0.281
	5	0.0471	0.0589	0.0447	0.0612	0.283	0.0799	0.104	0.0772	0.107	0.282
	8	0.0353	0.0447	0.0376	0.0471	0.282	0.0622	0.0758	0.0622	0.0798	0.281
DR27	3	0.0634	0.104	0.0589	0.0952	0.281	0.0812	0.131	0.0742	0.120	0.283
	5	0.161	0.212	0.161	0.221	0.281	0.206	0.267	0.206	0.278	0.282
	8	0.112	0.131	0.107	0.140	0.284	0.136	0.169	0.139	0.176	0.282
DR29	3	0.0515	0.0831	0.0499	0.0815	0.281	0.133	0.212	0.119	0.199	0.285
	5	0.0333	0.0433	0.0333	0.0467	0.280	0.0800	0.107	0.0800	0.113	0.287
	8	0.0484	0.0585	0.0484	0.0618	0.282	0.121	0.148	0.121	0.154	0.282
DR30	3	0.119	0.190	0.114	0.182	0.281	0.199	0.318	0.185	0.300	0.281
	5	0.224	0.293	0.224	0.303	0.283	0.381	0.498	0.386	0.520	0.282
	8	0.141	0.173	0.143	0.182	0.280	0.241	0.295	0.242	0.308	0.282
DR31	3	0.0825	0.134	0.0747	0.130	0.283	0.108	0.176	0.105	0.170	0.281
	5	0.105	0.136	0.101	0.136	0.283	0.141	0.181	0.138	0.184	0.282
	8	0.105	0.128	0.109	0.140	0.283	0.144	0.173	0.144	0.181	0.282
DR32	3	0.147	0.237	0.137	0.224	0.282	0.246	0.400	0.231	0.375	0.282
	5	0.104	0.134	0.104	0.139	0.282	0.176	0.229	0.173	0.235	0.282
	8	0.0771	0.0945	0.0771	0.0969	0.281	0.128	0.157	0.131	0.165	0.281
DR34	3	0.169	0.275	0.161	0.261	0.283	0.335	0.542	0.320	0.510	0.282
	5	0.119	0.153	0.119	0.160	0.283	0.238	0.307	0.239	0.320	0.282
	8	0.0928	0.113	0.0928	0.117	0.282	0.185	0.224	0.179	0.234	0.279
DR35	3	0.200	0.315	0.185	0.308	0.284	0.227	0.368	0.221	0.355	0.281
	5	0.137	0.190	0.145	0.190	0.282	0.165	0.212	0.165	0.225	0.284
	8	0.0975	0.128	0.105	0.128	0.278	0.117	0.143	0.117	0.150	0.280
DR36	3	0.242	0.397	0.234	0.380	0.280	0.324	0.531	0.308	0.502	0.280
	5	0.152	0.198	0.148	0.202	0.280	0.203	0.262	0.197	0.265	0.281
	8	0.108	0.132	0.108	0.136	0.281	0.141	0.172	0.144	0.182	0.282
DR37	3	0.0980	0.161	0.0980	0.156	0.283	0.124	0.200	0.114	0.191	0.286
	5	0.0520	0.0635	0.0520	0.0693	0.277	0.0621	0.0812	0.0621	0.0812	0.282
	8	0.0755	0.0929	0.0755	0.0988	0.279	0.0914	0.115	0.0962	0.115	0.279
DR39	3	0.209	0.335	0.201	0.324	0.284	0.338	0.553	0.323	0.522	0.282
	5	0.102	0.134	0.102	0.139	0.281	0.162	0.213	0.164	0.221	0.281
	8	0.0615	0.0721	0.0615	0.0775	0.283	0.0970	0.119	0.0970	0.124	0.281

Table B.7 (cont.).

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		Δ^N95	Δ^N98	Δ^N95	Δ^N98	Δ^N95	Δ^N95	Δ^N98	Δ^N95	Δ^N98	Δ^N95
DR40	3	0.0723	0.117	0.0695	0.111	0.281	0.116	0.187	0.109	0.174	0.281
	5	0.126	0.167	0.126	0.170	0.282	0.201	0.260	0.198	0.267	0.283
	8	0.0847	0.104	0.0875	0.109	0.282	0.135	0.165	0.137	0.172	0.281
DR41	3	0.0791	0.131	0.0756	0.124	0.282	0.115	0.180	0.107	0.173	0.280
	5	0.0517	0.0689	0.0517	0.0689	0.283	0.0734	0.0929	0.0709	0.0978	0.281
	8	0.0620	0.0757	0.0620	0.0792	0.279	0.0855	0.107	0.0879	0.110	0.281
DR42	3	0.195	0.318	0.187	0.303	0.283	0.301	0.490	0.281	0.458	0.281
	5	0.0904	0.117	0.0904	0.122	0.283	0.140	0.182	0.136	0.186	0.281
	8	0.0641	0.0816	0.0641	0.0816	0.283	0.101	0.121	0.0995	0.124	0.281
DR43	3	0.153	0.242	0.144	0.229	0.280	0.198	0.317	0.185	0.301	0.282
	5	0.139	0.177	0.135	0.182	0.279	0.177	0.232	0.181	0.242	0.284
	8	0.0844	0.105	0.0844	0.110	0.283	0.109	0.135	0.113	0.145	0.280
DR44	3	0.0964	0.165	0.0964	0.152	0.282	0.118	0.188	0.112	0.177	0.277
	5	0.0752	0.103	0.0752	0.103	0.280	0.0876	0.117	0.0876	0.117	0.280
	8	0.0960	0.123	0.103	0.130	0.281	0.117	0.147	0.117	0.147	0.281

Table B.8. Amplitudes of the confidence intervals of differences between DR means $(\overline{DR}_{x;i} - \overline{DR}_{y;i})$ (Δ), defined by the MCM and S-t methods considering 95% and 98% confidence levels, and SC method for ratio formats $A/(A+B)$ and A/B and different replicate injections of sample x ($n_x = 3, 5, 8$) and duplicate injections of sample y .

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		Δ_{95}	Δ_{98}	Δ_{95}	Δ_{98}	Δ_{SC}	Δ_{95}	Δ_{98}	Δ_{95}	Δ_{98}	Δ_{SC}
DR19	3	0.148	0.374	0.0190	0.0271	0.178	1.06	2.58	0.143	0.204	0.488
	5	0.229	0.563	0.0148	0.0200	0.178	1.93	4.98	0.111	0.150	0.488
	8	0.288	0.721	0.0144	0.0205	0.178	2.12	5.27	0.108	0.154	0.486
DR20	3	0.121	0.305	0.0984	0.247	0.165	0.711	1.73	0.577	1.44	0.402
	5	0.209	0.509	0.0941	0.235	0.165	1.28	3.14	0.550	1.38	0.402
	8	0.391	1.000	0.0958	0.241	0.165	2.25	5.66	0.561	1.40	0.400
DR21	3	0.341	0.853	0.0282	0.0402	0.197	3.87	9.72	0.320	0.456	0.662
	5	0.414	1.05	0.0183	0.0247	0.197	4.87	12.2	0.207	0.279	0.660
	8	0.490	1.25	0.0172	0.0246	0.196	5.29	13.3	0.194	0.277	0.658
DR22	3	0.251	0.633	0.0296	0.0422	0.182	2.11	5.23	0.237	0.338	0.516
	5	0.393	0.983	0.0229	0.0301	0.182	3.43	8.86	0.185	0.242	0.516
	8	0.588	1.46	0.0220	0.0313	0.181	4.41	11.2	0.178	0.252	0.514
DR23	3	0.163	0.422	0.108	0.270	0.128	0.594	1.48	0.370	0.927	0.236
	5	0.353	0.855	0.0416	0.0674	0.128	1.27	3.25	0.142	0.231	0.236
	8	0.592	1.48	0.0395	0.0640	0.128	2.23	5.69	0.135	0.219	0.236
DR24	3	0.171	0.437	0.121	0.303	0.134	0.620	1.53	0.446	1.12	0.258
	5	0.335	0.839	0.124	0.311	0.135	1.28	3.14	0.458	1.15	0.260
	8	0.402	1.02	0.119	0.297	0.135	1.55	3.87	0.437	1.10	0.260
DR26	3	0.172	0.445	0.0195	0.0316	0.119	0.500	1.23	0.0591	0.0957	0.206
	5	0.262	0.660	0.0083	0.0108	0.119	0.835	2.08	0.0250	0.0327	0.206
	8	0.289	0.737	0.0055	0.0069	0.119	0.937	2.32	0.0167	0.0210	0.206
DR27	3	0.141	0.353	0.113	0.284	0.0616	0.231	0.565	0.186	0.465	0.0788
	5	0.271	0.680	0.0449	0.0726	0.0610	0.464	1.15	0.0732	0.119	0.0780
	8	0.359	0.897	0.122	0.305	0.0608	0.548	1.38	0.199	0.498	0.0776
DR29	3	0.150	0.373	0.0168	0.0240	0.169	1.01	2.47	0.106	0.151	0.424
	5	0.283	0.710	0.0150	0.0214	0.168	1.82	4.47	0.0947	0.135	0.422
	8	0.571	1.48	0.0142	0.0186	0.168	3.48	8.64	0.0878	0.115	0.422
DR30	3	0.230	0.580	0.0246	0.0350	0.113	0.620	1.51	0.0687	0.0985	0.190
	5	0.628	1.55	0.0400	0.0523	0.115	1.94	4.71	0.115	0.151	0.195
	8	0.784	2.01	0.0252	0.0318	0.115	2.27	5.84	0.0723	0.0917	0.196
DR31	3	0.125	0.300	0.0259	0.0419	0.0718	0.221	0.539	0.139	0.348	0.0968
	5	0.360	0.905	0.0295	0.0477	0.0724	0.658	1.69	0.0536	0.0868	0.0976
	8	0.562	1.44	0.0289	0.0468	0.0724	1.07	2.63	0.0524	0.0849	0.0974
DR32	3	0.235	0.577	0.0284	0.0404	0.113	0.671	1.67	0.0792	0.113	0.189
	5	0.571	1.43	0.0230	0.0310	0.113	1.68	4.18	0.0649	0.0875	0.190
	8	0.735	1.87	0.0216	0.0309	0.113	2.08	5.18	0.0608	0.0868	0.189
DR34	3	0.374	0.961	0.0457	0.0741	0.139	1.47	3.61	0.175	0.283	0.276
	5	0.536	1.36	0.0263	0.0355	0.140	2.28	5.54	0.103	0.140	0.280
	8	0.657	1.64	0.0155	0.0196	0.140	2.73	6.95	0.0607	0.0769	0.280
DR35	3	0.0255	0.0519	0.0142	0.0229	0.0370	0.0336	0.0680	0.0187	0.0302	0.0428
	5	0.143	0.365	0.0084	0.0113	0.0372	0.189	0.465	0.0111	0.0150	0.0430
	8	0.283	0.703	0.0060	0.0077	0.0374	0.398	1.01	0.0080	0.0102	0.0432
DR36	3	0.284	0.702	0.0313	0.0446	0.0684	0.465	1.14	0.0547	0.0781	0.0904
	5	0.478	1.20	0.0273	0.0390	0.0688	0.853	2.11	0.0480	0.0684	0.0912
	8	0.517	1.31	0.0320	0.0517	0.0688	0.939	2.41	0.0564	0.0913	0.0910
DR37	3	0.0311	0.0752	0.0083	0.0119	0.0484	0.0474	0.112	0.0122	0.0174	0.0586
	5	0.110	0.273	0.0055	0.0074	0.0484	0.165	0.388	0.0080	0.0108	0.0584
	8	0.274	0.682	0.0060	0.0076	0.0482	0.421	1.05	0.0088	0.0111	0.0584
DR39	3	0.192	0.455	0.0346	0.0494	0.105	0.500	1.20	0.0887	0.127	0.168
	5	0.414	1.03	0.0190	0.0248	0.105	1.08	2.65	0.0487	0.0639	0.169
	8	0.639	1.65	0.0181	0.0259	0.105	1.68	4.17	0.0466	0.0664	0.169

Table B.8 (cont.).

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		$\Delta 95$	$\Delta 98$	$\Delta 95$	$\Delta 98$	ΔSC	$\Delta 95$	$\Delta 98$	$\Delta 95$	$\Delta 98$	ΔSC
DR40	3	0.0902	0.227	0.0120	0.0172	0.101	0.235	0.570	0.0295	0.0421	0.159
	5	0.631	1.55	0.0211	0.0285	0.102	1.54	3.84	0.0526	0.0710	0.161
	8	0.633	1.62	0.0118	0.0148	0.102	1.56	3.88	0.0293	0.0367	0.161
DR41	3	0.148	0.378	0.0915	0.230	0.0812	0.282	0.684	0.181	0.454	0.114
	5	0.218	0.543	0.0886	0.222	0.0810	0.435	1.09	0.175	0.439	0.114
	8	0.318	0.821	0.0884	0.221	0.0812	0.668	1.71	0.175	0.438	0.114
DR42	3	0.329	0.808	0.0295	0.0421	0.0968	0.752	1.83	0.0681	0.0972	0.148
	5	0.405	1.02	0.0157	0.0206	0.0968	0.919	2.27	0.0394	0.0531	0.148
	8	0.452	1.15	0.0157	0.0224	0.0968	1.04	2.65	0.0366	0.0522	0.148
DR43	3	0.126	0.312	0.0368	0.0596	0.0658	0.212	0.520	0.0628	0.102	0.0860
	5	0.270	0.672	0.0384	0.0622	0.0658	0.495	1.23	0.0657	0.106	0.0862
	8	0.355	0.902	0.102	0.255	0.0658	0.609	1.55	0.174	0.436	0.0860
DR44	3	0.0629	0.160	0.0078	0.0111	0.0406	0.0804	0.197	0.0107	0.0152	0.0474
	5	0.177	0.446	0.0066	0.0089	0.0408	0.253	0.608	0.0090	0.0122	0.0476
	8	0.326	0.841	0.0070	0.0092	0.0406	0.419	1.07	0.0096	0.0125	0.0476

Table B.9. Amplitudes of the confidence intervals of differences between DR means ($\overline{DR}_{x;i} - \overline{DR}_{y;i}$) (Δ), defined by the MCM and S-t methods considering 95% and 98% confidence levels, and SC method for ratio formats $A/(A+B)$ and A/B and different replicate injections of sample x ($n_x = 3, 5, 8$) and triplicate injections of sample y .

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		Δ_{95}	Δ_{98}	Δ_{95}	Δ_{98}	Δ_{SC}	Δ_{95}	Δ_{98}	Δ_{95}	Δ_{98}	Δ_{SC}
DR19	3	0.0245	0.0390	0.0169	0.0242	0.178	0.185	0.285	0.127	0.181	0.488
	5	0.0148	0.0204	0.0119	0.0155	0.178	0.111	0.152	0.0880	0.115	0.486
	8	0.0117	0.0163	0.0086	0.0108	0.178	0.0869	0.121	0.0641	0.0805	0.486
DR20	3	0.0244	0.0380	0.0143	0.0192	0.165	0.147	0.229	0.0840	0.113	0.402
	5	0.0198	0.0314	0.0147	0.0209	0.165	0.116	0.181	0.0862	0.123	0.402
	8	0.0192	0.0301	0.0151	0.0216	0.165	0.112	0.178	0.0774	0.104	0.402
DR21	3	0.0382	0.0593	0.0352	0.0568	0.197	0.437	0.696	0.401	0.648	0.662
	5	0.0185	0.0254	0.0145	0.0190	0.196	0.208	0.286	0.166	0.216	0.660
	8	0.0142	0.0200	0.0106	0.0133	0.196	0.159	0.228	0.120	0.150	0.658
DR22	3	0.0513	0.0815	0.0290	0.0390	0.181	0.411	0.650	0.230	0.311	0.512
	5	0.0374	0.0558	0.0247	0.0317	0.181	0.306	0.443	0.198	0.254	0.514
	8	0.0334	0.0518	0.0220	0.0288	0.181	0.265	0.407	0.176	0.231	0.512
DR23	3	0.0282	0.0449	0.0185	0.0263	0.128	0.0974	0.156	0.0631	0.0901	0.236
	5	0.0282	0.0430	0.0182	0.0234	0.128	0.0954	0.143	0.0619	0.0795	0.236
	8	0.0263	0.0401	0.0170	0.0218	0.128	0.0885	0.134	0.0578	0.0742	0.234
DR24	3	0.0306	0.0482	0.0203	0.0289	0.135	0.115	0.185	0.0747	0.107	0.260
	5	0.0282	0.0443	0.0187	0.0252	0.135	0.104	0.163	0.0692	0.0934	0.260
	8	0.0274	0.0433	0.0198	0.0282	0.135	0.0997	0.158	0.0729	0.104	0.260
DR26	3	0.0208	0.0330	0.0193	0.0311	0.119	0.0623	0.0993	0.0584	0.0944	0.206
	5	0.0092	0.0121	0.0087	0.0117	0.119	0.0278	0.0366	0.0263	0.0354	0.206
	8	0.0066	0.0084	0.0060	0.0076	0.119	0.0199	0.0250	0.0181	0.0230	0.206
DR27	3	0.0362	0.0579	0.0348	0.0563	0.0610	0.0592	0.0968	0.0568	0.0918	0.0782
	5	0.0381	0.0594	0.0270	0.0364	0.0606	0.0612	0.0953	0.0439	0.0592	0.0772
	8	0.0364	0.0566	0.0283	0.0404	0.0604	0.0593	0.0929	0.0460	0.0657	0.0770
DR29	3	0.0268	0.0420	0.0153	0.0206	0.168	0.169	0.263	0.0961	0.130	0.422
	5	0.0192	0.0295	0.0128	0.0167	0.168	0.123	0.185	0.0803	0.105	0.422
	8	0.0211	0.0306	0.0144	0.0181	0.168	0.130	0.189	0.0912	0.116	0.420
DR30	3	0.0318	0.0505	0.0214	0.0305	0.113	0.0886	0.140	0.0591	0.0843	0.190
	5	0.0434	0.0580	0.0418	0.0564	0.115	0.125	0.166	0.121	0.163	0.195
	8	0.0299	0.0381	0.0268	0.0338	0.115	0.0862	0.111	0.0768	0.0973	0.196
DR31	3	0.0232	0.0364	0.0156	0.0222	0.0720	0.0414	0.0660	0.0282	0.0403	0.0970
	5	0.0217	0.0324	0.0151	0.0198	0.0726	0.0393	0.0584	0.0275	0.0360	0.0980
	8	0.0206	0.0309	0.0144	0.0185	0.0724	0.0373	0.0555	0.0261	0.0336	0.0976
DR32	3	0.0390	0.0620	0.0262	0.0373	0.113	0.109	0.173	0.0730	0.104	0.188
	5	0.0253	0.0352	0.0184	0.0236	0.113	0.0711	0.0970	0.0520	0.0668	0.189
	8	0.0210	0.0297	0.0149	0.0187	0.113	0.0584	0.0812	0.0418	0.0525	0.189
DR34	3	0.0490	0.0779	0.0460	0.0744	0.139	0.188	0.301	0.176	0.285	0.276
	5	0.0269	0.0347	0.0265	0.0358	0.140	0.106	0.139	0.104	0.140	0.280
	8	0.0183	0.0229	0.0177	0.0228	0.140	0.0713	0.0893	0.0696	0.0894	0.278
DR35	3	0.0166	0.0265	0.0113	0.0161	0.0370	0.0215	0.0340	0.0149	0.0212	0.0426
	5	0.0105	0.0144	0.0085	0.0111	0.0372	0.0139	0.0186	0.0112	0.0147	0.0428
	8	0.0090	0.0121	0.0074	0.0093	0.0372	0.0120	0.0160	0.0099	0.0124	0.0430
DR36	3	0.0413	0.0650	0.0279	0.0398	0.0682	0.0710	0.112	0.0487	0.0694	0.0902
	5	0.0259	0.0380	0.0181	0.0231	0.0686	0.0458	0.0666	0.0315	0.0405	0.0910
	8	0.0224	0.0336	0.0155	0.0198	0.0684	0.0391	0.0599	0.0271	0.0348	0.0906
DR37	3	0.0113	0.0181	0.0077	0.0111	0.0484	0.0164	0.0256	0.0113	0.0161	0.0584
	5	0.0058	0.0082	0.0042	0.0054	0.0484	0.0084	0.0120	0.0061	0.0079	0.0584
	8	0.0073	0.0095	0.0062	0.0079	0.0482	0.0107	0.0139	0.0091	0.0115	0.0584
DR39	3	0.0477	0.0774	0.0447	0.0723	0.105	0.120	0.194	0.115	0.185	0.168
	5	0.0209	0.0286	0.0171	0.0224	0.105	0.0539	0.0742	0.0439	0.0575	0.169
	8	0.0153	0.0217	0.0116	0.0146	0.105	0.0393	0.0555	0.0298	0.0374	0.169

Table B.9 (cont.).

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		$\Delta 95$	$\Delta 98$	$\Delta 95$	$\Delta 98$	ΔSC	$\Delta 95$	$\Delta 98$	$\Delta 95$	$\Delta 98$	ΔSC
DR40	3	0.0204	0.0323	0.0121	0.0164	0.101	0.0513	0.0803	0.0296	0.0400	0.159
	5	0.0247	0.0338	0.0203	0.0266	0.102	0.0611	0.0817	0.0506	0.0662	0.161
	8	0.0178	0.0241	0.0137	0.0173	0.102	0.0441	0.0604	0.0341	0.0428	0.161
DR41	3	0.0293	0.0460	0.0190	0.0271	0.0814	0.0584	0.0929	0.0376	0.0538	0.115
	5	0.0246	0.0403	0.0181	0.0258	0.0814	0.0499	0.0788	0.0359	0.0512	0.115
	8	0.0254	0.0398	0.0183	0.0261	0.0814	0.0498	0.0789	0.0363	0.0517	0.115
DR42	3	0.0400	0.0642	0.0379	0.0613	0.0968	0.0955	0.150	0.0874	0.142	0.148
	5	0.0172	0.0236	0.0139	0.0182	0.0968	0.0401	0.0539	0.0321	0.0419	0.148
	8	0.0126	0.0173	0.0096	0.0120	0.0968	0.0290	0.0407	0.0221	0.0278	0.148
DR43	3	0.0336	0.0527	0.0196	0.0265	0.0660	0.0566	0.0890	0.0335	0.0453	0.0864
	5	0.0278	0.0425	0.0193	0.0253	0.0662	0.0479	0.0729	0.0331	0.0434	0.0866
	8	0.0254	0.0397	0.0184	0.0247	0.0660	0.0434	0.0675	0.0314	0.0424	0.0864
DR44	3	0.0209	0.0337	0.0148	0.0211	0.0408	0.0297	0.0477	0.0204	0.0290	0.0478
	5	0.0201	0.0316	0.0147	0.0209	0.0410	0.0267	0.0426	0.0202	0.0288	0.0480
	8	0.0195	0.0306	0.0149	0.0213	0.0408	0.0263	0.0421	0.0206	0.0293	0.0478

Table B.10. Amplitudes of the confidence intervals of differences between DR means ($\overline{DR}_{x,i} - \overline{DR}_{y,i}$) (Δ), defined by the MCM and S-t methods considering 95% and 98% confidence levels, and SC method for ratio formats $A/(A+B)$ and A/B and duplicate injections of sample x and sample y .

DR Code	$A/(A+B)$					A/B				
	MCM		S-t		SC	MCM		S-t		SC
	Δ_{95}	Δ_{98}	Δ_{95}	Δ_{98}	Δ_{SC}	Δ_{95}	Δ_{98}	Δ_{95}	Δ_{98}	Δ_{SC}
DR19	0.0391	0.0618	0.0357	0.0579	0.178	0.288	0.458	0.265	0.430	0.486
DR20	0.0249	0.0393	0.0221	0.0357	0.165	0.149	0.232	0.132	0.214	0.404
DR21	0.0460	0.0730	0.129	0.322	0.197	0.523	0.839	1.47	3.67	0.660
DR22	0.0558	0.0881	0.149	0.372	0.180	0.442	0.690	1.18	2.95	0.506
DR23	0.0652	0.104	0.0582	0.0942	0.127	0.219	0.352	0.194	0.314	0.234
DR24	0.0317	0.0512	0.0863	0.216	0.135	0.119	0.189	0.325	0.814	0.262
DR26	0.0388	0.0607	0.0342	0.0555	0.119	0.116	0.182	0.104	0.168	0.206
DR27	0.0509	0.0800	0.140	0.351	0.0608	0.0830	0.131	0.228	0.572	0.0776
DR29	0.0595	0.0952	0.166	0.415	0.167	0.366	0.596	1.00	2.51	0.416
DR30	0.0904	0.144	0.247	0.618	0.114	0.251	0.400	0.695	1.74	0.193
DR31	0.0666	0.104	0.0588	0.0952	0.0718	0.120	0.189	0.106	0.172	0.0964
DR32	0.0721	0.114	0.194	0.486	0.112	0.202	0.318	0.546	1.37	0.188
DR34	0.0694	0.109	0.0636	0.103	0.139	0.271	0.424	0.246	0.398	0.274
DR35	0.0266	0.0412	0.0237	0.0385	0.0376	0.0349	0.0546	0.0318	0.0514	0.0434
DR36	0.0641	0.101	0.0573	0.0928	0.0680	0.111	0.173	0.100	0.162	0.0898
DR37	0.0197	0.0314	0.0544	0.136	0.0484	0.0287	0.0461	0.0797	0.199	0.0586
DR39	0.0195	0.0310	0.0172	0.0278	0.104	0.0496	0.0787	0.0436	0.0708	0.167
DR40	0.0668	0.105	0.0608	0.0984	0.102	0.165	0.259	0.151	0.244	0.161
DR41	0.0275	0.0425	0.0723	0.181	0.0818	0.0543	0.0840	0.0488	0.0789	0.115
DR42	0.0562	0.0897	0.0515	0.0833	0.0962	0.131	0.206	0.119	0.193	0.146
DR43	0.0420	0.0661	0.0378	0.0612	0.0664	0.0726	0.114	0.0650	0.105	0.0870
DR44	0.0321	0.0502	0.0284	0.0459	0.0410	0.0440	0.0699	0.0390	0.0631	0.0480

Table B.11. True acceptance probability of *DR* equivalence (γ) assessed by the MCM and S-t methods considering 95% and 98% confidence levels, and by the SC method for ratio formats $A/(A+B)$ and A/B , and different replicate injections of sample x ($n_x = 3, 5, 8$) and single analysis of sample y .

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{sc}	γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{sc}
DR19	3	94.9	98.0	94.5	97.9	99.7	95.0	97.9	94.7	97.8	98.0
	5	95.2	98.1	95.2	98.4	100	95.0	97.9	95.1	98.2	99.8
	8	95.3	98.3	95.6	98.6	100	94.8	97.8	95.1	98.3	100
DR20	3	95.2	98.1	94.5	97.8	99.8	94.9	98.0	94.1	97.6	99.3
	5	95.2	98.1	94.7	98.1	100	95.0	98.0	94.6	98.0	100
	8	95.1	98.1	95.0	98.4	100	94.9	97.9	94.8	98.2	100
DR21	3	95.3	98.1	94.7	98.0	99.5	94.9	98.0	94.3	97.7	94.4
	5	95.2	98.1	95.1	98.3	100	95.1	98.2	95.1	98.4	99.6
	8	95.1	98.0	95.2	98.4	100	94.9	98.0	95.5	98.5	100
DR22	3	95.3	98.1	94.7	97.9	99.3	95.0	97.9	94.2	97.5	95.1
	5	95.2	98.0	94.8	98.2	100	95.2	98.1	94.8	98.1	98.3
	8	95.1	98.0	95.2	98.3	100	94.9	97.9	95.1	98.3	100
DR23	3	95.4	98.1	94.6	97.8	99.8	94.9	98.0	94.1	97.6	99.3
	5	95.1	98.0	94.7	98.1	100	95.1	98.2	94.8	98.3	99.6
	8	95.2	98.2	95.1	98.5	100	95.0	97.9	95.0	98.2	99.8
DR24	3	95.4	98.1	94.9	97.9	99.8	94.9	97.9	94.3	97.7	99.3
	5	95.1	98.3	94.8	98.4	100	94.9	98.0	94.8	98.1	99.9
	8	95.2	98.1	94.9	98.4	100	94.9	97.9	94.5	98.1	100
DR26	3	95.3	98.1	94.6	97.8	99.5	94.9	98.0	94.2	97.8	98.5
	5	95.1	97.9	94.8	98.0	100	95.1	98.0	94.8	98.1	100
	8	95.2	98.0	95.4	98.4	100	95.2	98.1	95.4	98.5	100
DR27	3	95.4	98.1	94.8	97.8	99.7	94.9	98.0	94.2	97.7	99.4
	5	95.2	98.0	95.2	98.3	99.3	94.9	97.9	94.8	98.2	98.2
	8	94.9	97.8	95.1	98.3	100	95.2	98.0	95.4	98.4	99.9
DR29	3	95.0	98.0	94.5	97.8	99.7	94.8	97.9	94.3	97.7	98.8
	5	95.1	98.2	95.1	98.5	100	95.1	98.2	95.1	98.4	99.9
	8	95.0	98.0	95.6	98.5	100	94.9	98.0	95.1	98.5	100
DR30	3	95.4	98.1	94.8	98.0	99.0	95.0	97.9	94.4	97.7	97.4
	5	95.1	98.1	95.2	98.3	97.7	95.1	97.8	95.3	98.1	89.0
	8	95.0	98.1	95.4	98.5	99.9	95.1	97.9	95.1	98.3	97.5
DR31	3	95.1	98.1	94.8	98.0	99.5	94.9	97.9	94.7	97.8	99.1
	5	95.1	98.1	94.9	98.2	99.9	95.1	98.0	94.9	98.1	99.6
	8	94.9	98.0	95.2	98.5	100	95.5	98.1	95.7	98.5	99.9
DR32	3	94.9	98.0	94.5	97.8	98.6	95.0	97.9	94.4	97.6	96.1
	5	94.9	97.7	94.7	97.9	99.9	95.0	97.9	94.7	98.1	99.1
	8	95.0	98.1	95.0	98.4	100	95.2	98.0	95.4	98.4	100
DR34	3	95.4	98.1	94.9	97.9	98.1	94.9	97.9	94.3	97.7	92.9
	5	95.2	98.1	95.4	98.4	99.8	95.0	97.9	95.2	98.3	97.3
	8	94.9	97.9	95.2	98.3	100	95.1	98.0	95.2	98.3	99.5
DR35	3	95.1	98.1	94.7	97.9	97.5	95.1	97.9	94.6	97.8	96.6
	5	95.1	98.0	95.1	98.3	99.6	95.1	98.0	95.3	98.3	99.2
	8	95.1	98.0	95.6	98.6	100	95.1	98.1	95.6	98.7	100
DR36	3	95.1	98.1	94.7	97.9	96.4	94.9	97.9	94.7	97.7	93.6
	5	95.2	98.1	94.8	98.2	99.6	95.1	98.1	94.7	98.3	98.6
	8	94.9	98.0	95.0	98.4	100	95.2	98.0	95.2	98.3	99.9
DR37	3	95.1	98.1	94.7	97.9	99.4	95.0	97.9	94.6	97.7	98.9
	5	95.1	98.1	95.2	98.4	100	95.1	98.0	95.2	98.3	100
	8	94.9	98.1	95.3	98.5	100	95.2	98.0	95.4	98.5	100
DR39	3	95.2	98.1	94.8	98.0	97.4	95.0	97.9	94.7	97.7	93.3
	5	95.1	98.2	95.1	98.3	99.9	95.1	98.1	95.1	98.3	99.3
	8	94.9	97.9	95.0	98.3	100	95.1	98.0	95.0	98.3	100

Table B.11 (cont.).

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{SC}	γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{SC}
DR40	3	94.8	98.0	94.3	97.8	99.6	94.9	97.9	94.4	97.7	99.0
	5	95.2	98.1	95.0	98.3	99.8	95.0	97.9	94.8	98.1	98.4
	8	95.1	98.2	95.4	98.6	100	94.9	98.0	95.1	98.3	99.9
DR41	3	95.4	98.1	94.8	97.9	99.5	95.0	97.9	94.4	97.7	99.1
	5	95.0	97.8	94.8	98.0	100	94.7	97.8	94.6	98.0	100
	8	95.2	98.0	95.1	98.4	100	94.8	98.0	95.0	98.4	100
DR42	3	94.9	98.0	94.4	97.8	97.5	94.9	97.9	94.3	97.6	94.2
	5	95.1	98.0	94.8	98.1	99.9	95.0	97.9	94.7	98.0	99.6
	8	95.1	97.9	95.1	98.3	100	95.2	98.1	95.1	98.4	100
DR43	3	95.1	98.1	94.7	97.9	98.4	95.0	97.9	94.7	97.7	97.3
	5	95.0	98.0	94.9	98.2	99.6	95.1	98.1	95.2	98.3	98.9
	8	95.1	98.1	95.6	98.5	100	95.0	97.9	95.5	98.5	100
DR44	3	94.8	98.0	94.2	97.8	99.3	94.9	97.9	94.4	97.7	99.0
	5	95.1	98.1	94.6	98.2	100	95.0	98.0	94.5	98.1	99.9
	8	94.9	98.0	94.8	98.4	100	95.2	98.0	95.1	98.3	100
Min.	3	94.8	98.0	94.2	97.8	96.4	94.8	97.9	94.1	97.5	92.9
Max.		95.4	98.1	94.9	98.0	99.8	95.1	98.0	94.7	97.8	99.4
Min.	5	94.9	97.7	94.6	97.9	97.7	94.7	97.8	94.5	98.0	89.0
Max.		95.2	98.3	95.4	98.5	100	95.2	98.2	95.3	98.4	100
Min.	8	94.9	97.8	94.8	98.3	99.9	94.8	97.8	94.5	98.1	97.5
Max.		95.3	98.3	95.6	98.6	100	95.5	98.1	95.7	98.7	100

Table B.12. True acceptance probability of *DR* equivalence (γ) assessed by the MCM and S-t methods considering 95% and 98% confidence levels, and by the SC method for ratio formats $A/(A+B)$ and A/B , and different replicate injections of sample x ($n_x = 3, 5, 8$) and duplicate injections of sample y .

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{sc}	γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{sc}
DR19	3	95.0	98.2	58.5	70.1	95.9	94.7	97.8	60.3	71.2	88.0
	5	94.5	97.6	38.1	47.1	92.8	95.7	98.3	40.5	49.9	82.3
	8	95.5	98.3	36.7	47.6	92.7	95.3	97.9	36.9	48.1	78.7
DR20	3	94.6	98.0	93.0	97.4	96.1	94.4	97.6	93.2	97.2	89.3
	5	94.9	97.8	88.6	95.5	93.5	94.8	98.1	88.6	95.3	83.5
	8	95.5	98.1	81.6	92.7	89.2	95.1	98.1	80.2	92.0	72.2
DR21	3	95.3	98.2	48.1	60.0	91.6	95.0	97.9	46.9	58.8	69.9
	5	95.2	98.0	31.6	40.2	90.2	95.0	98.0	29.5	37.6	64.7
	8	95.2	98.1	25.7	35.1	87.6	95.0	98.1	26.7	35.2	62.2
DR22	3	94.6	97.9	53.2	65.1	92.1	94.5	97.9	53.5	65.2	76.5
	5	94.4	97.8	34.5	42.3	87.6	95.8	98.4	39.6	47.9	71.4
	8	95.4	98.3	28.2	37.7	84.3	94.7	97.7	27.5	37.3	59.0
DR23	3	94.6	98.0	91.5	96.9	92.8	94.5	97.8	91.0	96.6	85.0
	5	95.1	98.0	61.0	73.9	85.7	94.7	97.8	56.3	71.1	70.3
	8	95.3	98.3	44.8	59.8	78.4	95.3	98.2	40.8	56.6	57.1
DR24	3	94.6	98.1	92.2	97.1	92.9	94.6	97.6	92.2	96.8	86.1
	5	95.0	98.0	86.3	94.6	87.4	95.6	98.2	87.7	95.3	77.8
	8	95.0	97.8	83.8	93.5	85.6	95.4	98.1	83.5	93.4	71.6
DR26	3	95.8	98.5	62.5	76.3	93.8	95.6	98.3	62.5	76.0	88.8
	5	95.3	98.1	23.3	29.8	89.5	96.2	98.4	24.9	31.6	83.9
	8	95.0	98.0	14.1	17.6	88.0	94.9	98.0	14.2	17.8	77.7
DR27	3	94.6	97.8	93.2	97.3	87.0	94.3	97.8	92.9	97.2	83.4
	5	95.1	98.0	71.2	81.6	78.5	95.0	98.1	69.1	80.4	70.7
	8	95.7	98.3	87.3	94.9	74.7	95.4	98.2	86.7	94.9	68.1
DR29	3	94.5	97.8	52.8	64.6	95.2	94.8	97.9	52.6	64.3	86.7
	5	94.9	98.0	35.1	45.7	91.1	95.2	98.2	35.5	46.0	78.4
	8	95.4	98.2	19.9	25.2	83.8	94.6	97.7	17.6	22.9	59.6
DR30	3	95.5	98.3	57.9	68.8	89.7	95.2	98.2	60.3	70.8	79.3
	5	95.6	98.3	41.5	51.0	74.8	94.9	97.9	36.9	45.3	54.0
	8	95.2	98.1	23.0	28.4	67.2	95.6	98.2	27.7	34.0	57.7
DR31	3	96.1	98.4	80.1	88.0	92.7	95.4	98.2	92.7	97.1	89.1
	5	95.3	98.2	49.1	64.3	75.7	94.4	98.0	45.4	60.9	64.1
	8	95.3	98.2	36.7	51.9	65.3	95.5	98.1	38.9	54.9	59.4
DR32	3	94.7	97.8	53.7	65.8	88.0	94.5	97.9	55.1	66.3	79.2
	5	94.7	98.0	27.3	35.2	73.7	96.0	98.5	35.7	45.0	68.9
	8	95.2	98.0	20.8	29.1	68.5	94.2	97.7	19.2	26.7	49.1
DR34	3	96.0	98.6	65.5	78.4	88.3	95.4	98.3	62.2	76.0	72.1
	5	95.3	98.1	34.5	43.2	81.7	95.0	97.9	29.5	38.0	59.7
	8	94.9	97.8	17.0	21.1	75.5	95.0	97.9	16.9	20.9	56.3
DR35	3	95.7	98.4	89.7	94.8	97.0	95.6	98.2	89.6	95.0	96.3
	5	95.2	97.9	37.4	47.7	80.6	94.7	97.9	37.7	47.2	76.7
	8	95.2	98.1	17.2	21.5	66.2	95.7	98.2	16.8	21.0	61.8
DR36	3	95.4	98.2	56.0	67.2	76.6	95.1	98.0	58.0	68.9	70.1
	5	94.7	98.0	37.0	48.1	66.1	95.6	98.1	39.8	51.3	60.1
	8	95.5	98.1	44.2	59.7	67.8	95.1	98.2	39.8	55.3	54.7
DR37	3	94.9	98.1	74.6	83.0	97.0	94.7	97.9	74.7	82.7	95.7
	5	94.8	97.9	32.7	41.3	87.8	95.2	98.0	33.7	42.7	86.0
	8	94.9	98.0	15.9	19.5	71.6	95.3	98.3	17.7	22.1	69.3
DR39	3	95.7	98.3	70.9	79.9	91.2	95.2	98.2	68.5	78.6	84.1
	5	96.0	98.4	38.3	46.9	83.9	96.2	98.5	39.9	48.5	75.8
	8	95.1	98.1	21.7	30.3	71.5	95.1	98.1	21.0	28.9	57.9

Table B.12 (cont.).

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{sc}	γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{sc}
DR40	3	95.0	98.0	58.7	70.2	95.5	94.8	98.0	57.8	69.3	91.9
	5	94.9	98.0	22.9	30.1	69.4	94.5	97.8	21.2	28.3	53.5
	8	95.2	98.1	13.4	16.9	69.0	95.5	98.2	16.1	20.0	60.5
DR41	3	94.8	98.2	91.3	96.8	90.1	94.7	97.8	91.5	96.8	86.2
	5	95.1	98.1	88.7	95.1	87.6	95.3	98.0	87.9	95.3	81.4
	8	95.3	98.2	82.3	92.8	80.8	95.1	98.1	81.6	92.8	72.2
DR42	3	95.0	98.0	46.2	58.2	80.3	94.6	97.9	47.2	59.1	71.1
	5	94.6	97.9	25.6	32.6	77.5	94.3	97.6	26.5	34.4	65.6
	8	94.8	97.8	26.3	35.6	76.8	95.2	98.2	26.5	36.2	67.0
DR43	3	96.2	98.7	85.0	91.5	92.4	95.5	98.2	83.9	90.3	88.7
	5	95.3	98.1	68.4	80.4	81.1	95.3	98.1	64.2	77.2	71.7
	8	95.2	97.9	82.8	93.3	73.2	95.5	98.3	84.0	93.3	69.1
DR44	3	95.5	98.2	60.3	71.5	92.5	94.9	98.1	63.5	73.7	91.5
	5	94.6	97.9	25.0	32.3	76.4	95.3	98.1	26.7	34.8	75.4
	8	95.3	98.1	16.4	21.5	64.1	94.7	98.0	16.1	20.6	58.3
Min. Max.	3	94.5	97.8	46.2	58.2	76.6	94.3	97.6	46.9	58.8	69.9
		96.2	98.7	93.2	97.4	97.0	95.6	98.3	93.2	97.2	96.3
Min. Max.	5	94.4	97.6	22.9	29.8	66.1	94.3	97.6	21.2	28.3	53.5
		96.0	98.4	88.7	95.5	93.5	96.2	98.5	88.6	95.3	86.0
Min. Max.	8	94.8	97.8	13.4	16.9	64.1	94.2	97.7	14.2	17.8	49.1
		95.7	98.3	87.3	94.9	92.7	95.7	98.3	86.7	94.9	78.7

Table B.13. True acceptance probability of *DR* equivalence (γ) assessed by the MCM and S-t methods considering 95% and 98% confidence levels, and by the SC method for ratio formats $A/(A+B)$ and A/B , and different replicate injections of sample x ($n_x = 3, 5, 8$) and triplicate injections of sample y .

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{sc}	γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{sc}
DR19	3	95.2	98.2	90.1	95.0	99.9	95.8	98.1	91.0	95.5	99.4
	5	95.5	98.1	91.5	96.0	100	95.2	97.9	91.3	95.6	99.9
	8	94.9	98.1	88.3	93.4	100	94.9	98.1	88.7	93.3	99.9
DR20	3	95.4	98.1	87.1	92.7	99.9	95.1	97.9	85.4	91.5	99.3
	5	95.5	98.3	92.1	96.0	99.9	95.5	98.1	91.8	96.2	99.6
	8	95.0	98.2	92.2	96.1	99.9	95.3	98.0	92.9	96.2	99.6
DR21	3	95.3	98.0	94.6	97.9	99.7	95.3	98.1	94.5	97.8	97.8
	5	95.3	98.0	90.8	95.5	100	95.2	98.1	90.8	95.8	99.8
	8	95.3	98.2	88.5	93.5	100	95.1	98.1	88.4	93.4	99.7
DR22	3	95.0	97.9	84.6	91.2	99.6	95.0	98.1	85.0	91.5	96.8
	5	94.4	97.9	85.8	91.9	99.7	95.0	98.0	85.9	92.1	98.6
	8	95.1	98.3	89.5	94.4	99.7	94.7	98.0	89.1	94.1	98.7
DR23	3	94.8	97.9	88.3	94.1	99.7	94.9	98.0	89.0	94.2	99.1
	5	95.4	98.1	87.5	93.0	99.7	95.7	98.2	87.1	93.0	99.3
	8	95.1	98.0	87.5	92.8	99.8	95.5	98.0	88.5	94.0	99.3
DR24	3	94.8	97.9	88.6	94.4	99.7	95.2	97.9	89.1	94.4	98.9
	5	95.1	98.2	89.1	93.9	99.8	95.4	98.1	89.8	94.4	99.3
	8	95.0	98.1	90.9	95.6	99.8	95.3	98.1	91.9	95.8	99.3
DR26	3	95.4	98.0	94.6	97.7	99.8	95.3	98.0	94.6	97.8	99.5
	5	95.0	98.2	94.0	98.0	100	94.7	97.9	93.7	97.7	100
	8	95.1	97.8	92.7	96.4	100	94.7	97.9	91.9	96.3	99.9
DR27	3	94.6	97.9	94.2	97.9	98.0	95.8	98.6	95.4	98.4	97.5
	5	94.9	97.9	89.3	94.4	98.0	95.2	98.2	89.9	94.8	97.1
	8	95.4	98.3	91.7	96.1	98.4	95.1	98.1	91.5	95.9	97.1
DR29	3	94.7	97.9	84.9	91.2	99.8	95.0	97.9	85.8	91.9	99.2
	5	94.8	97.9	87.2	92.9	99.9	95.2	98.0	86.8	92.8	99.6
	8	95.2	98.2	87.1	92.5	99.9	95.0	98.0	87.1	92.8	99.5
DR30	3	94.9	98.0	88.9	94.4	99.4	95.2	98.1	89.2	94.7	97.3
	5	95.2	98.2	94.4	98.0	99.8	95.3	98.2	94.5	98.1	98.7
	8	95.1	97.9	92.3	96.2	99.8	94.7	98.0	91.7	96.1	99.6
DR31	3	95.2	97.9	89.1	94.8	99.5	95.4	98.3	90.1	95.2	99.3
	5	94.8	98.0	88.1	93.6	99.6	95.0	98.2	88.3	94.0	99.4
	8	95.4	98.2	87.8	93.5	99.7	94.8	98.0	87.8	92.8	99.4
DR32	3	95.1	98.0	89.3	94.5	99.4	95.6	98.2	90.5	95.2	98.5
	5	95.1	98.0	89.2	94.3	99.8	95.3	98.0	89.1	94.4	99.6
	8	95.3	98.1	87.2	92.9	99.8	95.2	98.0	86.9	92.6	99.6
DR34	3	95.1	98.0	94.4	97.8	99.3	95.2	98.0	94.4	97.8	96.6
	5	94.8	97.8	94.7	97.9	100	95.2	98.1	94.9	98.1	99.7
	8	95.3	98.2	93.6	97.5	100	95.1	98.3	93.7	97.5	99.8
DR35	3	95.1	98.1	89.6	94.8	98.8	94.9	98.0	89.2	94.7	98.5
	5	95.3	98.2	91.2	96.0	99.7	95.0	98.0	90.9	95.8	99.8
	8	95.5	98.4	90.2	95.2	99.9	95.2	98.1	90.2	94.7	99.8
DR36	3	94.9	97.9	88.7	94.4	97.8	95.0	98.2	89.5	94.7	95.8
	5	95.0	98.1	87.4	93.3	99.3	95.1	98.1	87.4	93.0	98.9
	8	95.3	98.2	88.3	93.5	99.5	94.8	98.1	87.5	92.9	98.8
DR37	3	94.9	98.0	89.0	94.6	99.6	94.9	98.1	89.4	94.7	99.6
	5	95.1	98.0	88.9	94.2	99.9	95.2	98.1	88.0	94.1	99.9
	8	95.4	98.3	90.2	95.4	99.9	94.7	97.8	89.5	94.5	99.9
DR39	3	95.0	98.2	94.5	97.9	98.9	94.9	98.0	94.5	98.0	97.5
	5	94.7	97.6	91.6	95.8	99.8	95.3	98.2	91.3	96.0	99.7
	8	95.0	98.0	88.7	93.4	99.8	95.1	98.0	87.9	93.1	99.7

Table B.13 (cont.).

DR Code	n_x	$A/(A+B)$					A/B				
		MCM		S-t		SC	MCM		S-t		SC
		γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{SC}	γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{SC}
DR40	3	94.6	97.7	84.9	91.5	99.8	95.3	98.2	86.2	92.4	99.5
	5	95.2	98.1	91.3	96.1	99.8	95.3	98.2	91.4	96.4	99.7
	8	95.1	98.1	89.4	94.0	99.9	95.0	98.0	88.9	94.1	99.7
DR41	3	94.9	97.8	87.8	94.0	99.3	95.2	97.9	89.5	94.5	98.6
	5	94.7	97.9	90.7	95.3	99.4	95.3	97.9	90.8	95.7	99.0
	8	95.1	98.1	90.6	95.4	99.6	95.1	98.0	90.6	95.5	98.9
DR42	3	95.0	97.9	94.6	97.7	99.0	95.6	98.0	94.8	97.8	97.9
	5	95.8	98.1	91.8	96.3	99.8	95.1	98.0	91.0	95.7	99.7
	8	95.3	98.2	89.5	94.3	99.8	95.1	98.0	88.5	93.8	99.7
DR43	3	94.9	97.9	85.4	91.7	98.7	95.3	98.3	86.4	92.4	98.2
	5	94.8	97.9	88.1	93.6	99.1	95.1	98.2	87.9	93.5	98.7
	8	95.2	98.2	89.9	94.6	99.4	94.7	98.1	88.9	94.5	98.7
DR44	3	94.5	97.9	89.5	94.6	98.5	94.9	98.1	89.3	94.7	98.1
	5	95.6	98.1	92.2	96.1	98.7	95.2	98.2	91.9	95.9	98.7
	8	95.3	98.3	92.3	96.1	99.0	95.2	98.2	92.0	96.0	98.6
Min.	3	94.5	97.7	84.6	91.2	97.8	94.9	97.9	85.0	91.5	95.8
Max.		95.4	98.2	94.6	97.9	99.9	95.8	98.6	95.4	98.4	99.6
Min.	5	94.4	97.6	85.8	91.9	98.0	94.7	97.9	85.9	92.1	97.1
Max.		95.8	98.3	94.7	98.0	100	95.7	98.2	94.9	98.1	100
Min.	8	94.9	97.8	87.1	92.5	98.4	94.7	97.8	86.9	92.6	97.1
Max.		95.5	98.4	93.6	97.5	100	95.5	98.3	93.7	97.5	99.9

Table B.14. True acceptance probability of *DR* equivalence (γ) assessed by the MCM and S-t methods considering 95% and 98% confidence levels, and by the SC method for ratio formats $A/(A+B)$ and A/B , and duplicate injections of sample x and sample y .

<i>DR</i> Code	$A/(A+B)$					A/B				
	MCM		S-t		SC	MCM		S-t		SC
	γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{sc}	γ_{95}	γ_{98}	γ_{95}	γ_{98}	γ_{sc}
<i>DR19</i>	94.8	98.0	94.0	97.7	99.7	95.2	98.1	94.3	97.9	98.2
<i>DR20</i>	95.3	98.1	93.9	97.7	99.9	95.0	98.1	93.5	97.8	99.3
<i>DR21</i>	95.3	98.2	99.3	99.9	99.7	95.1	98.1	99.4	99.9	96.6
<i>DR22</i>	94.9	98.0	99.3	99.9	99.5	95.1	98.1	99.4	99.8	96.4
<i>DR23</i>	95.0	98.0	93.9	97.5	98.6	95.2	98.2	94.0	97.8	95.8
<i>DR24</i>	95.0	98.1	99.2	99.9	99.7	95.2	98.0	99.4	99.9	98.9
<i>DR26</i>	95.0	98.1	93.7	97.7	99.5	95.1	98.2	93.9	97.8	98.5
<i>DR27</i>	95.1	98.0	99.3	99.9	96.4	95.2	98.2	99.4	99.8	94.3
<i>DR29</i>	94.9	97.9	99.3	99.8	99.4	95.0	98.1	99.2	99.9	96.0
<i>DR30</i>	95.0	98.0	99.1	99.9	96.3	95.1	98.0	99.3	99.9	86.2
<i>DR31</i>	95.0	97.9	93.7	97.4	95.6	95.1	98.1	93.9	97.7	92.5
<i>DR32</i>	94.8	97.8	99.2	99.9	97.8	95.0	97.9	99.3	99.8	93.8
<i>DR34</i>	95.0	98.1	94.1	97.9	98.7	95.1	98.1	94.2	97.8	94.6
<i>DR35</i>	95.1	97.9	93.8	97.7	97.4	95.2	98.0	94.2	97.7	96.6
<i>DR36</i>	95.1	98.0	94.0	97.6	95.3	94.8	97.9	93.7	97.6	91.0
<i>DR37</i>	95.2	98.0	99.3	99.9	99.2	95.1	98.1	99.3	99.8	98.7
<i>DR39</i>	94.8	97.9	93.4	97.4	99.7	95.1	98.3	93.7	97.8	99.6
<i>DR40</i>	95.2	98.0	94.1	97.8	97.9	95.2	98.0	94.3	97.7	94.9
<i>DR41</i>	95.2	97.8	99.3	99.8	99.4	94.9	98.1	93.7	97.8	98.8
<i>DR42</i>	95.2	98.1	94.1	97.8	98.2	95.1	98.0	94.3	97.7	95.8
<i>DR43</i>	94.9	97.9	93.6	97.6	97.6	95.0	98.3	93.6	98.0	95.6
<i>DR44</i>	94.7	97.8	93.3	97.4	96.8	95.0	98.2	93.6	97.8	95.8
Min.	94.7	97.8	93.3	97.4	95.3	94.8	97.9	93.5	97.6	86.2
Max.	95.3	98.2	99.3	99.9	99.9	95.2	98.3	99.4	99.9	99.6

Table B.15. Confidence intervals of *DR* means difference obtained from the first comparison of the Round Robin Test spill (Sp) and suspected source samples 1 and 2 (SS1 and SS2, respectively) by the MCM, S-t and SC methods.

DR Code	Sp vs. SS1					Sp vs. SS2				
	MCM		S-t		SC	MCM		S-t		SC
	<i>P2.5 - P97.5</i>	<i>P1 - P99</i>	<i>P2.5 - P97.5</i>	<i>P1 - P99</i>	<i>SC_{LL} - SC_{UL}</i>	<i>P2.5 - P97.5</i>	<i>P1 - P99</i>	<i>P2.5 - P97.5</i>	<i>P1 - P99</i>	<i>SC_{LL} - SC_{UL}</i>
DR01	-0.189 - 0.0723	-0.274 - 0.139	-0.405 - 0.300	-0.935 - 0.830	-0.294 - 0.189	-0.117 - 0.0715	-0.174 - 0.117	-0.102 - 0.0646	-0.154 - 0.116	-0.258 - 0.220
DR02	-0.249 - 0.242	-0.397 - 0.360	-0.214 - 0.217	-0.347 - 0.350	-0.336 - 0.339	-0.0970 - 0.259	-0.201 - 0.357	-0.396 - 0.564	-1.12 - 1.29	-0.248 - 0.416
DR03	-0.0165 - 0.360	-0.140 - 0.455	0.0053 - 0.351	-0.102 - 0.458	-0.0287 - 0.385	-0.0250 - 0.273	-0.111 - 0.364	-0.302 - 0.550	-0.943 - 1.19	-0.0870 - 0.334
DR04	0.0278 - 0.0607	0.0180 - 0.0702	-0.0018 - 0.0906	-0.0713 - 0.160	-0.0699 - 0.159	0.0295 - 0.185	-0.0154 - 0.232	-0.108 - 0.319	-0.430 - 0.641	-0.0044 - 0.216
DR06	-0.0155 - 0.0141	-0.0233 - 0.0226	-0.0139 - 0.0124	-0.0220 - 0.0205	-0.0184 - 0.0170	-0.0162 - 0.0089	-0.0232 - 0.0161	-0.0149 - 0.0074	-0.0218 - 0.0144	-0.0216 - 0.0142
DR07	-0.0978 - 0.0140	-0.130 - 0.0433	-0.0908 - 0.0080	-0.121 - 0.0386	-0.179 - 0.0961	-0.0140 - 0.0783	-0.0442 - 0.102	-0.0071 - 0.0751	-0.0325 - 0.101	-0.0982 - 0.166
DR08	-0.201 - 0.104	-0.291 - 0.184	-0.447 - 0.357	-1.05 - 0.961	-0.284 - 0.194	-0.312 - 0.156	-0.448 - 0.275	-0.281 - 0.134	-0.410 - 0.263	-0.315 - 0.168
DR09	-5.09 - 2.11	-7.37 - 3.99	-10.9 - 8.11	-25.2 - 22.4	-3.46 - 0.647	-10.2 - -4.74	-11.8 - -3.34	-9.79 - -4.92	-11.3 - -3.41	-9.83 - -4.88
DR10	-0.0424 - 0.0174	-0.0575 - 0.0349	-0.0396 - 0.0130	-0.0558 - 0.0292	-0.0378 - 0.0112	-0.0897 - -0.0229	-0.107 - -0.0011	-0.0878 - -0.0274	-0.106 - -0.0087	-0.0852 - -0.0300
DR11	-0.109 - 0.116	-0.185 - 0.176	-0.310 - 0.328	-0.789 - 0.807	-0.155 - 0.172	0.172 - 0.306	0.133 - 0.340	0.180 - 0.301	0.143 - 0.338	0.0934 - 0.388
DR12	-0.0016 - 0.327	-0.0934 - 0.413	-0.263 - 0.593	-0.907 - 1.24	-0.0012 - 0.331	-0.0224 - 0.352	-0.122 - 0.453	0.0014 - 0.326	-0.0990 - 0.427	-0.0022 - 0.330
DR13	-0.0170 - 0.168	-0.0686 - 0.222	-0.0091 - 0.159	-0.0610 - 0.211	-0.198 - 0.347	-0.106 - 0.168	-0.201 - 0.235	-0.338 - 0.418	-0.907 - 0.986	-0.235 - 0.315
DR14	-0.106 - 0.0395	-0.142 - 0.0814	-0.0987 - 0.0283	-0.138 - 0.0676	-0.175 - 0.104	-0.194 - 0.0277	-0.251 - 0.0950	-0.184 - 0.0107	-0.244 - 0.0708	-0.230 - 0.0566
DR15	-0.377 - 0.248	-0.574 - 0.411	-0.335 - 0.218	-0.506 - 0.389	-0.325 - 0.208	-0.108 - 0.557	-0.335 - 0.729	-0.0667 - 0.544	-0.256 - 0.733	-0.0067 - 0.484
DR16	-0.0201 - 0.0362	-0.0386 - 0.0500	-0.0662 - 0.0851	-0.180 - 0.199	-0.0404 - 0.0593	-0.144 - -0.0643	-0.168 - -0.0436	-0.139 - -0.0672	-0.161 - -0.0451	-0.161 - -0.0452
DR17	-3.35 - 0.677	-4.74 - 1.60	-3.01 - 0.566	-4.12 - 1.67	-4.07 - 1.62	0.361 - 4.18	-0.944 - 5.18	0.649 - 4.11	-0.422 - 5.18	-0.211 - 4.97
DR19	-0.513 - 0.145	-0.742 - 0.316	-1.07 - 0.741	-2.43 - 2.10	-0.436 - 0.109	-1.05 - -0.830	-1.11 - -0.766	-1.04 - -0.842	-1.10 - -0.781	-1.27 - -0.613
DR20	-0.369 - 0.245	-0.527 - 0.451	-0.351 - 0.186	-0.517 - 0.351	-0.528 - 0.363	1.05 - 1.40	0.967 - 1.54	1.05 - 1.37	0.955 - 1.47	0.857 - 1.57
DR21	-0.674 - -0.115	-0.833 - 0.0612	-1.15 - 0.354	-2.29 - 1.49	-0.813 - 0.0138	-1.09 - -0.601	-1.23 - -0.469	-1.05 - -0.627	-1.18 - -0.495	-1.28 - -0.395
DR45	-0.430 - 0.176	-0.612 - 0.352	-0.402 - 0.151	-0.573 - 0.323	-0.833 - 0.583	-1.30 - -0.602	-1.50 - -0.386	-1.27 - -0.635	-1.47 - -0.438	-1.72 - -0.187
DR46	-0.101 - 0.0716	-0.153 - 0.117	-0.0895 - 0.0631	-0.137 - 0.110	-0.254 - 0.228	0.120 - 0.235	0.0874 - 0.266	0.128 - 0.230	0.0969 - 0.261	-0.0485 - 0.407
DR47	-0.0404 - 0.0345	-0.0609 - 0.0559	-0.103 - 0.0952	-0.251 - 0.244	-0.0626 - 0.0552	-0.0085 - 0.0361	-0.0209 - 0.0493	-0.0060 - 0.0337	-0.0183 - 0.0460	-0.0438 - 0.0715
DR48	-0.0567 - 0.0204	-0.0777 - 0.0435	-0.0533 - 0.0164	-0.0748 - 0.0379	-0.120 - 0.0828	-0.0612 - 0.0679	-0.107 - 0.0972	-0.166 - 0.184	-0.430 - 0.448	-0.0904 - 0.108
DR49	-0.181 - 0.126	-0.319 - 0.197	-0.426 - 0.408	-1.05 - 1.03	-0.117 - 0.0983	-0.0848 - -0.0377	-0.0966 - -0.0193	-0.131 - 0.0043	-0.232 - 0.106	-0.174 - 0.0482
DR51	-0.0046 - 0.0478	-0.0197 - 0.0605	-0.0006 - 0.0450	-0.0148 - 0.0592	-0.0435 - 0.0879	0.0465 - 0.115	0.0286 - 0.133	0.0503 - 0.111	0.0316 - 0.129	0.0188 - 0.142
DR52	-0.0400 - 0.0456	-0.0574 - 0.0749	-0.112 - 0.111	-0.280 - 0.278	-0.0682 - 0.0663	0.0955 - 0.178	0.0781 - 0.208	0.0233 - 0.244	-0.143 - 0.410	0.0758 - 0.191
DR53	-0.0687 - 0.0016	-0.0878 - 0.0238	-0.0667 - -0.0034	-0.0862 - 0.0162	-0.0999 - 0.0299	0.0043 - 0.0747	-0.0139 - 0.0967	0.0068 - 0.0700	-0.0128 - 0.0895	-0.0213 - 0.0981
DR54	-0.354 - 0.129	-0.481 - 0.276	-0.325 - 0.0864	-0.453 - 0.214	-0.471 - 0.232	0.0787 - 0.659	-0.0739 - 0.842	0.0990 - 0.610	-0.0589 - 0.768	0.0358 - 0.673
DR56	-0.186 - 0.274	-0.340 - 0.393	-0.158 - 0.269	-0.291 - 0.401	-0.264 - 0.375	0.517 - 0.773	0.435 - 0.844	0.292 - 1.00	-0.243 - 1.54	0.369 - 0.926
DR57	-0.0515 - 0.116	-0.0904 - 0.177	-0.0479 - 0.0983	-0.0931 - 0.144	-0.0901 - 0.141	0.0112 - 0.161	-0.0224 - 0.216	0.0140 - 0.146	-0.0267 - 0.186	-0.0317 - 0.191
DR61	-0.129 - 0.108	-0.208 - 0.173	-0.325 - 0.311	-0.804 - 0.789	-0.122 - 0.107	-0.143 - 0.0807	-0.203 - 0.149	-0.337 - 0.269	-0.792 - 0.724	-0.151 - 0.0824
DR62	-0.0396 - 0.0664	-0.0626 - 0.105	-0.132 - 0.150	-0.344 - 0.362	-0.0568 - 0.0746	0.0690 - 0.162	0.0481 - 0.198	-0.0185 - 0.240	-0.213 - 0.434	0.0520 - 0.169

Blue background – Confidence interval that does not include the zero (non-equivalent *DR*).

Table B.16. Confidence intervals of *DR* means difference obtained from the second comparison of the Round Robin Test spill (Sp) and suspected source samples 1 and 2 (SS1 and SS2, respectively) by the MCM, S-t and SC methods.

DR Code	Sp vs. SS1					Sp vs. SS2				
	MCM		S-t		SC	MCM		S-t		SC
	<i>P2.5 - P97.5</i>	<i>P1 - P99</i>	<i>P2.5 - P97.5</i>	<i>P1 - P99</i>	<i>SC_{LL} - SC_{UL}</i>	<i>P2.5 - P97.5</i>	<i>P1 - P99</i>	<i>P2.5 - P97.5</i>	<i>P1 - P99</i>	<i>SC_{LL} - SC_{UL}</i>
DR01	-0.316 - 0.141	-0.437 - 0.298	-0.305 - 0.104	-0.431 - 0.231	-0.338 - 0.138	-0.252 - 0.146	-0.347 - 0.291	-0.615 - 0.483	-1.44 - 1.31	-0.302 - 0.170
DR02	-0.258 - 0.163	-0.392 - 0.271	-0.219 - 0.144	-0.331 - 0.256	-0.372 - 0.297	-0.0922 - 0.169	-0.173 - 0.231	-0.0686 - 0.159	-0.139 - 0.230	-0.284 - 0.374
DR03	-0.0725 - 0.430	-0.227 - 0.566	-0.487 - 0.870	-1.51 - 1.89	-0.0163 - 0.399	-0.0831 - 0.344	-0.209 - 0.466	-0.480 - 0.754	-1.41 - 1.68	-0.0746 - 0.348
DR04	-0.0186 - 0.0854	-0.0437 - 0.128	-0.117 - 0.175	-0.337 - 0.395	-0.0841 - 0.142	-0.0005 - 0.191	-0.0459 - 0.251	0.0040 - 0.177	-0.0494 - 0.230	-0.0186 - 0.199
DR06	-0.0149 - 0.0145	-0.0226 - 0.0242	-0.0139 - 0.0120	-0.0219 - 0.0200	-0.0186 - 0.0167	-0.0153 - 0.0090	-0.0211 - 0.0177	-0.0149 - 0.0070	-0.0217 - 0.0138	-0.0218 - 0.0139
DR07	-0.142 - 0.117	-0.231 - 0.192	-0.359 - 0.339	-0.884 - 0.864	-0.149 - 0.130	-0.0629 - 0.185	-0.138 - 0.250	-0.274 - 0.405	-0.784 - 0.916	-0.0687 - 0.200
DR08	-0.217 - 0.138	-0.332 - 0.233	-0.511 - 0.443	-1.23 - 1.16	-0.274 - 0.206	-0.323 - 0.184	-0.475 - 0.307	-0.288 - 0.163	-0.427 - 0.302	-0.304 - 0.180
DR09	-5.10 - 1.85	-7.45 - 3.61	-10.6 - 7.70	-24.4 - 21.5	-3.51 - 0.596	-10.2 - -5.10	-12.0 - -4.00	-9.68 - -5.13	-11.1 - -3.72	-9.87 - -4.94
DR10	-0.0329 - 0.0132	-0.0449 - 0.0280	-0.0306 - 0.0096	-0.0431 - 0.0220	-0.0352 - 0.0142	-0.0807 - -0.0268	-0.0947 - -0.0085	-0.0798 - -0.0298	-0.0953 - -0.0143	-0.0826 - -0.0270
DR11	-0.110 - 0.0919	-0.189 - 0.149	-0.298 - 0.293	-0.742 - 0.737	-0.165 - 0.160	0.180 - 0.274	0.149 - 0.300	0.0972 - 0.361	-0.101 - 0.559	0.0827 - 0.375
DR12	0.0331 - 0.335	-0.0559 - 0.415	0.0532 - 0.322	-0.0299 - 0.405	0.0200 - 0.355	0.0113 - 0.358	-0.0870 - 0.448	0.0336 - 0.339	-0.0610 - 0.434	0.0189 - 0.354
DR13	-0.0317 - 0.188	-0.103 - 0.244	-0.0130 - 0.179	-0.0724 - 0.238	-0.190 - 0.356	-0.111 - 0.181	-0.214 - 0.248	-0.354 - 0.450	-0.959 - 1.06	-0.228 - 0.323
DR14	-0.118 - 0.0102	-0.152 - 0.0499	-0.111 - 0.0014	-0.146 - 0.0362	-0.193 - 0.0834	-0.207 - -0.0002	-0.260 - 0.0590	-0.199 - -0.0135	-0.256 - 0.0437	-0.248 - 0.0357
DR15	-0.380 - 0.196	-0.574 - 0.343	-0.832 - 0.676	-1.97 - 1.81	-0.343 - 0.187	-0.107 - 0.510	-0.338 - 0.667	-0.627 - 1.07	-1.90 - 2.34	-0.0250 - 0.463
DR16	-0.0204 - 0.0249	-0.0355 - 0.0354	-0.0161 - 0.0234	-0.0284 - 0.0357	-0.0458 - 0.0531	-0.145 - -0.0746	-0.166 - -0.0565	-0.141 - -0.0769	-0.160 - -0.0572	-0.166 - -0.0515
DR17	-3.42 - 0.657	-4.81 - 1.57	-2.96 - 0.579	-4.05 - 1.67	-4.03 - 1.66	0.445 - 4.15	-0.800 - 5.01	0.709 - 4.12	-0.346 - 5.18	-0.177 - 5.01
DR19	-0.533 - 0.167	-0.798 - 0.338	-1.09 - 0.770	-2.49 - 2.17	-0.432 - 0.113	-1.07 - -0.797	-1.15 - -0.715	-1.06 - -0.814	-1.13 - -0.738	-1.26 - -0.609
DR20	-0.312 - 0.206	-0.461 - 0.369	-0.756 - 0.636	-1.80 - 1.68	-0.507 - 0.387	1.13 - 1.34	1.08 - 1.40	0.957 - 1.51	0.538 - 1.93	0.879 - 1.59
DR21	-0.631 - -0.101	-0.806 - 0.0502	-1.07 - 0.349	-2.14 - 1.42	-0.778 - 0.0542	-1.03 - -0.595	-1.17 - -0.486	-1.38 - -0.227	-2.24 - 0.639	-1.25 - -0.355
DR45	-0.442 - 0.169	-0.660 - 0.329	-0.393 - 0.152	-0.562 - 0.321	-0.829 - 0.588	-1.30 - -0.622	-1.52 - -0.439	-1.26 - -0.634	-1.46 - -0.439	-1.72 - -0.182
DR46	-0.150 - 0.0911	-0.211 - 0.178	-0.144 - 0.0686	-0.210 - 0.134	-0.277 - 0.202	0.0674 - 0.260	0.0229 - 0.326	-0.111 - 0.420	-0.509 - 0.819	-0.0713 - 0.381
DR47	-0.0428 - 0.0431	-0.0643 - 0.0705	-0.0386 - 0.0354	-0.0614 - 0.0583	-0.0607 - 0.0575	-0.0121 - 0.0459	-0.0273 - 0.0636	-0.0093 - 0.0413	-0.0250 - 0.0569	-0.0419 - 0.0738
DR48	-0.112 - 0.0771	-0.152 - 0.155	-0.268 - 0.211	-0.628 - 0.571	-0.129 - 0.0719	-0.106 - 0.112	-0.163 - 0.181	-0.0955 - 0.0930	-0.154 - 0.151	-0.0999 - 0.0974
DR49	-0.188 - 0.155	-0.334 - 0.236	-0.444 - 0.447	-1.11 - 1.12	-0.107 - 0.110	-0.117 - 0.0097	-0.156 - 0.0463	-0.223 - 0.119	-0.481 - 0.376	-0.164 - 0.0598
DR51	-0.0235 - 0.0614	-0.0512 - 0.0815	-0.0872 - 0.131	-0.251 - 0.295	-0.0437 - 0.0877	0.0302 - 0.126	0.0012 - 0.150	0.0383 - 0.122	0.0124 - 0.148	0.0186 - 0.142
DR52	-0.0139 - 0.0463	-0.0354 - 0.0603	-0.0083 - 0.0447	-0.0248 - 0.0612	-0.0504 - 0.0868	0.121 - 0.179	0.101 - 0.192	0.127 - 0.179	0.111 - 0.195	0.0936 - 0.212
DR53	-0.0690 - -0.0008	-0.0894 - 0.0186	-0.0665 - -0.0044	-0.0857 - 0.0147	-0.100 - 0.0294	0.0038 - 0.0716	-0.0154 - 0.0905	0.0070 - 0.0689	-0.0122 - 0.0880	-0.0218 - 0.0976
DR54	-0.460 - 0.140	-0.634 - 0.327	-0.973 - 0.633	-2.18 - 1.84	-0.518 - 0.178	-0.0209 - 0.665	-0.192 - 0.866	-0.0068 - 0.615	-0.199 - 0.807	-0.0109 - 0.619
DR56	-0.323 - 0.276	-0.496 - 0.481	-0.310 - 0.240	-0.480 - 0.410	-0.349 - 0.278	0.362 - 0.795	0.261 - 0.967	-0.0649 - 1.18	-1.00 - 2.11	0.285 - 0.829
DR57	-0.0274 - 0.0903	-0.0631 - 0.130	-0.0224 - 0.0847	-0.0555 - 0.118	-0.0847 - 0.147	0.0377 - 0.134	0.0112 - 0.163	0.0427 - 0.129	0.0160 - 0.155	-0.0263 - 0.198
DR61	-0.139 - 0.121	-0.219 - 0.207	-0.126 - 0.101	-0.196 - 0.171	-0.127 - 0.102	-0.151 - 0.0911	-0.214 - 0.173	-0.147 - 0.0692	-0.214 - 0.136	-0.155 - 0.0771
DR62	-0.0208 - 0.0558	-0.0390 - 0.0844	-0.0201 - 0.0492	-0.0415 - 0.0706	-0.0515 - 0.0807	0.0887 - 0.150	0.0752 - 0.173	0.0310 - 0.202	-0.0974 - 0.330	0.0573 - 0.175

Blue background – Confidence interval that does not include the zero (non-equivalent *DR*).

B.3. Spreadsheets used to simulate diagnostic ratios and estimate the probability of true acceptance of compositional equivalence between samples

Available to download using this [weblink](#) 

File: Single&Multi_DR_Flex_Modelling_EN15522.xlsm

Annex C

Supplementary material of Chapter 4

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C.1. Instrumental analysis

Table C.1. Compound classes analysed and fragments (m/z) used for peak identification and quantification.

Compound or compound class	m/z
<i>n</i> -Alkanes	85; 169
Branched alkanes	169; 225
Isoprenoids	85; 113
Alkylcycloalkanes	83
Decalins	138; 152; 166; 180
Biphenyl	154
Alkylbenzenes	92
Alkyltoluenes (<i>meta</i> and <i>ortho</i>) and Phytanyl-toluene	106
C2-Benzothiophenes	162
Tetrahydronaphthalenes	104
C0- to C4-Naphthalenes	128; 142; 156; 170; 184
Acenaphthylene	152
C1- and C2-Fluorenes	180; 194
C1- to C4-Phenanthrenes/Anthracenes	192; 206; 220; 234
C1- to C3-Dibenzothiophenes	198; 212; 226
C1- and C2-Fluoranthenes/Pyrenes	216; 230
C1-Chrysenes	242
Octahydrophenanthrene/Anthracene	186
1-Methyl-7-isopropylphenanthrene (Retene)	219
Benzo(b)naphtho(1,2-d)thiophene	234
Tetramethylphenanthrene	234
Benzo(e)pyrene and Benzo(a)pyrene	252
Tricyclic terpanes	191; 290
Hopanes	191
Diasteranes and Steranes	217; 218
Triaromatic steranes	231
Bicyclic sesquiterpanes	123; 179; 193
Adamantanes	135; 149; 163; 177
Diamantanes	187; 188
Fatty acid methyl esters	74

C.2. List of compounds and labels

Table C.2. List of analysed compounds and their labels according to EN 15522-2 standard.

ID number	Compounds/ Set of compounds	Label
1	1-Methyladamantane	1-M-Adam
2	1,2-Dimethyladamantane	1,2-DM-Adam
3	2,6-Dimethylundecane	i-C13
4	2-Methyl-1,2,3,4-tetrahydronaphthalene	2-M-tetralin
5	<i>cis</i> -1,3,4-Trimethyladamantane	c-1,3,4-TM-Adam
6	Hexylbenzene	C6-Benz
7	2,6,10-Trimethylundecane	i-C14
8	2-Ethyl-adamantane	2-E-Adam
9	Sesquiterpane C ₁₄ H ₂₆ ⁽¹⁾	BS1
10	Unknown compound designation (*)	C3-de peak
11	Sesquiterpane C ₁₄ H ₂₆	BS2
12	Heptylbenzene	C7-Benz
13	Biphenyl	B
14	2-Ethyl-naphthalene	2-E-N
15	2,6 + 2,7-Dimethylnaphthalene	2,6 + 2,7-DM-N
16	3 rd eluted branched alkane with <i>m/z</i> 169 ⁽²⁾	Br-alk-169-3
17	Sesquiterpane C ₁₅ H ₂₈ ⁽¹⁾	BS4
18	8β(H)-Drimane ⁽¹⁾	BS5
19	Sesquiterpane C ₁₅ H ₂₈ ⁽¹⁾	BS6
20	Pentadecane	n-C15
21	Sesquiterpane C ₁₆ H ₂₀ ⁽¹⁾	BS8
22	Sesquiterpane C ₁₆ H ₂₀ ⁽¹⁾	BS9
23	<i>meta</i> -Octyltoluene	m-C8-Tol
24	8β(H)-Homodrimane ⁽¹⁾	BS10
25	<i>ortho</i> -Octyltoluene	o-C8-Tol
26	Norpristane	Norpri
27	<i>meta</i> -Nonyltoluene	m-C9-Tol
28	Decylbenzene	C10-Benz
29	Heptadecane	n-C17
30	Pristane	Pri
31	Undecylcyclohexane	n-C11-CyC6
32	Octadecane	n-C18
33	Phytane	Phy
34	4-Methyldibenzothiophene	4-M-Dbt
35	3 rd eluted branched alkane with <i>m/z</i> 225 ⁽²⁾	Br-alk-225-3
36	Nonadecane	n-C19
37	1-Methyldibenzothiophene	1-M-Dbt
38	2-Methylphenanthrene	2-M-Phe
39	Hexadecanoic acid methyl ester	FAME C16:0
40	1-Methylphenanthrene	1-M-Phe
41	C2-Dibenzothiophenes	C2-dbt_s
42	C2-Phenanthrenes/Anthracenes	C2-phe_s
43	Octadecanoic acid methyl ester	FAME C18:0
44	2-Methylfluoranthene	2-M-Fl
45	Pentadecylbenzene	C15-Benz
46	Benzo(a)fluorene	BaF
47	Retene	Retene
48	2-Methylpyrene	2-M-Py
49	4-Methylpyrene	4-M-Py
50	1-Methylpyrene	1-M-Py
51	C23-Tricyclic terpane	C23Tr
52	C24-Tricyclic terpane	C24Tr
53	Heptadecylbenzene	C17-Benz
54	5α(H),14β(H),17β(H),20(R+S)-Cholestane,	27bbR+S

(1) The label identifies the elution order of sesquiterpanes, e.g., BS1 and BS2 are the first and the second sesquiterpanes to elute.

(2) Compound identified by quantification *m/z* and elution order.

(*) Compound with quantification *m/z* 180 and the same retention time as BS2, eluting outside the elution range of C3-Decalins.

Table C.2 (cont.).

ID number	Compounds/ Set of compounds	Label
55	18 α (H)-22,29,30-Trisnorneohopane	27Ts
56	C26,20S-Triaromatic sterane	SC26 TA
57	17 α (H)-22,29,30-Trisnorhopane	27Tm
58	C26,20R + C27,20S-Triaromatic sterane	RC26+SC27 TA
59	24-Ethyl-5 α (H),14 β (H),17 β (H),20(R+S)-cholestane	29bbR+S
60	17 α (H),21 β (H)-28,30-Bisnorhopane	28ab
61	C28,20S-Triaromatic sterane	SC28 TA
62	17 α (H),21 β (H)-30-Norhopane	29ab
63	18 α (H)-Oleanane	30O
64	17 α (H),21 β (H)-Hopane	30ab
65	C28,20R-Triaromatic sterane	RC28 TA
66	17 α (H),21 β (H),22(S)-Homohopane	31abS
67	Gammacerane	30G
68	Decalin	De
69	1,3,5-Trimethyladamantane	1,3,5-TM-Adam
70	C1-Decalins	C1-de_s
71	2-Methyladamantane	2-M-Adam
72	1,2,3,4-Tetrahydronaphthalene	Tetralin
73	<i>cis</i> -1,4-Dimethyladamantane	c-1,4-DM-Adam
74	Naphthalene	N
75	<i>trans</i> -1,4-Dimethyladamantane	tr-1,4-DM-Adam
76	1,3,6-Trimethyladamantane	1,3,6-TM-Adam
77	C2-Decalins	C2-de_s
78	<i>trans</i> -1,3,4-Trimethyladamantane	tr-1,3,4-TM-Adam
79	1,2,5,7-Tetramethyladamantane	1,2,5,7-TeM-Adam
80	1-Methylnaphthalene	1-M-N
81	<i>meta</i> -Hexyltoluene	m-C6-Tol
82	1 st eluted branched alkane with <i>m/z</i> 169 ⁽²⁾	Br-Alk-169-1
83	<i>ortho</i> -Hexyltoluene	o-C6-Tol
84	2,6,10-Trimethyldodecane	i-C15
85	1,3 + 1,7-Dimethylnaphthalene	1,3+1,7-DM-N
86	1,6-Dimethylnaphthalene	1,6-DM-N
87	Sesquiterpane C ₁₅ H ₂₈ ⁽¹⁾	BS3
88	C2-Benzothiophenes	C2-bt_s
89	Acenaphthylene	ANY
90	<i>meta</i> -Heptyltoluene	m-C7-Tol
91	2 nd eluted branched alkane with <i>m/z</i> 169 ⁽²⁾	Br-Alk-169-2
92	1,2-Dimethylnaphthalene	1,2-DM-N
93	2,6,10-Trimethyltridecane	i-C16
94	<i>ortho</i> -Heptyltoluene	o-C7-Tol
95	Diamantane	Diam
96	Dodecanoic acid methyl ester	FAME C12:0
97	4-Methyldiamantane	4-M-Diam
98	1,3,7-Trimethylnaphthalene	1,3,7-TM-N
99	1,3,6-Trimethylnaphthalene	1,3,6-TM-N
100	Nonylcyclohexane	n-C9-CyC6
101	<i>ortho</i> -Nonyltoluene	o-C9-Tol
102	1,2,3,4,5,6,7,8-Octahydro-anthracene	8H-A
103	1-Methylfluorene	1-M-F
104	1,2,3,4,5,6,7,8-Octahydrophenanthrene	8H-Phe
105	Tetradecanoic acid methyl ester	FAME C14:0
106	1 st eluted branched alkane with <i>m/z</i> 225 ⁽²⁾	Br-alk-225-1
107	C2-Fluorenes	C2-f_s
108	2 nd eluted branched alkane with <i>m/z</i> 225 ⁽²⁾	Br-alk-225-2
109	<i>meta</i> -Undecyltoluene	m-C11-Tol
110	Dodecylbenzene	C12-Benz
111	<i>ortho</i> -Undecyltoluene	o-C11-Tol
112	<i>cis</i> -9-Hexadecenoic acid methyl ester	FAME C16:1
113	2-Methylantracene	2-M-A

(1) The label identifies the elution order of sesquiterpanes, e.g., BS1 and BS2 are the first and the second sesquiterpanes to elute.

(2) Compound identified by quantification *m/z* and elution order.

Table C.2 (cont.).

ID number	Compounds/ Set of compounds	Label
114	1-Ethylphenanthrene	1-E-Phe
115	1,7-Dimethylphenanthrene	1,7-DM-Phe
116	C3-Dibenzothiophenes	C3-dbt_s
117	<i>cis</i> -9,12-Octadecadienoic acid methyl ester	FAME C18:2
118	<i>cis</i> -9-Octadecenoic acid methyl ester + 9,12,15-Octadecatrienoic acid methyl ester	FAME C18:1+C18:3
119	C21-Tricyclic terpane	C21Tr
120	C3-Phenanthrenes/Anthracenes	C3-phe_s
121	C4-Phenanthrenes/Anthracenes	C4-phe_s
122	<i>cis</i> -11-Eicosenoic acid methyl ester	FAME C20:1
123	Tetramethylphenanthrene	Te-M-Phe
124	Eicosanoic acid methyl ester	FAME C20:0
125	C2-Fluoranthenes	C2-fl_s
126	Benzo(b)naphtho(1,2-d)thiophene	BNT
127	C20-Triaromatic sterane	C20TA
128	C25-Tricyclic terpane (a+b)	C25Trab
129	C21-Triaromatic sterane	C21TA
130	Phytanyl-toluene	phy-tol
131	C1-Chrysenes	C1-chr
132	13 β (H),17 α (H),20S-Cholestane	27dbS
133	13 β (H),17 α (H),20R-Cholestane	27dbR
134	C28-Tricyclic terpane (22S)	C28(22S)
135	C29-Tricyclic terpane (22S)	C29(22S)
136	Benzo(e)pyrene	BePy
137	Benzo(a)pyrene	BaPy
138	24-Methyl-5 α (H),14 β (H),17 β (H),20(R+S)-cholestane	28bbR+S
139	24-Methyl-5 α (H),14 α (H),17 α (H),20R-cholestane	28aaR
140	24-Ethyl-5 α (H),14 α (H),17 α (H),20S-cholestane	29aaS
141	17 α (H),21 β (H)-25,28,30-Trisnorhopane	25nor30ab
142	24-Ethyl-5 α (H),14 α (H),17 α (H),20R-cholestane	29aaR
143	18 α (H)-30-Norneohopane	29Ts
144	17 β (H),21 α (H)-Hopane	30ba
145	17 α (H),21 β (H),22S-Bishomohopane	32abS

C.3. Experimental details

The experimental details present the list of quantified and unquantified compounds (**Table C.3**) and the determined *DR* (**Table C.4**) in each Sp and SS, known to be and not to be the source of the spill (SS1 and SS2, respectively) of the RR2018, RR2019 and RR2020, as well as the combined SIM chromatograms (**Figure C.1**) and the weathering assessment for each Sp (**Figures C.2** and **C.3**).

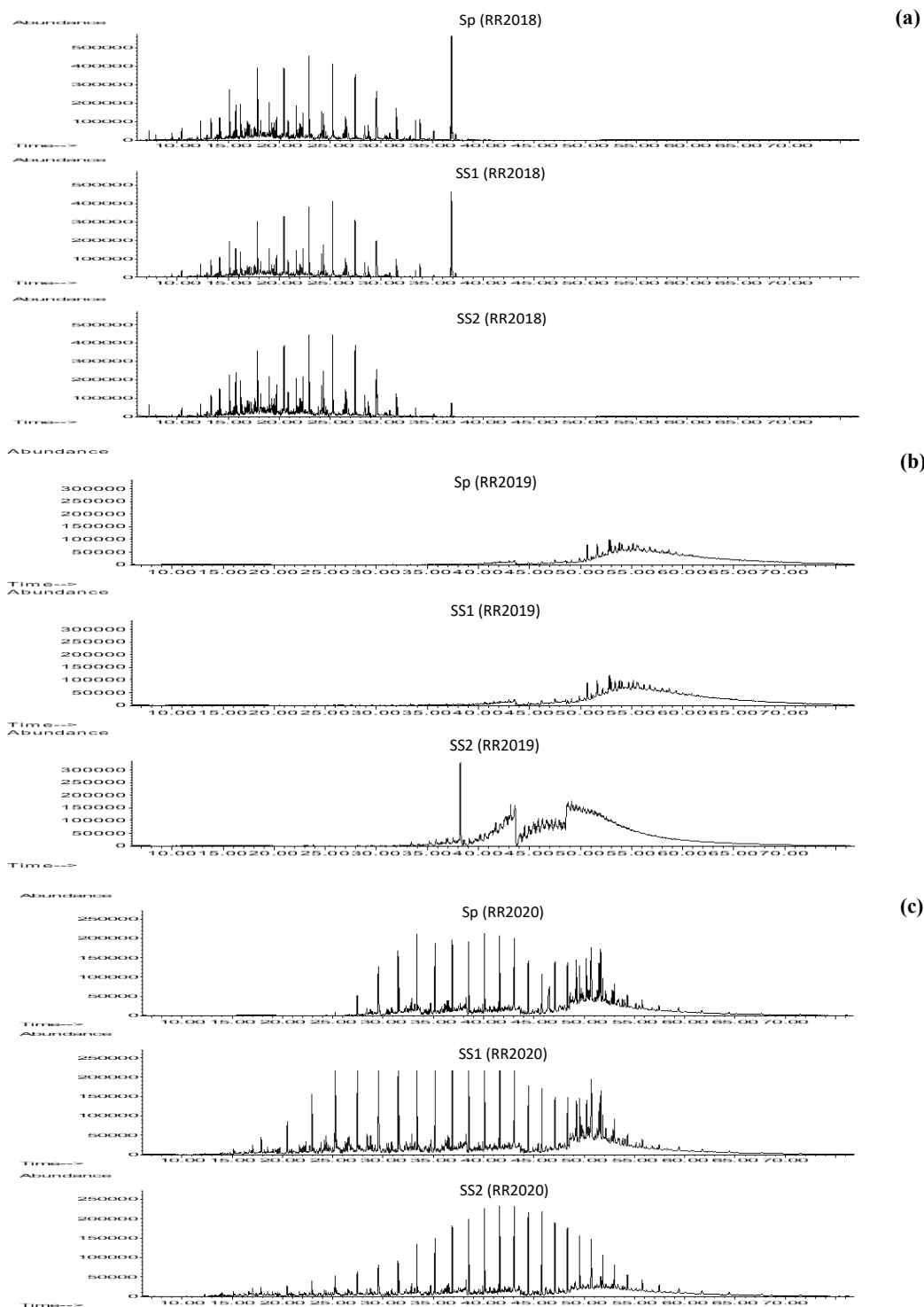


Figure C.1. Combined SIM chromatograms of the spill (Sp) and suspected source samples, known to be and not to be the origin of the spills (SS1 and SS2, respectively), of the Round Robin Tests (RR) (a) 2018, (b) 2019 and (c) 2020.

Table C.3. List of quantified and unquantified compounds in the spill (Sp) and suspected source (SS1 and SS2) samples of the Round Robin Tests (RR) 2018, 2019 and 2020.

Compounds		RR2018			RR2019			RR2020		
		Sp	SS1	SS2	Sp	SS1	SS2	Sp	SS1	SS2
1	1-M-Adam	●	●	●	○	○	○	○	●	●
2	1,2-DM-Adam	●	●	●	○	○	○	○	●	●
3	i-C13	●	●	●	○	○	○	○	●	●
4	2-M-Tetralin	●	●	●	○	○	○	○	●	●
5	c-1,3,4-TM-Adam	●	●	●	○	○	○	○	●	●
6	C6_Benz	●	●	●	○	○	○	○	●	●
7	i-C14	●	●	●	○	○	○	○	●	●
8	2-E-Adam	●	●	●	○	○	○	○	●	S/N < 5
9	BS1	●	●	●	○	○	○	○	●	
10	C3-de peak	●	●	●	○	○	○	○	●	
11	BS2	●	●	●	○	○	○	○	●	
12	C7_Benz	●	●	●	○	○	○	○	●	
13	B	●	●	●	○	○	○	○	●	●
14	2-E-N	●	●	●	○	○	○	○	●	●
15	2,6+2,7-DM-N	●	●	●	○	○	○	○	●	●
16	Br-Alk 169-3	●	●	●	○	S/N < 5	○	○	●	●
17	BS4	●	●	●	○	○	○	S/N < 3	●	●
18	BS5	●	●	●	○	S/N < 5	○	S/N < 5	●	●
19	BS6	●	●	●	○	○	○	S/N < 5	●	●
20	n-C15	●	●	●	○	S/N < 3	○	●	●	●
21	BS8	●	●	●	○	○	○	S/N < 5	●	●
22	BS9	●	●	●	○	○	○	S/N < 5	●	●
23	m-C8-Tol	●	●	●	○	S/N < 5	○	●	●	●
24	BS10	●	●	●	S/N < 5	●	○	●	●	●
25	o-C8-Tol	●	●	●		○	S/N < 5	○	●	●
26	Norpri	●	●	●	○	S/N < 5	○	●	●	●
27	m-C9-Tol	●	●	●	○	S/N < 5	○	●	●	●
28	C10_Benz	●	●	●	○	S/N < 5	○	●	●	●
29	n-C17	●	●	●	●	●	○	Both not determined (poor resolution)	Both not determined (poor resolution)	Both not determined (poor resolution)
30	Pri	●	●	●	○	○	○			
31	n-C11-CyC6	●	●	●	○	●	S/N < 3	●	●	●
32	n-C18	●	●	●	●	●	S/N < 5	●	●	●

S/N - signal-to-noise ratio.

● Quantified compound/set of compounds.

○ Absence.

Table C.3 (cont.).

Compounds		RR2018			RR2019			RR2020		
		Sp	SS1	SS2	Sp	SS1	SS2	Sp	SS1	SS2
33	Phy	●	●	●	●	●	●	●	●	●
34	4-M-Dbt	$S/N < 3$	$S/N < 3$	○	$S/N < 5$	●	○	●	●	●
35	Br-Alk 225-3	●	●	●	$S/N < 3$	$S/N < 5$	●	●	●	●
36	n-C19	●	●	●	$S/N < 3$	$S/N < 5$	$S/N < 5$	●	●	●
37	1-M-Dbt	○	○	○	$S/N < 5$	●	○	●	●	●
38	2-M-Phe	○	○	○	○	○	○	●	●	●
39	FAME C16:0	●	●	●	○	○	○	○	○	○
40	1-M-Phe	○	○	○	○	○	○	●	●	●
41	C2-dbt_s	○	○	○	●	●	○	●	●	●
42	C2-phe_s	Not determined (pattern not detected)	Not determined (pattern not detected)	Not determined (pattern not detected)	●	●	○	●	●	●
43	FAME C18:0	$S/N < 3$	●	●	○	○	○	○	○	○
44	2-M-FI	○	○	○	○	○	○	$S/N < 3$	$S/N < 3$	○
45	C15-Benz	○	○	○	●	●	○	●	●	●
46	BaF	○	○	○	○	○	○	●	●	●
47	Retene	○	○	○	○	○	○	○	○	○
48	2-M-Py	○	○	○	○	○	○	●	●	●
49	4-M-Py	○	○	○	○	○	○	●	●	●
50	1-M-Py	○	○	○	○	○	○	●	●	●
51	C23Tr	○	○	○	●	●	$S/N < 3$	●	●	●
52	C24Tr	○	○	○	●	●	○	●	●	●
53	C17-Benz	○	○	○	●	●	○	●	●	●
54	27bbR+S	○	○	○	●	●	○	●	●	●
55	27Ts	○	○	○	○	○	○	●	●	●
56	SC26 TA	○	○	○	○	○	○	●	●	$S/N < 3$
57	27Tm	○	○	○	○	○	○	●	●	●
58	RC26TA+SC27 TA	○	○	○	○	○	○	●	●	●
59	29bbR+S	○	○	○	●	●	○	●	●	●
60	28ab	○	○	○	○	○	○	○	○	○
61	SC28 TA	○	○	○	○	○	○	●	●	●
62	29ab	○	○	○	●	●	$S/N < 3$	●	●	○
63	30O	○	○	○	○	○	○	●	●	○
64	30ab	○	○	○	●	●	$S/N < 5$	●	●	●

S/N - signal-to-noise ratio.

● Quantified compound/set of compounds.

○ Absence.

Table C.3 (cont.).

Compounds		RR2018			RR2019			RR2020		
		Sp	SS1	SS2	Sp	SS1	SS2	Sp	SS1	SS2
65	RC28 TA	○	○	○	○	○	○	●	●	●
66	3labS	○	○	○	●	●	○	●	●	●
67	30G	○	○	○	●	●	○	●	●	●
68	De	●	●	●	○	○	<i>S/N</i> < 3	○	●	●
69	1,3,5-TM-Adam	●	●	●	○	○	○	○	●	<i>S/N</i> < 5
70	C1-de_s	●	●	●	○	○	<i>S/N</i> < 3	○	●	●
71	2-M-Adam	●	●	●	○	○	○	○	●	<i>S/N</i> < 5
72	Tetralin	●	●	●	○	○	○	○	●	●
73	c-1,4-DM-Adam	●	●	●	○	○	○	○	●	●
74	N	●	●	●	○	○	○	○	●	●
75	tr-1,4-DM-Adam	●	●	●	○	○	○	○	●	●
76	1,3,6-TM-Adam	●	●	●	○	○	○	○	●	●
77	C2-de_s	●	●	●	○	○	○	○	●	●
78	tr-1,3,4-TM-Adam	●	●	●	○	○	○	○	●	●
79	1,2,5,7-TeM-Adam	●	●	●	○	○	○	○	●	●
80	1-M-N	●	●	●	○	○	○	○	●	●
81	m-C6-Tol	●	●	●	○	○	○	○	●	●
82	Br-Alk-169-1	●	●	●	○	○	○	○	●	●
83	o-C6-Tol	●	●	●	○	○	○	○	●	●
84	i-C15	●	●	●	○	○	○	○	●	●
85	1,3+1,7-DM-N	●	●	●	○	<i>S/N</i> < 5	○	○	●	●
86	1,6-DM-N	●	●	●	○	<i>S/N</i> < 5	○	○	●	●
87	BS3	●	●	●	○	○	○	○	●	●
88	C2-bt_s	○	○	○	○	○	○	○	○	○
89	ANY	○	○	○	○	○	○	○	○	○
90	m-C7-Tol	●	●	●	○	<i>S/N</i> < 5	○	○	●	●
91	Br-Alk-169-2	●	●	●	○	<i>S/N</i> < 5	○	○	●	●
92	1,2 -DM-N	<i>S/N</i> < 3	<i>S/N</i> < 3	<i>S/N</i> < 3	○	<i>S/N</i> < 3	○	○	●	●
93	i-C16	●	●	●	○	○	○	<i>S/N</i> < 5	●	●
94	o-C7-Tol	●	●	●	○	<i>S/N</i> < 5	○	<i>S/N</i> < 5	●	●
95	Diam	●	●	●	○	○	○	○	●	●
96	FAME C12:0	●	●	●	○	○	○	○	○	○
97	4-M-Diam	○	○	○	○	○	○	○	○	○
98	1,3,7-TM-N	●	●	●	○	<i>S/N</i> < 5	○	●	●	●

S/N - signal-to-noise ratio.

● Quantified compound/set of compounds.

○ Absence.

Table C.3 (cont.).

Compounds		RR2018			RR2019			RR2020		
		Sp	SS1	SS2	Sp	SS1	SS2	Sp	SS1	SS2
99	1,3,6-TM-N	●	●	●	○	$S/N < 5$	○	●	●	●
100	n-C9-CyC6	●	●	●	○	●	○	●	●	●
101	o-C9-Tol	●	●	●	○	$S/N < 5$	○	●	●	●
102	8H-A	○	○	○	○	○	○	○	○	○
103	1-M-F	○	○	○	○	○	○	○	○	○
104	8H-Phe	○	○	○	○	○	○	○	○	○
105	FAME C14:0	○	●	●	○	○	○	○	○	○
106	Br-alk-225-1	●	●	●	$S/N < 3$	●	●	●	●	●
107	C2-f_s	Not determined (pattern not detected)	Not determined (pattern not detected)	Not determined (pattern not detected)	○	○	○	●	●	●
108	Br-alk-225-2	●	●	●	$S/N < 5$	●	●	●	●	●
109	m-C11-Tol	$S/N < 5$	$S/N < 5$	$S/N < 5$	$S/N < 5$	$S/N < 5$	○	●	●	●
110	C12-Benz	$S/N < 5$	$S/N < 5$	$S/N < 5$	$S/N < 5$	$S/N < 5$	○	●	●	●
111	o-C11-Tol	$S/N < 3$	$S/N < 3$	$S/N < 3$	$S/N < 5$	$S/N < 5$	○	●	●	●
112	FAME C16:1	$S/N < 3$	●	●	○	○	○	○	○	○
113	2-M-A	○	○	○	○	○	○	○	○	○
114	1-E-Phe	○	○	○	○	○	○	○	○	○
115	1,7 DM-Phe	○	○	○	$S/N < 5$	$S/N < 5$	○	●	●	●
116	C3-dbt_s	○	○	○	●	●	○	●	●	●
117	FAME C18:2	●	●	●	○	○	○	○	○	○
118	FAME C18:1+C18:3	●	●	●	○	○	○	○	○	○
119	C21Tr	○	○	○	○	○	○	$S/N < 5$	$S/N < 5$	$S/N < 3$
120	C3-phe_s	○	○	○	○	○	○	●	●	●
121	C4-phe_s	○	○	○	○	○	○	●	●	●
122	FAME C20:1	$S/N < 3$	●	●	○	○	○	○	○	○
123	Te-M-Phe	○	○	○	○	○	○	○	○	○
124	FAME C20:0	○	●	●	○	○	○	○	○	○
125	C2-fl_s	○	○	○	○	○	○	●	●	●
126	BNT	○	○	○	○	○	○	●	●	●
127	C20TA	○	○	○	○	○	○	●	●	●
128	C25Trab	○	○	○	$S/N < 5$	$S/N < 5$	○	●	●	$S/N < 3$
129	C21 TA	○	○	○	○	○	○	●	●	●
130	Phy-Tol	○	○	○	●	●	○	●	●	●
131	C1-chr	○	○	○	○	○	○	●	●	●

 S/N - signal-to-noise ratio.

● Quantified compound/set of compounds.

○ Absence.

Table C.3 (cont.).

Compounds		RR2018			RR2019			RR2020		
		Sp	SS1	SS2	Sp	SS1	SS2	Sp	SS1	SS2
132	27dbS	○	○	○	●	●	○	$S/N < 5$	$S/N < 5$	●
133	27dbR	○	○	○	●	●	○	$S/N < 3$	$S/N < 3$	$S/N < 5$
134	C28 (22S)	○	○	○	$S/N < 5$	$S/N < 5$	○	○	○	$S/N < 3$
135	C29 (22S)	○	○	○	$S/N < 5$	$S/N < 5$	○	$S/N < 5$	$S/N < 5$	●
136	BePy	○	○	○	○	○	○	○	○	○
137	BaPy	○	○	○	○	○	○	○	○	○
138	28bbR+S	○	○	○	●	●	○	●	●	●
139	28aaR	○	○	○	$S/N < 5$	$S/N < 5$	○	●	●	●
140	29aaS	○	○	○	●	●	○	●	●	●
141	25nor30ab	○	○	○	○	○	○	●	●	○
142	29aaR	○	○	○	●	●	○	●	●	●
143	29Ts	○	○	○	●	●	$S/N < 3$	●	●	●
144	30ba	○	○	○	●	●	○	●	●	●
145	32abS	○	○	○	●	●	○	●	●	●

S/N - signal-to-noise ratio.

● Quantified compound/set of compounds.

○ Absence.

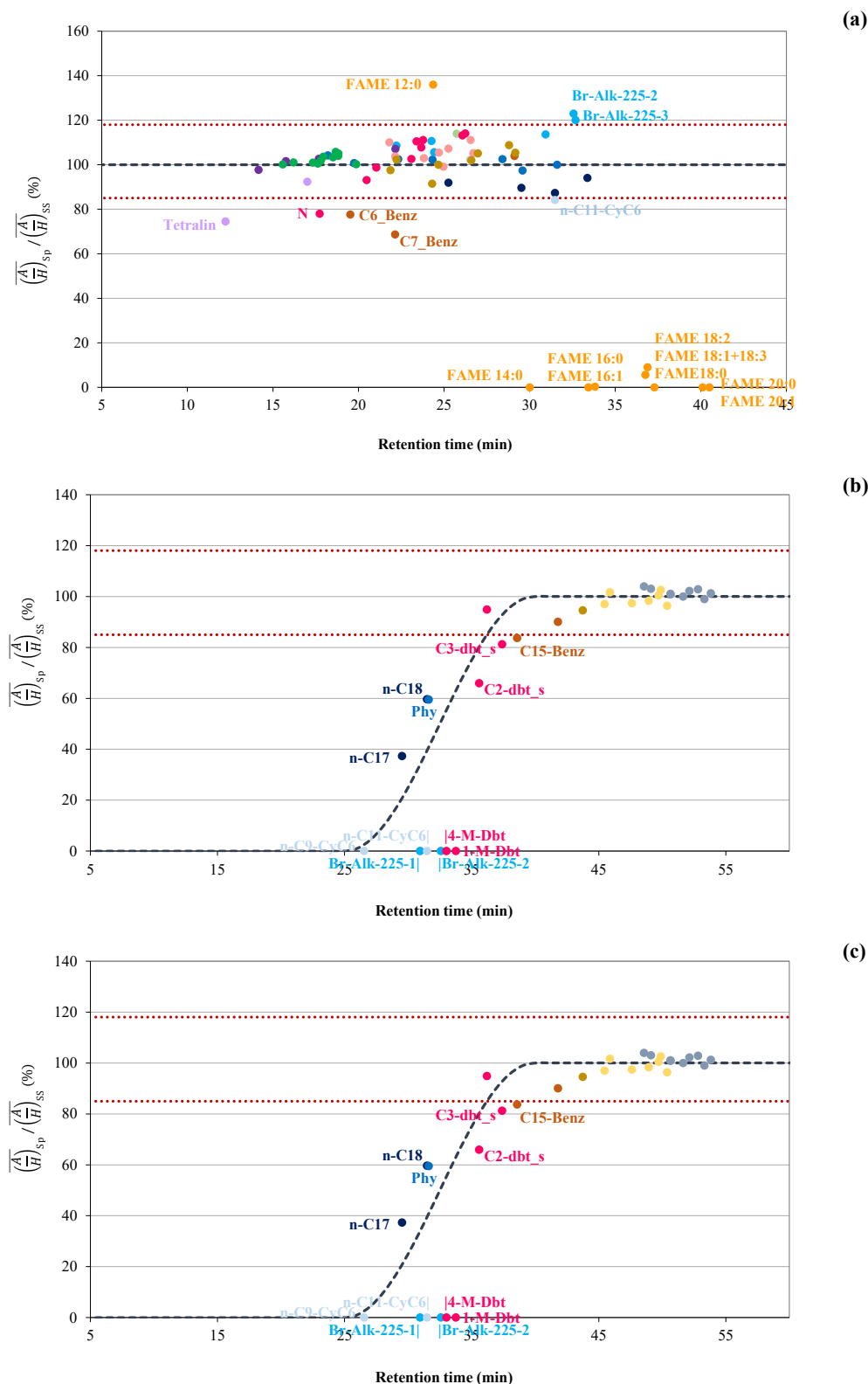


Figure C.2. Weathering assessment, using PW-plots, of the compounds analysed in the spill samples of the Round Robin Tests 2018, 2019 and 2020 used in the first comparison trial: (a) RR2018, (b) RR2019 and (c) RR2020. ● *n*-Alkanes; ● Isoprenoids; ● Branched alkanes; ● *n*-Alkylcyclohexanes; ● Decalins; ● Tetralins; ● Adamantanes; ● Diamantanes; ● Sesquiterpanes; ● Alkylbenzenes; ● Alkyltoluenes; ● PAH; ● Tricyclic terpanes; ● Hopanes; ● Steranes; ● Triaromatic steranes; ● FAME; ---- evaporation curve, according to EN 15522-2, and acceptable range for equivalence of compounds' contents in the spill and suspected source samples compared (85% to 118%).

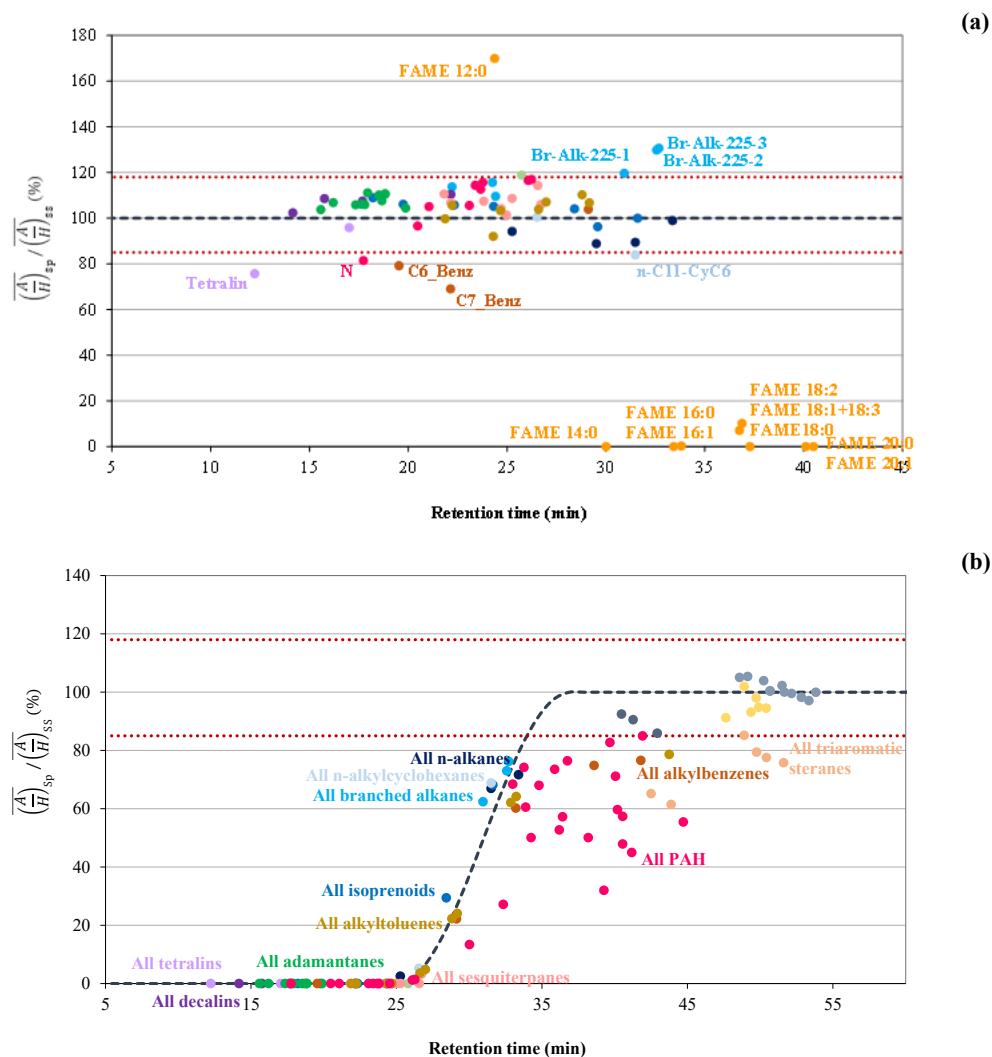


Figure C.3. Weathering assessment, using PW-plots, of the compounds analysed in the spill samples of the Round Robin Tests 2018 and 2020 used in the second comparison trial: (a) RR2018, and (b) RR2020. ● *n*-Alkanes; ● Isoprenoids; ● Branched alkanes; ● *n*-Alkylcyclohexanes; ● Decalins; ● Tetralins; ● Adamantanes; ● Diamantanes; ● Sesquiterpanes; ● Alkylbenzenes; ● Alkyltoluenes; ● PAH; ● Tricyclic terpanes; ● Hopanes; ● Steranes; ● Triaromatic steranes; ● FAME; ---- evaporation curve, according to EN 15522-2, and acceptable range for equivalence of compounds' contents in the spill and suspected source samples compared (85% to 118%).

Table C.4. List of quantified diagnostic ratios in the spill and suspected source samples of the Round Robin Tests (RR) 2018, 2019 and 2020.

DR code	Diagnostic ratio	RR2018	RR2019	RR2020
DR01	1-M-Adam/1,2-DM-Adam	●	-	-
DR02	1-M-Adam/2-E-Adam	●	-	-
DR03	i-C13/2-M-tetralin	●	-	-
DR04	c-1,3,4-TM-Adam/2-E-Adam	●	-	-
DR05	C6-/C7-Benz	○ ⁽¹⁾	-	-
DR06	2-E-Adam/i-C14	●	-	-
DR07	BS1/BS2	●	-	-
DR08	C3-de peak/BS2	●	-	-
DR09	B/2-E-N	●	-	-
DR10	2-E-N/2,6+2,7-DM-N	●	-	-
DR11	BS4/BS5	●	-	-
DR12	Br-alk-169-3/n-C15	●	-	-
DR13	BS5/BS6	●	-	-
DR14	BS8/BS9	●	-	-
DR15	m-/o-C8-Tol	●	-	-
DR16	BS10/Norpri	●	-	-
DR17	Norpri/m-C9-Tol	●	-	-
DR18	C10-Benz/n-C11-CyC6	○ ⁽¹⁾	○ ⁽¹⁾	-
DR19	n-C17/Pri	●	-	○ ⁽⁴⁾
DR20	Pri/Phy	●	-	○ ^(1; 4)
DR21	n-C18/Phy	●	-	○ ⁽¹⁾
DR22	4-M-Dbt/1-M-Dbt	○ ⁽²⁾	-	○ ⁽¹⁾
DR23	Br-alk-225-3/n-C19	-	-	○ ⁽¹⁾
DR24	2-M-Phe/1-M-Phe	○ ⁽²⁾	-	○ ⁽¹⁾
DR25	FAME C16:0/C18:0	○ ⁽³⁾	-	○ ⁽²⁾
DR26	C2-dbt_s/C2-phe_s	-	-	○ ⁽¹⁾
DR27	2-M-Fl/4-M-Py	-	-	○ ⁽¹⁾
DR28	C15-/C17-Benz	-	○ ⁽¹⁾	-
DR29	BaF/4-M-Py	-	-	○ ⁽¹⁾
DR30	Retene/29bb	-	-	-
DR31	2-M-Py/4-M-Py	-	-	○ ⁽¹⁾
DR32	1-M-Py/4-M-Py	-	-	○ ⁽¹⁾
DR33	C23Tr/C24Tr	-	●	●
DR34	27bb/29bb	-	●	●
DR35	27Ts/30ab	-	●	●
DR36	SC26/RC26+SC27 TA	-	-	○ ^(1; 2)
DR37	27Tm/30ab	-	●	●
DR38	28ab/30ab	-	○ ⁽²⁾	○ ⁽²⁾
DR39	SC28/RC26+SC27 TA	-	-	○ ⁽¹⁾
DR40	29ab/30ab	-	●	●
DR41	30O/30ab	-	○ ⁽²⁾	● (Sp vs. SS1) ○ ⁽²⁾ (Sp vs. SS2)
DR42	RC28/RC26+SC27 TA	-	-	○ ⁽¹⁾
DR43	31abS/30ab	-	●	●
DR44	30G/30ab	-	●	●

● Determined normative ratio for the oil type of the samples.

○ Not determined normative ratio for the oil type of the samples.

(1) DR not determined because at least one of the compounds that define the ratio was weathered in the Sp; weathering assessed by the sample pair known to have equivalent composition (Sp and SS1); DR not determined for the sample with different composition (Sp and SS2).

(2) DR not determined because at least one of the compounds that define the ratio is absent or shows the chromatographic signal with $S/N < 5$ in one of both Sp and SS.

(3) DR not determined because the chromatographic signal of at least one of the compounds that define the ratio has not been accurately quantified in one of both Sp and SS.

(4) DR not determined because the chromatographic signal(s) of one or both compound(s) have no resolution.

Table C.4 (cont.).

DR Code	Diagnostic ratio	RR2018	RR2019	RR2020
DR45	De/1-M-Adam	■	□ (2)	□ (2)
DR46	1-M-Adam/2-M-Adam	■	□ (2)	□ (2)
DR47	1,3,5-TM-Adam/tr-1,4-DM-Adam	■	□ (2)	□ (2)
DR48	1,3,5-TM-Adam/1,3,6-TM-Adam	■	□ (2)	□ (2)
DR49	C1-de_s/C2-de_s	■	□ (2)	□ (2)
DR50	Tetralin/2-M-Tetralin	(1)	□ (2)	□ (2)
DR51	1,2,5,7-TeM-Adam/2-E-Adam	■	□ (2)	□ (2)
DR52	1,2,5,7-TeM-Adam/BS10	■	□ (2)	□ (1; 2)
DR53	m-C6-Tol/BS10	■	□ (2)	□ (1; 2)
DR54	m-/o-C6-Tol	■	□ (2)	□ (2)
DR55	C7-/C10-Benz	□ (1)	□ (2)	□ (1; 2)
DR56	BS3/BS5	■	□ (2)	□ (2)
DR57	1,6-DM-N/1,3+1,7-DM-N	■	□ (2)	□ (2)
DR58	ANY/1,2-DM-N	□ (1)	□ (2)	□ (2)
DR59	Diam/4-M-Diam	□ (1)	□ (2)	□ (2)
DR60	FAME C12:0/C16:0	□ (1; 3)	□ (2)	□ (2)
DR61	1,3,7-TM-N/1,3,6-TM-N	■	□ (2)	□ (1)
DR62	BS8/BS10	■	□ (2)	□ (1; 2)
DR63	8H-A/8H-Phe	□ (2)	□ (2)	□ (2)
DR64	1-M-F/8H-Phe	□ (2)	□ (2)	□ (2)
DR65	FAME C14:0/C16:0	□ (1; 2; 3)	□ (2)	□ (2)
DR66	FAME C16:1/C16:0	□ (1; 2; 3)	□ (2)	□ (2)
DR67	1-E-Phe/1,7-DM-Phe	□ (2)	□ (2)	□ (1)
DR68	C3-dbt_s/C3-phe_s	□ (2)	□ (1; 2)	□ (1)
DR69	FAME C18:2/C18:0	□ (3)	□ (2)	□ (2)
DR70	FAME C18:1+C18:3/C18:0	□ (1; 2; 3)	□ (2)	□ (2)
DR71	C21Tr/C23Tr	□ (2)	□ (2)	□ (2)
DR72	C23Tr/phy-tol	□ (2)	■	□ (1)
DR73	FAME C20:0/C18:0	□ (2)	□ (2)	□ (2)
DR74	C20TA/C21TA	□ (2)	□ (2)	□ (1)
DR75	C21TA/RC26+SC27 TA	□ (2)	□ (2)	□ (1)
DR76	C28(22S)/30ab	□ (2)	□ (2)	□ (2)
DR77	BaPy/BePy	□ (2)	□ (2)	□ (2)
DR78	29aaS/29aaR	□ (2)	■	■
Normative ratios determined (of 44)		19	7	8 (Sp vs. SS1) 7 (Sp vs. SS2)
Informative ratios determined (of 34)		13	2	1
Total ratios determined (of 78)		32	9	9 (Sp vs. SS1) 8 (Sp vs. SS2)

■ Determined informative ratio.

□ Informative ratio not determined.

(1) DR not determined because at least one of the compounds that define the ratio was weathered in the Sp; weathering assessed by the sample pair known to have equivalent composition (Sp and SS1); DR not determined for the sample with different composition (Sp and SS2).

(2) DR not determined because at least one of the compounds that define the ratio is absent or shows the chromatographic signal with $S/N < 5$ in one of both Sp and SS.

(3) DR not determined because the chromatographic signal of at least one of the compounds that define the ratio has not been accurately quantified in one of both Sp and SS.

C.4. Detailed results

Table C.5. First trial of confidence limits of differences between DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering 95% and 98% confidence levels, for $A/(A+B)$ and A/B ratio formats, and triplicate and duplicate injections of the spill sample (Sp) and suspected source sample known to be the origin of the spill (SS1) of the Round Robin Test 2018 (RR2018), respectively.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp} = n_{SS1} = 3$					EN 15522-2 scenario: A/B and $n_{Sp} = n_{SS1} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR01	-0.0215 - 0.0070	-0.0296 - 0.0143	-0.0167 - 0.0025	-0.0208 - 0.0066	-0.0957 - 0.0815	-0.189 - 0.0707	-0.265 - 0.131	-0.405 - 0.300	-0.935 - 0.830	-0.294 - 0.189
DR02	-0.0174 - 0.0170	-0.0278 - 0.0262	-0.0097 - 0.0099	-0.0132 - 0.0134	-0.0988 - 0.0990	-0.250 - 0.238	-0.386 - 0.352	-0.214 - 0.217	-0.347 - 0.350	-0.336 - 0.339
DR03	0.0033 - 0.0521	-0.0126 - 0.0647	0.0145 - 0.0435	0.0095 - 0.0486	-0.0544 - 0.112	-0.0181 - 0.361	-0.125 - 0.457	0.0053 - 0.351	-0.102 - 0.458	-0.0287 - 0.385
DR04	0.0094 - 0.0176	0.0068 - 0.0201	0.0095 - 0.0174	0.0071 - 0.0199	-0.0494 - 0.0764	0.0279 - 0.0607	0.0182 - 0.0708	-0.0018 - 0.0906	-0.0713 - 0.160	-0.0699 - 0.159
DR06	-0.0098 - 0.0089	-0.0152 - 0.0144	-0.0060 - 0.0049	-0.0079 - 0.0068	-0.0163 - 0.0151	-0.0154 - 0.0139	-0.0231 - 0.0216	-0.0139 - 0.0124	-0.0220 - 0.0205	-0.0184 - 0.0170
DR07	-0.0221 - 0.0010	-0.0286 - 0.0072	-0.0171 - -0.0039	-0.0194 - -0.0016	-0.0799 - 0.0588	-0.0978 - 0.0134	-0.131 - 0.0420	-0.0908 - 0.0080	-0.121 - 0.0386	-0.179 - 0.0961
DR08	-0.0240 - 0.0100	-0.0349 - 0.0185	-0.0216 - 0.0092	-0.0312 - 0.0188	-0.0945 - 0.0821	-0.198 - 0.101	-0.291 - 0.179	-0.447 - 0.357	-1.05 - 0.961	-0.284 - 0.194
DR09	-0.0166 - 0.0064	-0.0225 - 0.0136	-0.0134 - 0.0021	-0.0167 - 0.0054	-0.137 - 0.125	-4.99 - 2.09	-6.98 - 3.91	-10.9 - 8.11	-25.2 - 22.4	-3.46 - 0.647
DR10	-0.0266 - 0.0082	-0.0361 - 0.0188	-0.0197 - 0.0004	-0.0232 - 0.0039	-0.0305 - 0.0112	-0.0420 - 0.0167	-0.0566 - 0.0353	-0.0396 - 0.0130	-0.0558 - 0.0292	-0.0378 - 0.0112
DR11	-0.0181 - 0.0212	-0.0296 - 0.0320	-0.0119 - 0.0158	-0.0178 - 0.0217	-0.0735 - 0.0773	-0.109 - 0.115	-0.182 - 0.168	-0.310 - 0.328	-0.789 - 0.807	-0.155 - 0.172
DR12	0.0068 - 0.0610	-0.0090 - 0.0746	0.0169 - 0.0521	0.0094 - 0.0596	-0.0413 - 0.110	-0.0014 - 0.326	-0.0916 - 0.410	-0.263 - 0.593	-0.907 - 1.24	-0.0012 - 0.331
DR13	-0.0002 - 0.0174	-0.0048 - 0.0223	0.0027 - 0.0145	0.0002 - 0.0171	-0.0838 - 0.101	-0.0176 - 0.168	-0.0654 - 0.217	-0.0091 - 0.159	-0.0610 - 0.211	-0.198 - 0.347
DR14	-0.0236 - 0.0062	-0.0320 - 0.0144	-0.0185 - 0.0008	-0.0227 - 0.0050	-0.0787 - 0.0610	-0.106 - 0.0392	-0.143 - 0.0825	-0.0987 - 0.0283	-0.138 - 0.0676	-0.175 - 0.104
DR15	-0.0368 - 0.0233	-0.0532 - 0.0408	-0.0263 - 0.0126	-0.0346 - 0.0209	-0.0986 - 0.0849	-0.376 - 0.247	-0.568 - 0.413	-0.335 - 0.218	-0.506 - 0.389	-0.325 - 0.208
DR16	-0.0078 - 0.0167	-0.0159 - 0.0230	-0.0033 - 0.0135	-0.0068 - 0.0171	-0.0316 - 0.0419	-0.0193 - 0.0356	-0.0381 - 0.0485	-0.0662 - 0.0851	-0.180 - 0.199	-0.0404 - 0.0593
DR17	-0.0063 - 0.0007	-0.0084 - 0.0026	-0.0050 - -0.0004	-0.0060 - 0.0006	-0.136 - 0.131	-3.38 - 0.654	-4.65 - 1.59	-3.01 - 0.566	-4.12 - 1.67	-4.07 - 1.62
DR19	-0.0474 - 0.0115	-0.0627 - 0.0294	-0.0455 - 0.0083	-0.0622 - 0.0250	-0.111 - 0.0738	-0.512 - 0.147	-0.727 - 0.293	-1.07 - 0.741	-2.43 - 2.10	-0.436 - 0.109
DR20	-0.0176 - 0.0105	-0.0243 - 0.0204	-0.0140 - 0.0046	-0.0179 - 0.0085	-0.111 - 0.102	-0.368 - 0.242	-0.510 - 0.440	-0.351 - 0.186	-0.517 - 0.351	-0.528 - 0.363
DR21	-0.0389 - -0.0110	-0.0458 - -0.0024	-0.0349 - -0.0163	-0.0389 - -0.0123	-0.130 - 0.0789	-0.674 - -0.120	-0.820 - 0.0338	-1.15 - 0.354	-2.29 - 1.49	-0.813 - 0.0138
DR45	-0.0102 - 0.0032	-0.0142 - 0.0068	-0.0074 - 0.0006	-0.0088 - 0.0020	-0.120 - 0.113	-0.430 - 0.179	-0.593 - 0.345	-0.402 - 0.151	-0.573 - 0.323	-0.833 - 0.583
DR46	-0.0112 - 0.0078	-0.0164 - 0.0131	-0.0072 - 0.0037	-0.0091 - 0.0056	-0.0903 - 0.0868	-0.102 - 0.0719	-0.148 - 0.114	-0.0895 - 0.0631	-0.137 - 0.110	-0.254 - 0.228
DR47	-0.0164 - 0.0136	-0.0244 - 0.0229	-0.0118 - 0.0082	-0.0161 - 0.0125	-0.0433 - 0.0396	-0.0402 - 0.0341	-0.0593 - 0.0565	-0.103 - 0.0952	-0.251 - 0.244	-0.0626 - 0.0552
DR48	-0.0167 - 0.0045	-0.0225 - 0.0109	-0.0133 - 0.0009	-0.0163 - 0.0039	-0.0650 - 0.0526	-0.0566 - 0.0204	-0.0770 - 0.0432	-0.0533 - 0.0164	-0.0748 - 0.0379	-0.120 - 0.0828
DR49	-0.0442 - 0.0348	-0.0710 - 0.0539	-0.0399 - 0.0345	-0.0630 - 0.0575	-0.0635 - 0.0581	-0.178 - 0.126	-0.301 - 0.193	-0.426 - 0.408	-1.05 - 1.03	-0.117 - 0.0983
DR51	0.0002 - 0.0199	-0.0056 - 0.0251	0.0047 - 0.0159	0.0027 - 0.0178	-0.0344 - 0.0550	-0.0043 - 0.0476	-0.0190 - 0.0601	-0.0006 - 0.0450	-0.0148 - 0.0592	-0.0435 - 0.0879
DR52	-0.0153 - 0.0162	-0.0226 - 0.0268	-0.0108 - 0.0099	-0.0153 - 0.0143	-0.0459 - 0.0450	-0.0398 - 0.0449	-0.0576 - 0.0744	-0.112 - 0.111	-0.280 - 0.278	-0.0682 - 0.0663
DR53	-0.0293 - -0.0026	-0.0360 - 0.0058	-0.0252 - -0.0075	-0.0290 - -0.0037	-0.0607 - 0.0280	-0.0690 - 0.0014	-0.0867 - 0.0235	-0.0667 - -0.0034	-0.0862 - 0.0162	-0.0999 - 0.0299

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

Table C.5 (cont.).

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{sp} = n_{ss1} = 3$					EN 15522-2 scenario: A/B and $n_{sp} = n_{ss1} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR54	-0.0256 - 0.0065	-0.0345 - 0.0155	-0.0200 - 0.0005	-0.0244 - 0.0049	-0.110 - 0.0904	-0.351 - 0.128	-0.471 - 0.274	-0.325 - 0.0864	-0.453 - 0.214	-0.471 - 0.232
DR56	-0.0124 - 0.0224	-0.0227 - 0.0317	-0.0068 - 0.0171	-0.0119 - 0.0223	-0.0922 - 0.103	-0.184 - 0.270	-0.327 - 0.375	-0.158 - 0.269	-0.291 - 0.401	-0.264 - 0.375
DR57	-0.0118 - 0.0287	-0.0214 - 0.0422	-0.0040 - 0.0192	-0.0081 - 0.0232	-0.0557 - 0.0708	-0.0499 - 0.115	-0.0855 - 0.172	-0.0479 - 0.0983	-0.0931 - 0.144	-0.0901 - 0.141
DR61	-0.0308 - 0.0274	-0.0466 - 0.0439	-0.0218 - 0.0176	-0.0302 - 0.0260	-0.0651 - 0.0609	-0.129 - 0.108	-0.204 - 0.169	-0.325 - 0.311	-0.804 - 0.789	-0.122 - 0.107
DR62	-0.0145 - 0.0250	-0.0239 - 0.0383	-0.0092 - 0.0173	-0.0148 - 0.0230	-0.0406 - 0.0488	-0.0396 - 0.0661	-0.0625 - 0.105	-0.132 - 0.150	-0.344 - 0.362	-0.0568 - 0.0746
τ (%)	18.8	6.3	28.1	25.0	0	6.3	3.1	6.3	0	0

Blue background – Confidence interval that does not include the zero (non-equivalent DR).
 τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table C.6. Second trial of confidence limits of differences between DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering 95% and 98% confidence levels, for $A/(A+B)$ and A/B ratio formats, and triplicate and duplicate injections of the spill sample (Sp) and suspected source sample known to be the origin of the spill (SS1) of the Round Robin Test 2018 (RR2018), respectively.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp} = n_{SS1} = 3$					EN 15522-2 scenario: A/B and $n_{Sp} = n_{SS1} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR01	-0.0405 - 0.0113	-0.0566 - 0.0247	-0.0312 - 0.0032	-0.0385 - 0.0105	-0.102 - 0.0741	-0.332 - 0.122	-0.466 - 0.241	-0.303 - 0.100	-0.428 - 0.225	-0.340 - 0.136
DR02	-0.0174 - 0.0139	-0.0271 - 0.0221	-0.0102 - 0.0077	-0.0134 - 0.0109	-0.100 - 0.0976	-0.251 - 0.198	-0.397 - 0.303	-0.211 - 0.182	-0.332 - 0.303	-0.351 - 0.322
DR03	0.0028 - 0.0608	-0.0125 - 0.0804	0.0112 - 0.0504	0.0028 - 0.0588	-0.0527 - 0.114	-0.0194 - 0.437	-0.129 - 0.606	-0.430 - 0.810	-1.36 - 1.74	-0.0174 - 0.398
DR04	-0.0016 - 0.0159	-0.0072 - 0.0207	0.0015 - 0.0135	-0.0011 - 0.0161	-0.0550 - 0.0700	-0.0110 - 0.0590	-0.0327 - 0.0783	-0.0719 - 0.121	-0.217 - 0.266	-0.0883 - 0.137
DR06	-0.0094 - 0.0058	-0.0140 - 0.0097	-0.0066 - 0.0035	-0.0088 - 0.0056	-0.0172 - 0.0141	-0.0142 - 0.0094	-0.0211 - 0.0153	-0.0333 - 0.0293	-0.0804 - 0.0765	-0.0196 - 0.0156
DR07	-0.0128 - 0.0154	-0.0196 - 0.0247	-0.0073 - 0.0087	-0.0100 - 0.0115	-0.0694 - 0.0709	-0.0628 - 0.0771	-0.0979 - 0.126	-0.0578 - 0.0636	-0.0954 - 0.101	-0.138 - 0.144
DR08	-0.0067 - 0.0053	-0.0105 - 0.0084	-0.0059 - 0.0050	-0.0093 - 0.0083	-0.0892 - 0.0882	-0.0615 - 0.0481	-0.0993 - 0.0738	-0.150 - 0.143	-0.370 - 0.363	-0.246 - 0.239
DR09	-0.0141 - 0.0055	-0.0186 - 0.0127	-0.0144 - 0.0039	-0.0201 - 0.0096	-0.136 - 0.126	-4.63 - 1.73	-6.66 - 3.40	-9.94 - 7.29	-22.9 - 20.3	-3.38 - 0.738
DR10	-0.0216 - 0.0015	-0.0277 - 0.0088	-0.0178 - -0.0027	-0.0211 - 0.0006	-0.0311 - 0.0106	-0.0337 - 0.0059	-0.0453 - 0.0171	-0.0316 - 0.0032	-0.0423 - 0.0140	-0.0386 - 0.0103
DR11	-0.0206 - 0.0181	-0.0324 - 0.0300	-0.0152 - 0.0121	-0.0210 - 0.0179	-0.0767 - 0.0736	-0.121 - 0.101	-0.191 - 0.158	-0.321 - 0.306	-0.792 - 0.777	-0.170 - 0.155
DR12	0.0168 - 0.0599	0.0058 - 0.0742	0.0248 - 0.0503	0.0203 - 0.0548	-0.0385 - 0.114	0.0571 - 0.315	-0.0085 - 0.393	0.0601 - 0.301	-0.0144 - 0.375	0.0134 - 0.347
DR13	-0.0011 - 0.0264	-0.0093 - 0.0335	0.0052 - 0.0207	0.0025 - 0.0234	-0.0798 - 0.106	-0.0338 - 0.262	-0.111 - 0.344	-0.0172 - 0.246	-0.0986 - 0.327	-0.161 - 0.390
DR14	-0.0319 - 0.0034	-0.0452 - 0.0113	-0.0243 - -0.0013	-0.0293 - 0.0036	-0.0824 - 0.0568	-0.142 - 0.0271	-0.202 - 0.0645	-0.271 - 0.170	-0.602 - 0.501	-0.189 - 0.0878
DR15	-0.0402 - 0.0235	-0.0601 - 0.0393	-0.0248 - 0.0112	-0.0311 - 0.0174	-0.0986 - 0.0849	-0.405 - 0.251	-0.614 - 0.406	-0.350 - 0.233	-0.530 - 0.414	-0.325 - 0.208
DR16	-0.0066 - 0.0127	-0.0130 - 0.0175	-0.0030 - 0.0099	-0.0058 - 0.0126	-0.0332 - 0.0401	-0.0166 - 0.0268	-0.0304 - 0.0370	-0.0133 - 0.0259	-0.0254 - 0.0380	-0.0433 - 0.0559
DR17	-0.0059 - 0.0009	-0.0077 - 0.0030	-0.0048 - -0.0003	-0.0058 - 0.0006	-0.136 - 0.131	-3.23 - 0.755	-4.59 - 1.79	-6.33 - 3.97	-14.1 - 11.7	-4.02 - 1.67
DR19	-0.0491 - 0.0130	-0.0667 - 0.0304	-0.0459 - 0.0099	-0.0632 - 0.0272	-0.110 - 0.0745	-0.530 - 0.161	-0.754 - 0.325	-1.09 - 0.772	-2.49 - 2.17	-0.431 - 0.115
DR20	-0.0274 - 0.0161	-0.0374 - 0.0314	-0.0212 - 0.0073	-0.0273 - 0.0134	-0.113 - 0.0994	-0.539 - 0.386	-0.741 - 0.716	-0.519 - 0.281	-0.766 - 0.528	-0.562 - 0.324
DR21	-0.0329 - -0.0080	-0.0394 - 0.0004	-0.0324 - -0.0096	-0.0394 - -0.0026	-0.126 - 0.0838	-0.591 - -0.0771	-0.739 - 0.0772	-1.04 - 0.370	-2.10 - 1.43	-0.752 - 0.0844
DR45	-0.0078 - 0.0038	-0.0115 - 0.0074	-0.0059 - 0.0021	-0.0076 - 0.0037	-0.119 - 0.115	-0.346 - 0.187	-0.511 - 0.330	-0.789 - 0.647	-1.87 - 1.73	-0.783 - 0.641
DR46	-0.0201 - 0.0095	-0.0301 - 0.0173	-0.0147 - 0.0056	-0.0190 - 0.0099	-0.0929 - 0.0838	-0.174 - 0.0934	-0.267 - 0.162	-0.156 - 0.0895	-0.232 - 0.165	-0.273 - 0.206
DR47	-0.0223 - 0.0242	-0.0364 - 0.0368	-0.0113 - 0.0149	-0.0158 - 0.0195	-0.0399 - 0.0435	-0.0553 - 0.0595	-0.0901 - 0.0901	-0.0467 - 0.0541	-0.0778 - 0.0852	-0.0557 - 0.0631
DR48	-0.0334 - 0.0158	-0.0481 - 0.0308	-0.0264 - 0.0077	-0.0337 - 0.0150	-0.0679 - 0.0492	-0.110 - 0.0666	-0.154 - 0.128	-0.270 - 0.215	-0.635 - 0.580	-0.128 - 0.0732
DR49	-0.0441 - 0.0438	-0.0755 - 0.0662	-0.0271 - 0.0318	-0.0397 - 0.0443	-0.0589 - 0.0635	-0.184 - 0.157	-0.320 - 0.229	-0.440 - 0.454	-1.11 - 1.13	-0.102 - 0.115
DR51	-0.0030 - 0.0270	-0.0133 - 0.0344	0.0027 - 0.0227	-0.0016 - 0.0270	-0.0322 - 0.0576	-0.0151 - 0.0654	-0.0419 - 0.0853	-0.0793 - 0.134	-0.240 - 0.295	-0.0385 - 0.0936
DR52	0.0012 - 0.0177	-0.0039 - 0.0219	0.0042 - 0.0149	0.0019 - 0.0172	-0.0366 - 0.0557	-0.0019 - 0.0428	-0.0149 - 0.0549	0.0016 - 0.0410	-0.0106 - 0.0531	-0.0476 - 0.0901
DR53	-0.0245 - -0.0017	-0.0309 - 0.0048	-0.0237 - -0.0025	-0.0302 - 0.0041	-0.0576 - 0.0315	-0.0595 - 0.0017	-0.0791 - 0.0200	-0.112 - 0.0555	-0.238 - 0.181	-0.0935 - 0.0372

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

Table C.6 (cont.).

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{sp} = n_{ss1} = 3$					EN 15522-2 scenario: A/B and $n_{sp} = n_{ss1} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR54	-0.0295 - 0.0042	-0.0411 - 0.0123	-0.0228 - -0.0005	-0.0275 - 0.0042	-0.112 - 0.0883	-0.408 - 0.0911	-0.566 - 0.209	-0.362 - 0.0774	-0.497 - 0.213	-0.492 - 0.208
DR56	-0.0240 - 0.0106	-0.0347 - 0.0206	-0.0184 - 0.0053	-0.0235 - 0.0104	-0.103 - 0.0900	-0.294 - 0.145	-0.433 - 0.256	-0.275 - 0.139	-0.404 - 0.267	-0.379 - 0.243
DR57	-0.0120 - 0.0277	-0.0217 - 0.0412	-0.0048 - 0.0178	-0.0088 - 0.0218	-0.0567 - 0.0697	-0.0527 - 0.108	-0.0902 - 0.163	-0.0499 - 0.0931	-0.0941 - 0.137	-0.0935 - 0.137
DR61	-0.0335 - 0.0312	-0.0514 - 0.0493	-0.0224 - 0.0203	-0.0315 - 0.0294	-0.0642 - 0.0620	-0.136 - 0.126	-0.217 - 0.194	-0.120 - 0.113	-0.193 - 0.185	-0.119 - 0.111
DR62	-0.0054 - 0.0158	-0.0118 - 0.0221	-0.0015 - 0.0124	-0.0045 - 0.0154	-0.0394 - 0.0503	-0.0175 - 0.0391	-0.0345 - 0.0545	-0.0132 - 0.0367	-0.0286 - 0.0521	-0.0542 - 0.0777
τ (%)	15.6	3.1	37.5	15.6	0	6.3	0	6.3	0	3.1

Blue background – Confidence interval that does not include the zero (non-equivalent DR).
 τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table C.7. Confidence limits of differences between DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering 95% and 98% confidence levels, for $A/(A+B)$ and A/B ratio formats, and triplicate and duplicate injections of the spill sample (Sp) and suspected source sample known to be the origin of the spill (SS1) of the Round Robin Test 2019 (RR2019), respectively.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp} = n_{SS1} = 3$					EN 15522-2 scenario: A/B and $n_{Sp} = n_{SS1} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR33	-0.0630 - 0.0604	-0.110 - 0.0900	-0.0359 - 0.0463	-0.0535 - 0.0639	-0.0890 - 0.0993	-0.689 - 0.736	-1.24 - 1.15	-1.80 - 1.91	-4.59 - 4.70	-0.234 - 0.342
DR34	-0.0549 - 0.0308	-0.0833 - 0.0546	-0.0355 - 0.0138	-0.0441 - 0.0224	-0.0542 - 0.0326	-0.136 - 0.0841	-0.212 - 0.138	-0.121 - 0.0752	-0.181 - 0.136	-0.0858 - 0.0402
DR35	-0.0137 - 0.0189	-0.0254 - 0.0262	-0.0054 - 0.0130	-0.0086 - 0.0163	-0.0117 - 0.0194	-0.0234 - 0.0273	-0.0426 - 0.0384	-0.0172 - 0.0269	-0.0308 - 0.0405	-0.0127 - 0.0224
DR37	-0.0124 - 0.0198	-0.0210 - 0.0299	-0.0078 - 0.0141	-0.0125 - 0.0187	-0.0135 - 0.0198	-0.0201 - 0.0314	-0.0353 - 0.0480	-0.0192 - 0.0273	-0.0336 - 0.0417	-0.0149 - 0.0229
DR40	-0.0363 - 0.0418	-0.0606 - 0.0656	-0.0207 - 0.0250	-0.0287 - 0.0329	-0.0611 - 0.0654	-0.155 - 0.173	-0.265 - 0.270	-0.138 - 0.152	-0.228 - 0.242	-0.108 - 0.122
DR43	-0.0119 - 0.0310	-0.0219 - 0.0493	-0.0140 - 0.0279	-0.0269 - 0.0409	-0.0600 - 0.0740	-0.0593 - 0.136	-0.102 - 0.219	-0.248 - 0.299	-0.659 - 0.710	-0.103 - 0.154
DR44	-0.0143 - 0.0098	-0.0232 - 0.0159	-0.0080 - 0.0053	-0.0104 - 0.0076	-0.0233 - 0.0206	-0.0241 - 0.0177	-0.0390 - 0.0293	-0.0197 - 0.0158	-0.0307 - 0.0268	-0.0280 - 0.0241
DR72	-0.0296 - 0.0310	-0.0524 - 0.0452	-0.0245 - 0.0314	-0.0418 - 0.0486	-0.0236 - 0.0304	-0.0554 - 0.0577	-0.0990 - 0.0856	-0.149 - 0.160	-0.382 - 0.392	-0.0280 - 0.0388
DR78	-0.0424 - 0.0553	-0.0807 - 0.0779	-0.0227 - 0.0433	-0.0368 - 0.0574	-0.0473 - 0.0679	-0.152 - 0.194	-0.268 - 0.279	-0.440 - 0.501	-1.15 - 1.21	-0.0676 - 0.128
τ (%)	0	0	0	0	0	0	0	0	0	0

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table C.8. First trial of confidence limits of differences between DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering 95% and 98% confidence levels, for $A/(A+B)$ and A/B ratio formats, and triplicate and duplicate injections of the spill sample (Sp) and suspected source sample known to be the origin of the spill (SS1) of the Round Robin Test 2020 (RR2020), respectively.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp} = n_{SS1} = 3$					EN 15522-2 scenario: A/B and $n_{Sp} = n_{SS1} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR33	-0.0098 - 0.0216	-0.0212 - 0.0288	-0.0011 - 0.0160	-0.0041 - 0.0190	-0.0720 - 0.0868	-0.0739 - 0.133	-0.149 - 0.190	-0.0469 - 0.126	-0.100 - 0.180	-0.144 - 0.223
DR34	-0.0333 - 0.0365	-0.0477 - 0.0658	-0.0261 - 0.0204	-0.0360 - 0.0303	-0.0630 - 0.0573	-0.121 - 0.138	-0.176 - 0.249	-0.127 - 0.109	-0.199 - 0.181	-0.114 - 0.0964
DR35	-0.0131 - 0.0303	-0.0242 - 0.0450	-0.0071 - 0.0223	-0.0134 - 0.0285	-0.0168 - 0.0320	-0.0269 - 0.0515	-0.0464 - 0.0785	-0.0245 - 0.0467	-0.0465 - 0.0687	-0.0185 - 0.0406
DR37	0.0003 - 0.0241	-0.0078 - 0.0306	0.0042 - 0.0199	0.0008 - 0.0233	-0.0144 - 0.0385	-0.0039 - 0.0407	-0.0183 - 0.0534	-0.0014 - 0.0379	-0.0135 - 0.0501	-0.0143 - 0.0509
DR40	-0.0296 - 0.0317	-0.0428 - 0.0552	-0.0206 - 0.0148	-0.0268 - 0.0210	-0.0594 - 0.0536	-0.100 - 0.111	-0.144 - 0.200	-0.103 - 0.0859	-0.161 - 0.144	-0.103 - 0.0865
DR41	-0.0366 - 0.0334	-0.0546 - 0.0567	-0.0222 - 0.0166	-0.0290 - 0.0234	-0.0531 - 0.0475	-0.109 - 0.102	-0.163 - 0.176	-0.0970 - 0.0833	-0.153 - 0.139	-0.0853 - 0.0717
DR43	-0.0141 - 0.0068	-0.0188 - 0.0147	-0.0107 - 0.0011	-0.0128 - 0.0032	-0.0321 - 0.0225	-0.0251 - 0.0151	-0.0338 - 0.0316	-0.0248 - 0.0099	-0.0355 - 0.0207	-0.0413 - 0.0265
DR44	-0.0122 - 0.0087	-0.0172 - 0.0158	-0.0085 - 0.0035	-0.0106 - 0.0056	-0.0138 - 0.0088	-0.0171 - 0.0134	-0.0242 - 0.0242	-0.0164 - 0.0105	-0.0247 - 0.0188	-0.0152 - 0.0093
DR78	-0.0287 - 0.0538	-0.0485 - 0.0844	-0.0195 - 0.0353	-0.0312 - 0.0470	-0.0384 - 0.0543	-0.0803 - 0.155	-0.127 - 0.256	-0.0838 - 0.120	-0.147 - 0.183	-0.0514 - 0.0872
τ (%)	11.1	0	11.1	11.1	0	0	0	0	0	0

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table C.9. Second trial of confidence limits of differences between *DR* means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering 95% and 98% confidence levels, for $A/(A+B)$ and A/B ratio formats, and triplicate and duplicate injections of the spill sample (Sp) and suspected source sample known to be the origin of the spill (SS1) of the Round Robin Test 2020 (RR2020), respectively.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp} = n_{SS1} = 3$					EN 15522-2 scenario: A/B and $n_{Sp} = n_{SS1} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR33	-0.0099 - 0.0191	-0.0213 - 0.0279	-0.0036 - 0.0140	-0.0073 - 0.0177	-0.0740 - 0.0844	-0.0727 - 0.118	-0.174 - 0.187	-0.0488 - 0.104	-0.0960 - 0.151	-0.155 - 0.210
DR34	-0.0388 - 0.0346	-0.0513 - 0.0663	-0.0327 - 0.0140	-0.0427 - 0.0240	-0.0690 - 0.0503	-0.136 - 0.138	-0.181 - 0.270	-0.146 - 0.0889	-0.219 - 0.162	-0.133 - 0.0754
DR35	-0.0110 - 0.0271	-0.0212 - 0.0420	-0.0107 - 0.0250	-0.0217 - 0.0360	-0.0172 - 0.0315	-0.0222 - 0.0473	-0.0408 - 0.0749	-0.0838 - 0.105	-0.226 - 0.246	-0.0191 - 0.0399
DR37	-0.0044 - 0.0193	-0.0135 - 0.0254	0.0003 - 0.0157	-0.0030 - 0.0190	-0.0181 - 0.0342	-0.0122 - 0.0324	-0.0303 - 0.0434	-0.0070 - 0.0313	-0.0189 - 0.0431	-0.0201 - 0.0443
DR40	-0.0276 - 0.0415	-0.0396 - 0.0710	-0.0182 - 0.0200	-0.0249 - 0.0267	-0.0559 - 0.0577	-0.0922 - 0.149	-0.136 - 0.259	-0.100 - 0.105	-0.164 - 0.169	-0.0931 - 0.0981
DR41	-0.0316 - 0.0375	-0.0556 - 0.0579	-0.0135 - 0.0240	-0.0201 - 0.0306	-0.0456 - 0.0561	-0.100 - 0.110	-0.176 - 0.172	-0.0753 - 0.101	-0.130 - 0.156	-0.0670 - 0.0928
DR43	-0.0141 - 0.0091	-0.0213 - 0.0165	-0.0091 - 0.0036	-0.0113 - 0.0058	-0.0302 - 0.0247	-0.0256 - 0.0186	-0.0394 - 0.0324	-0.0229 - 0.0144	-0.0345 - 0.0259	-0.0384 - 0.0298
DR44	-0.0125 - 0.0078	-0.0191 - 0.0137	-0.0078 - 0.0035	-0.0098 - 0.0055	-0.0135 - 0.0092	-0.0176 - 0.0119	-0.0270 - 0.0204	-0.0153 - 0.0102	-0.0232 - 0.0181	-0.0149 - 0.0098
DR78	-0.0111 - 0.0331	-0.0205 - 0.0530	-0.0115 - 0.0279	-0.0237 - 0.0401	-0.0382 - 0.0546	-0.0333 - 0.0877	-0.0588 - 0.147	-0.139 - 0.175	-0.375 - 0.411	-0.0511 - 0.0875
τ (%)	0	0	3.1	0	0	0	0	0	0	0

Blue background – Confidence interval that does not include the zero (non-equivalent *DR*).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent *DR*).

Table C.10. Confidence limits of differences between DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering 95% and 98% confidence levels, for $A/(A+B)$ and A/B ratio formats, and triplicate and duplicate injections of the spill sample (Sp) and suspected source sample known not to be the origin of the spill (SS2) of the Round Robin Test 2018 (RR2018), respectively.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp} = n_{SS2} = 3$					EN 15522-2 scenario: A/B and $n_{Sp} = n_{SS2} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR01	-0.0132 - 0.0075	-0.0194 - 0.0127	-0.0086 - 0.0034	-0.0106 - 0.0055	-0.0909 - 0.0857	-0.116 - 0.0709	-0.173 - 0.117	-0.102 - 0.0646	-0.154 - 0.116	-0.258 - 0.220
DR02	-0.0056 - 0.0197	-0.0133 - 0.0261	-0.0012 - 0.0159	-0.0049 - 0.0196	-0.0910 - 0.106	-0.0956 - 0.259	-0.198 - 0.351	-0.396 - 0.564	-1.12 - 1.29	-0.248 - 0.416
DR03	0.0006 - 0.0374	-0.0115 - 0.0473	0.0017 - 0.0375	-0.0093 - 0.0486	-0.0644 - 0.104	-0.0245 - 0.272	-0.111 - 0.365	-0.302 - 0.550	-0.943 - 1.19	-0.0870 - 0.334
DR04	0.0133 - 0.0552	0.0026 - 0.0685	0.0137 - 0.0528	0.0016 - 0.0648	-0.0283 - 0.0947	0.0294 - 0.185	-0.0130 - 0.232	-0.108 - 0.319	-0.430 - 0.641	-0.0044 - 0.216
DR06	-0.0109 - 0.0049	-0.0155 - 0.0094	-0.0076 - 0.0017	-0.0092 - 0.0033	-0.0188 - 0.0129	-0.0162 - 0.0086	-0.0232 - 0.0156	-0.0149 - 0.0074	-0.0218 - 0.0144	-0.0216 - 0.0142
DR07	-0.0011 - 0.0185	-0.0069 - 0.0235	0.0032 - 0.0147	0.0012 - 0.0167	-0.0590 - 0.0770	-0.0137 - 0.0777	-0.0423 - 0.101	-0.0071 - 0.0751	-0.0325 - 0.101	-0.0982 - 0.166
DR08	-0.0355 - 0.0155	-0.0499 - 0.0291	-0.0247 - 0.0049	-0.0298 - 0.0101	-0.0984 - 0.0787	-0.312 - 0.154	-0.453 - 0.275	-0.281 - 0.134	-0.410 - 0.263	-0.315 - 0.168
DR09	-0.0289 - -0.0155	-0.0332 - -0.0120	-0.0266 - -0.0174	-0.0285 - -0.0155	-0.154 - 0.110	-10.2 - -4.76	-11.9 - -3.38	-9.79 - -4.92	-11.3 - -3.41	-9.83 - -4.88
DR10	-0.0584 - -0.0209	-0.0679 - -0.0094	-0.0513 - -0.0291	-0.0552 - -0.0252	-0.0632 - -0.0172	-0.0893 - -0.0231	-0.106 - -0.0019	-0.0878 - -0.0274	-0.106 - -0.0087	-0.0852 - -0.0300
DR11	0.0440 - 0.0702	0.0368 - 0.0772	0.0497 - 0.0651	0.0470 - 0.0678	-0.0141 - 0.129	0.172 - 0.306	0.133 - 0.340	0.180 - 0.301	0.143 - 0.338	0.0934 - 0.388
DR12	0.0031 - 0.0658	-0.0146 - 0.0833	0.0167 - 0.0519	0.0105 - 0.0581	-0.0415 - 0.110	-0.0210 - 0.353	-0.121 - 0.456	0.0014 - 0.326	-0.0990 - 0.427	-0.0022 - 0.330
DR13	-0.0083 - 0.0168	-0.0162 - 0.0240	-0.0075 - 0.0166	-0.0149 - 0.0240	-0.0882 - 0.0973	-0.104 - 0.166	-0.201 - 0.234	-0.338 - 0.418	-0.907 - 0.986	-0.235 - 0.315
DR14	-0.0420 - 0.0011	-0.0528 - 0.0136	-0.0335 - -0.0087	-0.0379 - -0.0044	-0.0919 - 0.0496	-0.193 - 0.0270	-0.252 - 0.0887	-0.184 - 0.0107	-0.244 - 0.0708	-0.230 - 0.0566
DR15	-0.0052 - 0.0687	-0.0267 - 0.0894	0.0064 - 0.0571	-0.0044 - 0.0679	-0.0573 - 0.121	-0.116 - 0.553	-0.357 - 0.730	-0.0667 - 0.544	-0.256 - 0.733	-0.0067 - 0.484
DR16	-0.0682 - -0.0360	-0.0773 - -0.0277	-0.0611 - -0.0422	-0.0644 - -0.0389	-0.0924 - -0.0109	-0.144 - -0.0650	-0.166 - -0.0439	-0.139 - -0.0672	-0.161 - -0.0451	-0.161 - -0.0452
DR17	0.0020 - 0.0106	-0.0004 - 0.0130	0.0034 - 0.0092	0.0021 - 0.0105	-0.126 - 0.139	0.398 - 4.18	-0.822 - 5.12	0.649 - 4.11	-0.422 - 5.18	-0.211 - 4.97
DR19	-0.0937 - -0.0786	-0.0979 - -0.0742	-0.0907 - -0.0818	-0.0922 - -0.0802	-0.183 - 0.0109	-1.05 - -0.833	-1.11 - -0.769	-1.04 - -0.842	-1.10 - -0.781	-1.27 - -0.613
DR20	0.0890 - 0.112	0.0833 - 0.119	0.0933 - 0.107	0.0910 - 0.109	0.0008 - 0.199	1.05 - 1.40	0.971 - 1.53	1.05 - 1.37	0.955 - 1.47	0.857 - 1.57
DR21	-0.0593 - -0.0381	-0.0651 - -0.0320	-0.0548 - -0.0425	-0.0570 - -0.0404	-0.155 - 0.0574	-1.08 - -0.606	-1.23 - -0.476	-1.05 - -0.627	-1.18 - -0.495	-1.28 - -0.395
DR45	-0.0294 - -0.0163	-0.0327 - -0.0124	-0.0267 - -0.0190	-0.0281 - -0.0177	-0.141 - 0.0954	-1.29 - -0.601	-1.49 - -0.400	-1.27 - -0.635	-1.47 - -0.438	-1.72 - -0.187
DR46	0.0193 - 0.0324	0.0154 - 0.0358	0.0222 - 0.0298	0.0209 - 0.0311	-0.0606 - 0.113	0.121 - 0.235	0.0876 - 0.265	0.128 - 0.230	0.0969 - 0.261	-0.0485 - 0.407
DR47	-0.0021 - 0.0160	-0.0070 - 0.0208	0.0017 - 0.0122	-0.0001 - 0.0140	-0.0339 - 0.0478	-0.0082 - 0.0360	-0.0212 - 0.0481	-0.0060 - 0.0337	-0.0183 - 0.0460	-0.0438 - 0.0715
DR48	-0.0157 - 0.0200	-0.0272 - 0.0288	-0.0135 - 0.0197	-0.0237 - 0.0300	-0.0550 - 0.0612	-0.0618 - 0.0669	-0.109 - 0.0964	-0.166 - 0.184	-0.430 - 0.448	-0.0904 - 0.108
DR49	-0.0254 - -0.0132	-0.0286 - -0.0091	-0.0256 - -0.0136	-0.0293 - -0.0099	-0.0816 - 0.0424	-0.0848 - -0.0378	-0.0964 - -0.0206	-0.131 - 0.0043	-0.232 - 0.106	-0.174 - 0.0482
DR51	0.0256 - 0.0527	0.0188 - 0.0604	0.0298 - 0.0478	0.0260 - 0.0517	-0.0039 - 0.0815	0.0470 - 0.115	0.0282 - 0.134	0.0503 - 0.111	0.0316 - 0.129	0.0188 - 0.142
DR52	0.0517 - 0.0839	0.0439 - 0.0942	0.0563 - 0.0777	0.0518 - 0.0823	0.0263 - 0.108	0.0958 - 0.178	0.0778 - 0.208	0.0233 - 0.244	-0.143 - 0.410	0.0758 - 0.191
DR53	0.0052 - 0.0335	-0.0018 - 0.0421	0.0094 - 0.0284	0.0053 - 0.0324	-0.0230 - 0.0607	0.0049 - 0.0746	-0.0136 - 0.0976	0.0068 - 0.0700	-0.0128 - 0.0895	-0.0213 - 0.0981
DR54	0.0121 - 0.0566	0.0014 - 0.0705	0.0202 - 0.0461	0.0157 - 0.0507	-0.0639 - 0.130	0.0834 - 0.658	-0.0662 - 0.846	0.0990 - 0.610	-0.0589 - 0.768	0.0358 - 0.673
DR56	0.0627 - 0.0832	0.0562 - 0.0885	0.0664 - 0.0804	0.0634 - 0.0833	-0.0192 - 0.166	0.516 - 0.773	0.437 - 0.840	0.292 - 1.00	-0.243 - 1.54	0.369 - 0.926
DR57	0.0075 - 0.0441	-0.0011 - 0.0565	0.0126 - 0.0368	0.0074 - 0.0420	-0.0373 - 0.0867	0.0120 - 0.161	-0.0196 - 0.215	0.0140 - 0.146	-0.0267 - 0.186	-0.0317 - 0.191

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

Table C.10 (cont.).

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{sp} = n_{ss2} = 3$					EN 15522-2 scenario: A/B and $n_{sp} = n_{ss2} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR61	-0.0355 - 0.0174	-0.0496 - 0.0335	-0.0283 - 0.0081	-0.0360 - 0.0159	-0.0737 - 0.0535	-0.143 - 0.0797	-0.208 - 0.145	-0.337 - 0.269	-0.792 - 0.724	-0.151 - 0.0824
DR62	0.0387 - 0.0736	0.0300 - 0.0853	0.0385 - 0.0715	0.0284 - 0.0817	0.0139 - 0.0962	0.0690 - 0.162	0.0490 - 0.198	-0.0185 - 0.240	-0.213 - 0.434	0.0520 - 0.169
τ (%)	65.6	50.0	78.1	68.8	15.6	59.4	43.8	53.1	31.3	40.6

Blue background – Confidence interval that does not include the zero (non-equivalent DR).
 τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table C.11. Confidence limits of differences between DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering 95% and 98% confidence levels, for $A/(A+B)$ and A/B ratio formats, and triplicate and duplicate injections of the spill sample (Sp) and suspected source sample known not to be the origin of the spill (SS2) of the Round Robin Test 2020 (RR2020), respectively.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp} = n_{SS2} = 3$					EN 15522-2 scenario: A/B and $n_{Sp} = n_{SS2} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR33	-0.0488 - -0.0021	-0.0590 - 0.0154	-0.0427 - -0.0131	-0.0490 - -0.0068	-0.110 - 0.0540	-0.316 - 0.0250	-0.399 - 0.147	-0.605 - 0.280	-1.27 - 0.946	-0.360 - 0.0352
DR34	-0.0152 - 0.0369	-0.0324 - 0.0504	-0.0027 - 0.0276	-0.0079 - 0.0329	-0.0466 - 0.0715	-0.0644 - 0.127	-0.134 - 0.174	-0.0486 - 0.123	-0.102 - 0.176	-0.0648 - 0.139
DR35	0.0328 - 0.0765	0.0157 - 0.0865	0.0418 - 0.0716	0.0355 - 0.0780	0.0358 - 0.0777	0.0374 - 0.111	0.0069 - 0.127	0.0454 - 0.112	0.0250 - 0.132	0.0537 - 0.103
DR37	-0.0342 - 0.0030	-0.0453 - 0.0141	-0.0331 - 0.0004	-0.0435 - 0.0107	-0.0449 - 0.0121	-0.0613 - 0.0114	-0.0847 - 0.0337	-0.124 - 0.0718	-0.271 - 0.219	-0.0617 - 0.0099
DR40	-0.0705 - -0.0175	-0.0842 - -0.0008	-0.0601 - -0.0298	-0.0653 - -0.0245	-0.104 - 0.0145	-0.229 - -0.0310	-0.278 - 0.0384	-0.224 - -0.0477	-0.279 - 0.0070	-0.240 - -0.0323
DR43	-0.0862 - -0.0640	-0.0917 - -0.0564	-0.0817 - -0.0694	-0.0839 - -0.0672	-0.108 - -0.0433	-0.150 - -0.104	-0.161 - -0.0867	-0.148 - -0.108	-0.160 - -0.0956	-0.170 - -0.0855
DR44	-0.0736 - -0.0567	-0.0779 - -0.0510	-0.0731 - -0.0578	-0.0778 - -0.0531	-0.0812 - -0.0498	-0.0944 - -0.0699	-0.100 - -0.0609	-0.116 - -0.0503	-0.165 - -0.0008	-0.101 - -0.0652
DR78	-0.141 - -0.0603	-0.160 - -0.0318	-0.131 - -0.0774	-0.142 - -0.0659	-0.158 - -0.0500	-0.391 - -0.138	-0.443 - -0.0397	-0.390 - -0.168	-0.459 - -0.0993	-0.369 - -0.189
τ (%)	75.0	62.5	75.0	75.0	50.0	62.5	50.0	62.5	50.0	62.5

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table C.12. Mean value ($\bar{\delta}$) and relative standard deviation (RSD), based on three simulations, of total risk of true compositional equivalence claim between the spill sample (Sp) and the suspected source sample known to be the origin of the spill (SS1), from a single comparison trial, of the Round Robin Tests (RR) 2018, 2019 and 2020, estimated by the SC approach and by the MCM and S-t approaches considering 95% and 98% confidence levels, for $A/(A+B)$ and A/B ratio formats, and triplicate ($n_{Sp} = n_{SS1} = 3$) and duplicate ($n_{Sp} = n_{SS1} = 2$) injections of each sample.

RR	Number of <i>DR</i>	Simulation	Nordtest scenario: $A/(A+B)$ and $n_{Sp} = n_{SS1} = 3$					EN 15522-2 scenario: A/B and $n_{Sp} = n_{SS1} = 2$				
			MCM		S-t		SC	MCM		S-t		SC
			95%	98%	95%	98%		95%	98%	95%	98%	
2018	32	δ_1 (%)	83.2	93.7	62.0	78.6	91.3	83.3	93.0	82.2	93.1	18.6
		δ_2 (%)	83.4	93.5	62.4	78.8	91.8	82.8	93.4	81.7	93.5	17.9
		δ_3 (%)	83.3	93.0	62.6	78.6	91.3	82.7	93.1	81.4	93.3	18.3
		$\bar{\delta}$ (%)	83.3	93.4	62.3	78.7	91.5	82.9	93.2	81.8	93.3	18.3
		RSD (%)	0.11	0.37	0.49	0.19	0.35	0.35	0.18	0.51	0.22	1.8
2019	9	δ_1 (%)	85.9	94.6	68.1	81.7	85.2	85.6	94.3	85.8	94.8	53.8
		δ_2 (%)	86.1	94.3	67.9	81.2	85.4	85.9	94.4	86.7	95.1	55.0
		δ_3 (%)	86.2	94.4	67.5	81.6	85.8	85.7	94.4	86.4	94.5	55.0
		$\bar{\delta}$ (%)	86.1	94.4	67.8	81.5	85.5	85.7	94.36	86.3	94.8	54.6
		RSD (%)	0.16	0.13	0.43	0.28	0.33	0.20	0.049	0.49	0.32	1.2
2020	9	δ_1 (%)	87.2	94.9	67.0	81.4	89.9	86.5	94.5	83.4	93.4	72.1
		δ_2 (%)	87.1	95.0	66.6	80.9	89.9	87.1	94.8	83.6	93.6	71.5
		δ_3 (%)	87.4	95.0	66.7	80.9	89.5	88.0	95.2	84.6	94.1	73.0
		$\bar{\delta}$ (%)	87.2	94.99	66.8	81.1	89.7	87.2	94.9	83.9	93.7	72.2
		RSD (%)	0.19	0.058	0.38	0.37	0.22	0.89	0.36	0.73	0.38	1.1

Table C.13. Mean value ($\bar{\omega}$) and relative standard deviation (RSD), based on three simulations, of total risk of true compositional equivalence claim between the spill sample (Sp) and the suspected source sample known to be the origin of the spill (SS1), from two comparison trials, of the Round Robin Tests (RR) 2018, 2019 and 2020, estimated by the SC approach and by the MCM and S-t approaches considering 98% confidence levels, for $A/(A+B)$ and A/B ratio formats, and triplicate ($n_{Sp} = n_{SS1} = 3$) and duplicate ($n_{Sp} = n_{SS1} = 2$) injections of each sample.

RR	Number of <i>DR</i>	Simulation	Nordtest scenario: $A/(A+B)$ and $n_{Sp} = n_{SS1} = 3$			EN 15522-2 scenario: A/B and $n_{Sp} = n_{SS1} = 2$		
			MCM (98%)	S-t (98%)	SC	MCM (98%)	S-t (98%)	SC
2018	32	ω_1	100	97.1	100	100	99.7	91.6
		ω_2	100	97.0	100	100	99.9	91.6
		ω_3	100	97.0	100	100	99.8	91.4
		$\bar{\omega}$	100	97.0	100	100	99.8	91.5
		RSD (%)	-	0.052	0.015	-	0.11	0.10
2020	9	ω_1	100	98.0	99.8	100	99.8	98.4
		ω_2	100	97.6	99.9	100	99.7	98.4
		ω_3	100	98.2	99.9	100	99.8	98.7
		$\bar{\omega}$	100	97.9	99.9	100	99.8	98.5
		RSD (%)	-	0.32	0.061	-	0.038	0.15

Annex D

Supplementary material of Chapter 5

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D.1. List of compounds and labels

Table D.1. List of analysed compounds and their labels according to EN 15522-2 standard.

ID number	Compounds/ Set of compounds	Label
1	1-Methyladamantane	1-M-Adam
2	1,2-Dimethyladamantane	1,2-DM-Adam
3	2,6-Dimethylundecane	i-C13
4	2-Methyl-1,2,3,4-tetrahydronaphthalene	2-M-tetralin
5	<i>cis</i> -1,3,4-Trimethyladamantane	c-1,3,4-TM-Adam
6	Hexylbenzene	C6-Benz
7	2,6,10-Trimethylundecane	i-C14
8	2-Ethyladamantane	2-E-Adam
9	Sesquiterpane C ₁₄ H ₂₆ ⁽¹⁾	BS1
10	Unknown compound designation (*)	C3-de peak
11	Sesquiterpane C ₁₄ H ₂₆	BS2
12	Heptylbenzene	C7-Benz
13	Biphenyl	B
14	2-Ethyl-naphthalene	2-E-N
15	2,6 + 2,7-Dimethylnaphthalene	2,6+2,7-DM-N
16	3 rd eluted branched alkane with <i>m/z</i> 169 ⁽²⁾	Br-alk-169-3
17	Sesquiterpane C ₁₅ H ₂₈ ⁽¹⁾	BS4
18	8β(H)-Drimane ⁽¹⁾	BS5
19	Sesquiterpane C ₁₅ H ₂₈ ⁽¹⁾	BS6
20	Pentadecane	n-C15
21	Sesquiterpane C ₁₆ H ₂₀ ⁽¹⁾	BS8
22	Sesquiterpane C ₁₆ H ₂₀ ⁽¹⁾	BS9
23	<i>meta</i> -Octyltoluene	m-C8-Tol
24	8β(H)-Homodrimane ⁽¹⁾	BS10
25	<i>ortho</i> -Octyltoluene	o-C8-Tol
26	Norpristane	Norpri
27	<i>meta</i> -Nonyltoluene	m-C9-Tol
28	Decylbenzene	C10-Benz
29	Heptadecane	n-C17
30	Pristane	Pri
31	Undecylcyclohexane	n-C11-CyC6
32	Octadecane	n-C18
33	Phytane	Phy
34	4-Methyldibenzothiophene	4-M-Dbt
35	3 rd eluted branched alkane with <i>m/z</i> 225 ⁽²⁾	Br-alk-225-3
36	Nonadecane	n-C19
37	1-Methyldibenzothiophene	1-M-Dbt
38	2-Methylphenanthrene	2-M-Phe
39	Hexadecanoic acid methyl ester	FAME C16:0
40	1-Methylphenanthrene	1-M-Phe
41	C2-Dibenzothiophenes	C2-dbt_s
42	C2-Phenanthrenes/Anthracenes	C2-phe_s
43	Octadecanoic acid methyl ester	FAME C18:0
44	2-Methylfluoranthene	2-M-Fl
45	Pentadecylbenzene	C15-Benz
46	Benzo(a)fluorene	BaF
47	Retene	Retene
48	2-Methylpyrene	2-M-Py
49	4-Methylpyrene	4-M-Py
50	1-Methylpyrene	1-M-Py
51	C23-Tricyclic terpane	C23Tr
52	C24-Tricyclic terpane	C24Tr
53	Heptadecylbenzene	C17-Benz
54	5α(H),14β(H),17β(H),20(R+S)-Cholestane,	27bbR+S

(1) The label identifies the elution order of sesquiterpanes, e.g., BS1 and BS2 are the first and the second sesquiterpanes to elute.

(2) Compound identified by quantification *m/z* and elution order.

(*) Compound with quantification *m/z* 180 and the same retention time as BS2, eluting outside the elution range of C3-Decalins.

Table D.1 (cont.).

ID number	Compounds/ Set of compounds	Label
55	18 α (H)-22,29,30-Trisnorneohopane	27Ts
56	C26,20S-Triaromatic sterane	SC26 TA
57	17 α (H)-22,29,30-Trisnorhopane	27Tm
58	C26,20R + C27,20S-Triaromatic sterane	RC26+SC27 TA
59	24-Ethyl-5 α (H),14 β (H),17 β (H),20(R+S)-cholestane	29bbR+S
60	17 α (H),21 β (H)-28,30-Bisnorhopane	28ab
61	C28,20S-Triaromatic sterane	SC28 TA
62	17 α (H),21 β (H)-30-Norhopane	29ab
63	18 α (H)-Oleanane	30O
64	17 α (H),21 β (H)-Hopane	30ab
65	C28,20R-Triaromatic sterane	RC28 TA
66	17 α (H),21 β (H),22(S)-Homohopane	31abS
67	Gammacerane	30G
68	Decalin	De
69	1,3,5-Trimethyladamantane	1,3,5-TM-Adam
70	C1-Decalins	C1-de_s
71	2-Methyladamantane	2-M-Adam
72	1,2,3,4-Tetrahydronaphthalene	Tetralin
73	<i>cis</i> -1,4-Dimethyladamantane	c-1,4-DM-Adam
74	Naphthalene	N
75	<i>trans</i> -1,4-Dimethyladamantane	tr-1,4-DM-Adam
76	1,3,6-Trimethyladamantane	1,3,6-TM-Adam
77	C2-Decalins	C2-de_s
78	<i>trans</i> -1,3,4-Trimethyladamantane	tr-1,3,4-TM-Adam
79	1,2,5,7-Tetramethyladamantane	1,2,5,7-TeM-Adam
80	1-Methylnaphthalene	1-M-N
81	<i>meta</i> -Hexyltoluene	m-C6-Tol
82	1 st eluted branched alkane with <i>m/z</i> 169 ⁽²⁾	Br-Alk-169-1
83	<i>ortho</i> -Hexyltoluene	o-C6-Tol
84	2,6,10-Trimethyldodecane	i-C15
85	1,3 + 1,7-Dimethylnaphthalene	1,3+1,7-DM-N
86	1,6-Dimethylnaphthalene	1,6-DM-N
87	Sesquiterpane C ₁₅ H ₂₈ ⁽¹⁾	BS3
88	C2-Benzothiophenes	C2-bt_s
89	Acenaphthylene	ANY
90	<i>meta</i> -Heptyltoluene	m-C7-Tol
91	2 nd eluted branched alkane with <i>m/z</i> 169 ⁽²⁾	Br-Alk-169-2
92	1,2-Dimethylnaphtalene	1,2-DM-N
93	2,6,10-Trimethyltridecane	i-C16
94	<i>ortho</i> -Heptyltoluene	o-C7-Tol
95	Diamantane	Diam
96	Dodecanoic acid methyl ester	FAME C12:0
97	4-Methyldiamantane	4-M-Diam
98	1,3,7-Trimethylnaphthalene	1,3,7-TM-N
99	1,3,6-Trimethylnaphthalene	1,3,6-TM-N
100	Nonylcyclohexane	n-C9-CyC6
101	<i>ortho</i> -Nonyltoluene	o-C9-Tol
102	1,2,3,4,5,6,7,8-Octahydro-anthracene	8H-A
103	1-Methylfluorene	1-M-F
104	1,2,3,4,5,6,7,8-Octahydrophenanthrene	8H-Phe
105	Tetradecanoic acid methyl ester	FAME C14:0
106	1 st eluted branched alkane with <i>m/z</i> 225 ⁽²⁾	Br-alk-225-1
107	C2-Fluorenes	C2-f_s
108	2 nd eluted branched alkane with <i>m/z</i> 225 ⁽²⁾	Br-alk-225-2
109	<i>meta</i> -Undecyltoluene	m-C11-Tol
110	Dodecylbenzene	C12-Benz
111	<i>ortho</i> -Undecyltoluene	o-C11-Tol
112	<i>cis</i> -9-Hexadecenoic acid methyl ester	FAME C16:1
113	2-Methylantracene	2-M-A

(1) The label identifies the elution order of sesquiterpanes, e.g., BS1 and BS2 are the first and the second sesquiterpanes to elute.

(2) Compound identified by quantification *m/z* and elution order.

Table D.1 (cont.).

ID number	Compounds/ Set of compounds	Label
114	1-Ethylphenanthrene	1-E-Phe
115	1,7-Dimethylphenanthrene	1,7-DM-Phe
116	C3-Dibenzothiophenes	C3-dbt_s
117	<i>cis</i> -9,12-Octadecadienoic acid methyl ester	FAME C18:2
118	<i>cis</i> -9-Octadecenoic acid methyl ester + 9,12,15-Octadecatrienoic acid methyl ester	FAME C18:1+C18:3
119	C21-Tricyclic terpane	C21Tr
120	C3-Phenanthrenes/Anthracenes	C3-phe_s
121	C4-Phenanthrenes/Anthracenes	C4-phe_s
122	<i>cis</i> -11-Eicosenoic acid methyl ester	FAME C20:1
123	Tetramethylphenanthrene	Te-M-Phe
124	Eicosanoic acid methyl ester	FAME C20:0
125	C2-Fluoranthenes	C2-fl_s
126	Benzo(b)naphto(1,2-d)thiophene	BNT
127	C20-Triaromatic sterane	C20TA
128	C25-Tricyclic terpane (a+b)	C25Trab
129	C21-Triaromatic sterane	C21TA
130	Phytanyl-toluene	phy-tol
131	C1-Chrysenes	C1-chr
132	13 β (H),17 α (H),20S-Cholestane	27dbS
133	13 β (H),17 α (H),20R-Cholestane	27dbR
134	C28-Tricyclic terpane (22S)	C28(22S)
135	C29-Tricyclic terpane (22S)	C29(22S)
136	Benzo(e)pyrene	BePy
137	Benzo(a)pyrene	BaPy
138	24-Methyl-5 α (H),14 β (H),17 β (H),20(R+S)-cholestane	28bbR+S
139	24-Methyl-5 α (H),14 α (H),17 α (H),20R-cholestane	28aaR
140	24-Ethyl-5 α (H),14 α (H),17 α (H),20S-cholestane	29aaS
141	17 α (H),21 β (H)-25,28,30-Trisnorhopane	25nor30ab
142	24-Ethyl-5 α (H),14 α (H),17 α (H),20R-cholestane	29aaR
143	18 α (H)-30-Norneohopane	29Ts
144	17 β (H),21 α (H)-Hopane	30ba
145	17 α (H),21 β (H),22S-Bishomohopane	32abS

D.2. Experimental details

The experimental details present the combined SIM chromatograms of one of the injections performed for each sample (**Figure D.1**), the list of quantified and non-quantified compounds (**Table D.2**) for each analysed sample, the evaluation of compositional equivalence/difference and occurrence of weathering events (**Figures D.2, D.3 and D.4**), as well as the list of determined *DR* used in the comparison of each Sp with each SS (**Table D.3**).

▪ Analytical data

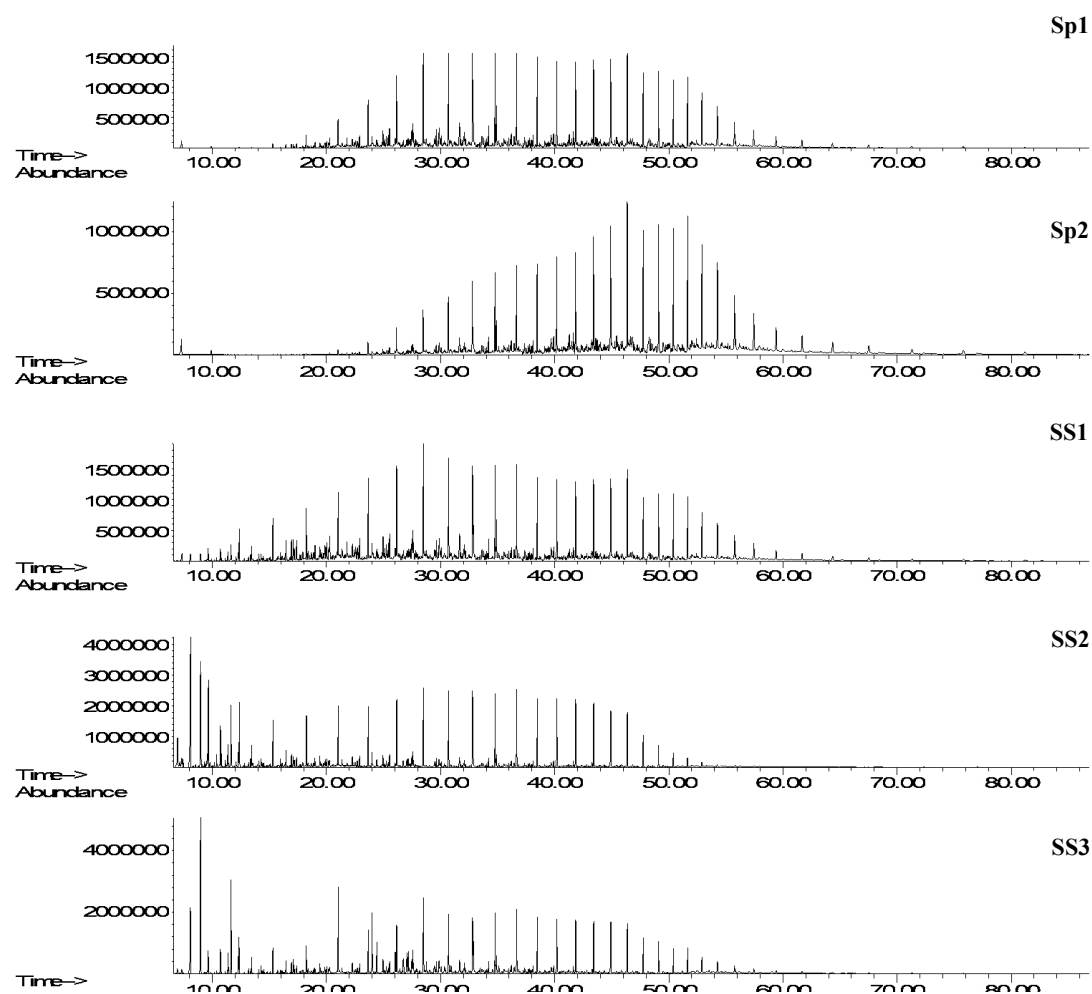


Figure D.1. Combined SIM chromatograms of the spill samples 1 and 2 (Sp1 and Sp2) and suspected source samples known to be the source of the spill (SS1) and not to be the origin of the spill (SS2 and SS3).

Figure D.1 shows that the chromatograms of Sp1 and Sp2 have some similarities with each other and with the chromatogram of SS1, suggesting that weathering events may have occurred, which explains the absence of compounds in the Sp that are first eluted. In contrast, the visual comparison of the Sp1 and Sp2 chromatograms with the SS2 and SS3 chromatograms revealed some differences in chemical composition.

Table D.2. List of quantified and unquantified compounds in the spill samples 1 and 2 (Sp1 and Sp2) and in the suspected source samples 1, 2 and 3 (SS1, SS2 and SS3).

Compounds		Sp1	Sp2	SS1	SS2	SS3
1	1-M-Adam	●	●	●	●	●
2	1,2-DM-Adam	●	●	●	●	●
3	i-C13	●	●	●	●	●
4	2-M-Tetralin	●	●	●	●	●
5	c-1,3,4-TM-Adam	●	●	●	●	●
6	C6_Benz	●	●	●	●	●
7	i-C14	●	●	●	●	●
8	2-E-Adam	●	●	●	●	●
9	BS1	●	●	●	●	●
10	C3-de peak	●	●	●	●	●
11	BS2	●	●	●	●	●
12	C7_Benz	●	●	●	●	●
13	B	●	●	●	●	●
14	2-E-N	●	●	●	●	●
15	2,6+2,7-DM-N	●	●	●	●	●
16	Br-Alk 169-3	●	●	●	●	●
17	BS4	●	●	●	●	●
18	BS5	●	●	●	●	●
19	BS6	●	●	●	●	●
20	n-C15	●	●	●	●	●
21	BS8	●	●	●	●	●
22	BS9	●	●	●	●	●
23	m-C8-Tol	●	●	●	●	●
24	BS10	●	●	●	●	●
25	o-C8-Tol	●	●	●	●	●
26	Norpri	●	●	●	●	●
27	m-C9-Tol	●	●	●	●	●
28	C10_Benz	●	●	●	●	●
29	n-C17	●	●	●	●	●
30	Pri	●	●	●	●	●
31	n-C11-CyC6	●	●	●	●	●
32	n-C18	●	●	●	●	●
33	Phy	●	●	●	●	●
34	4-M-Dbt	●	●	●	●	●
35	Br-Alk 225-3	●	●	●	●	●
36	n-C19	●	●	●	●	●
37	1-M-Dbt	●	●	●	●	●
38	2-M-Phe	●	●	●	●	●
39	FAME C16:0	○	○	○	●	○
40	1-M-Phe	●	●	●	●	●
41	C2-dbt_s	●	●	●	●	●
42	C2-phe_s	●	●	●	●	●
43	FAME C18:0	○	○	○	○	○
44	2-M-Fl	●	●	●	S/N < 5	S/N < 5
45	C15-Benz	●	●	●	●	●
46	BaF	●	●	●	●	●
47	Retene	○	○	○	○	●
48	2-M-Py	●	●	●	●	●
49	4-M-Py	●	●	●	●	●
50	1-M-Py	●	●	●	●	●
51	C23Tr	●	●	●	●	●
52	C24Tr	○	○	○	○	S/N < 5
53	C17-Benz	●	●	●	●	●
54	27bbR+S	●	●	●	●	●
55	27Ts	●	●	●	●	●
56	SC26 TA	●	●	●	●	●
57	27Tm	●	●	●	●	●
58	RC26TA+SC27 TA	●	●	●	●	●
59	29bbR+S	●	●	●	●	●

S/N – signal-to-noise ratio.

● Quantified compound/ set of compounds.

○ Absence.

Table D.2 (cont.).

Compounds	Sp1	Sp2	SS1	SS2	SS3
60 28ab	$S/N < 5$	$S/N < 3$	$S/N < 5$	○	$S/N < 3$
61 SC28 TA	●	●	●	●	●
62 29ab	●	●	●	●	●
63 30O	○	○	○	○	○
64 30ab	●	●	●	●	●
65 RC28 TA	●	●	●	●	●
66 31abS	●	●	●	●	●
67 30G	●	●	●	●	●
68 De	●	●	●	●	●
69 1,3,5-TM-Adam	●	●	●	●	●
70 C1-de_s	●	●	●	●	●
71 2-M-Adam	●	●	●	●	●
72 Tetralin	●	●	●	●	●
73 c-1,4-DM-Adam	●	●	●	●	●
74 N	●	●	●	●	●
75 tr-1,4-DM-Adam	●	●	●	●	●
76 1,3,6-TM-Adam	●	●	●	●	●
77 C2-de_s	●	●	●	●	●
78 tr-1,3,4-TM-Adam	●	●	●	●	●
79 1,2,5,7-TeM-Adam	●	●	●	●	●
80 1-M-N	●	●	●	●	●
81 m-C6-Tol	●	●	●	●	●
82 Br-Alk-169-1	●	●	●	●	●
83 o-C6-Tol	●	●	●	●	●
84 i-C15	●	●	●	●	●
85 1,3+1,7-DM-N	●	●	●	●	●
86 1,6-DM-N	●	●	●	●	●
87 BS3	●	●	●	●	●
88 C2-bt_s	○	○	○	●	●
89 ANY	●	●	●	●	●
90 m-C7-Tol	●	●	●	●	●
91 Br-Alk-169-2	●	●	●	●	●
92 1,2 -DM-N	●	●	●	●	●
93 i-C16	●	●	●	●	●
94 o-C7-Tol	●	●	●	●	●
95 Diam	●	●	●	●	●
96 FAME C12:0	○	○	○	○	○
97 4-M-Diam	○	○	○	○	●
98 1,3,7-TM-N	●	●	●	●	●
99 1,3,6-TM-N	●	●	●	●	●
100 n-C9-CyC6	●	●	●	●	●
101 o-C9-Tol	●	●	●	●	●
102 8H-A	●	●	●	●	○
103 1-M-F	●	●	●	●	●
104 8H-Phe	●	●	●	●	○
105 FAME C14:0	○	○	○	○	○
106 Br-alk-225-1	●	●	●	●	●
107 C2-f_s	●	●	●	●	●
108 Br-alk-225-2	●	●	●	●	●
109 m-C11-Tol	●	●	●	●	●
110 C12-Benz	●	●	●	●	●
111 o-C11-Tol	●	●	●	●	●
112 FAME C16:1	○	○	○	○	○
113 2-M-A	●	●	●	○	○
114 1-E-Phe	●	●	●	●	●
115 1,7 DM-Phe	●	●	●	●	●
116 C3-dbt_s	●	●	●	●	●
117 FAME C18:2	○	○	○	○	○
118 FAME C18:1+C18:3	○	○	○	○	○
119 C21Tr	●	●	●	●	●

S/N – signal-to-noise ratio.

● Quantified compound/ set of compounds.

○ Absence.

Table D.2 (cont.).

Compounds		Sp1	Sp2	SS1	SS2	SS3
120	C3-phe_s	●	●	●	●	●
121	C4-phe_s	●	●	●	●	●
122	FAME C20:1	○	○	○	○	○
123	Te-M-Phe	●	●	●	●	●
124	FAME C20:0	○	○	○	○	○
125	C2-fl_s	●	●	●	●	●
126	BNT	<i>S/N < 5</i>	<i>S/N < 5</i>	<i>S/N < 5</i>	●	●
127	C20TA	<i>S/N < 5</i>	<i>S/N < 5</i>	<i>S/N < 5</i>	●	●
128	C25Trab	●	●	●	●	●
129	C21 TA	<i>S/N < 5</i>	<i>S/N < 5</i>	<i>S/N < 5</i>	●	●
130	Phy-Tol	●	●	●	●	●
131	C1-chr	●	●	●	●	●
132	27dbS	<i>S/N < 5</i>	<i>S/N < 5</i>	<i>S/N < 5</i>	●	●
133	27dbR	<i>S/N < 5</i>	<i>S/N < 5</i>	<i>S/N < 5</i>	●	●
134	C28 (22S)	●	●	●	●	<i>S/N < 3</i>
135	C29 (22S)	●	●	●	●	<i>S/N < 3</i>
136	BePy	●	●	●	○	○
137	BaPy	●	●	●	○	○
138	28bbR+S	●	●	●	●	●
139	28aaR	●	●	●	●	●
140	29aaS	●	●	●	●	●
141	25nor30ab	○	○	○	○	●
142	29aaR	●	●	●	●	●
143	29Ts	n.q. (poor resolution)	n.q. (poor resolution)	n.q. (poor resolution)	n.q. (poor resolution)	n.q. (poor resolution)
144	30ba	●	●	●	●	●
145	32abS	●	●	●	●	●

S/N - signal-to-noise ratio.

n.q. – not quantified.

● Quantified compound/ set of compounds.

○ Absence.

▪ Percentage of weathering plots

A chromatographic signal of a given compound (*A*) was assumed to be adequately determined if the percentage of the lowest signal from the set of triplicate injections considered, relative to the highest signal from the same set, both normalised to the signal of an unweathered compound present in both injections (*H*) ($(A/H)_{\text{Min}}/(A/H)_{\text{Max}}$), are in the range of 85% and 118% (CEN, 2023). The weathering assessment was performed equivalently determining for each triplicate injection, the percentage of the *A* signal in Sp in relation to the *A* signal in SS, both normalised with the *H* signal ($(A/H)_{\text{Sp}}/(A/H)_{\text{SS}}$). The mean percentages ($\overline{(A/H)_{\text{Sp}}}/\overline{(A/H)_{\text{SS}}}$) determined for all compounds were represented as a function of the retention time of their chromatographic peaks. This representations are designated as Percentage Weathering (PW)-plots (**Figures D.2, D.3 and D.4**) and enables the assessment of the weathering occurrence or compositional discrepancies between Sp and SS, which are identified if, for some compounds, $\overline{(A/H)_{\text{Sp}}}/\overline{(A/H)_{\text{SS}}}$ is lower than 85% or higher than 118%, respectively (CEN, 2023).

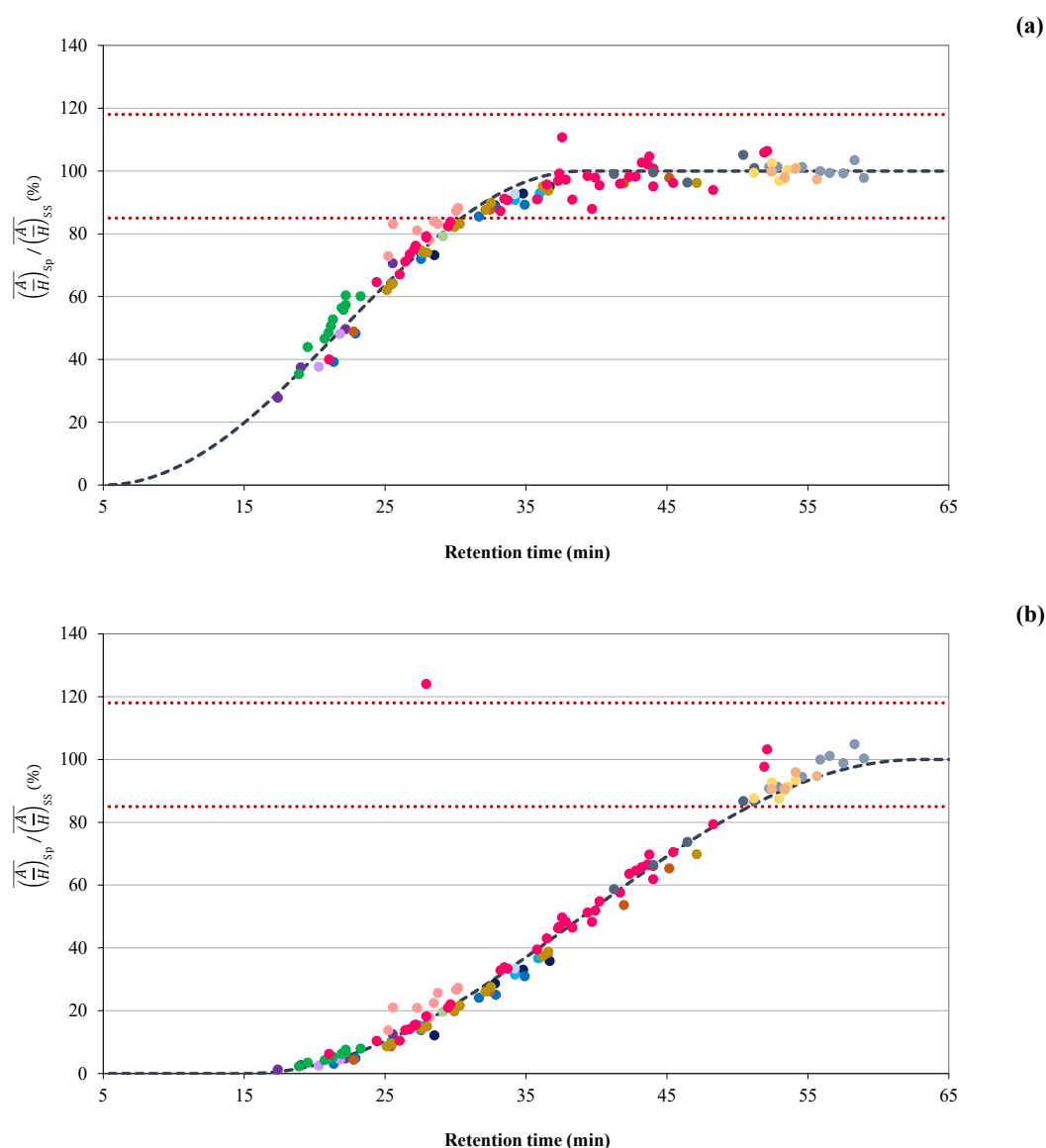


Figure D.2. Assessment of weathering and compositional equivalence of the spill samples 1 and 2 (Sp1 and Sp2, respectively) and the suspected source sample 1 (SS1), using PW-plots with data from the first *DR* comparison trial: (a) Sp1 vs. SS1 and (b) Sp2 vs. SS1. ● *n*-Alkanes; ● Isoprenoids; ● Branched alkanes; ● *n*-Alkylcyclohexanes; ● Decalins; ● Tetralins; ● Adamantanes; ● Diamantanes; ● Sesquiterpanes; ● Alkylbenzenes; ● Alkyltoluenes; ● PAH; ● Tricyclic terpanes; ● Hopanes; ● Steranes; ● Triaromatic steranes; ● FAME; --- evaporation curve, according to EN 15522-2; acceptable range for equivalence of compounds' contents in the spill and suspected source samples compared (85% to 118%). (1) Acenaphthylene, ANY, is often found at concentrations below the detection limit, yet abundant in burning residues. The EN 15522-2 standard defines it as a marker of the incidence of burning.

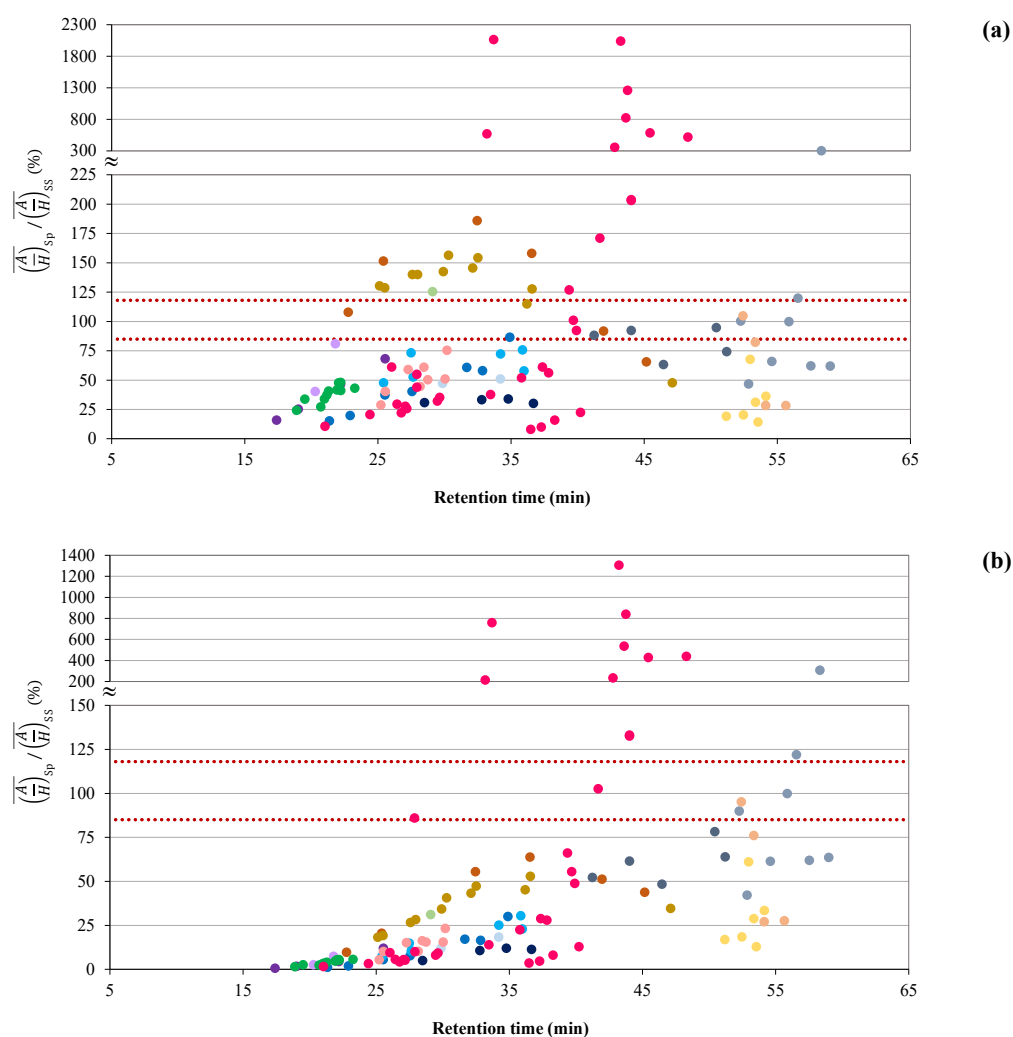


Figure D.3. Assessment of weathering and compositional equivalence of the spill samples 1 and 2 (Sp1 and Sp2, respectively) and the suspected source sample 2 (SS2), using PW-plots with data from the first *DR* comparison trial: (a) Sp1 vs. SS2 and (b) Sp2 vs. SS2. ● *n*-Alkanes; ● Isoprenoids; ● Branched alkanes; ● *n*-Alkylcyclohexanes; ● Decalins; ● Tetralins; ● Adamantanes; ● Diamantanes; ● Sesquiterpanes; ● Alkylbenzenes; ● Alkyltoluenes; ● PAH; ● Tricyclic terpanes; ● Hopanes; ● Steranes; ● Triaromatic steranes; ● FAME; acceptable range for equivalence of compounds' contents in the spill and suspected source samples compared (85% to 118%).

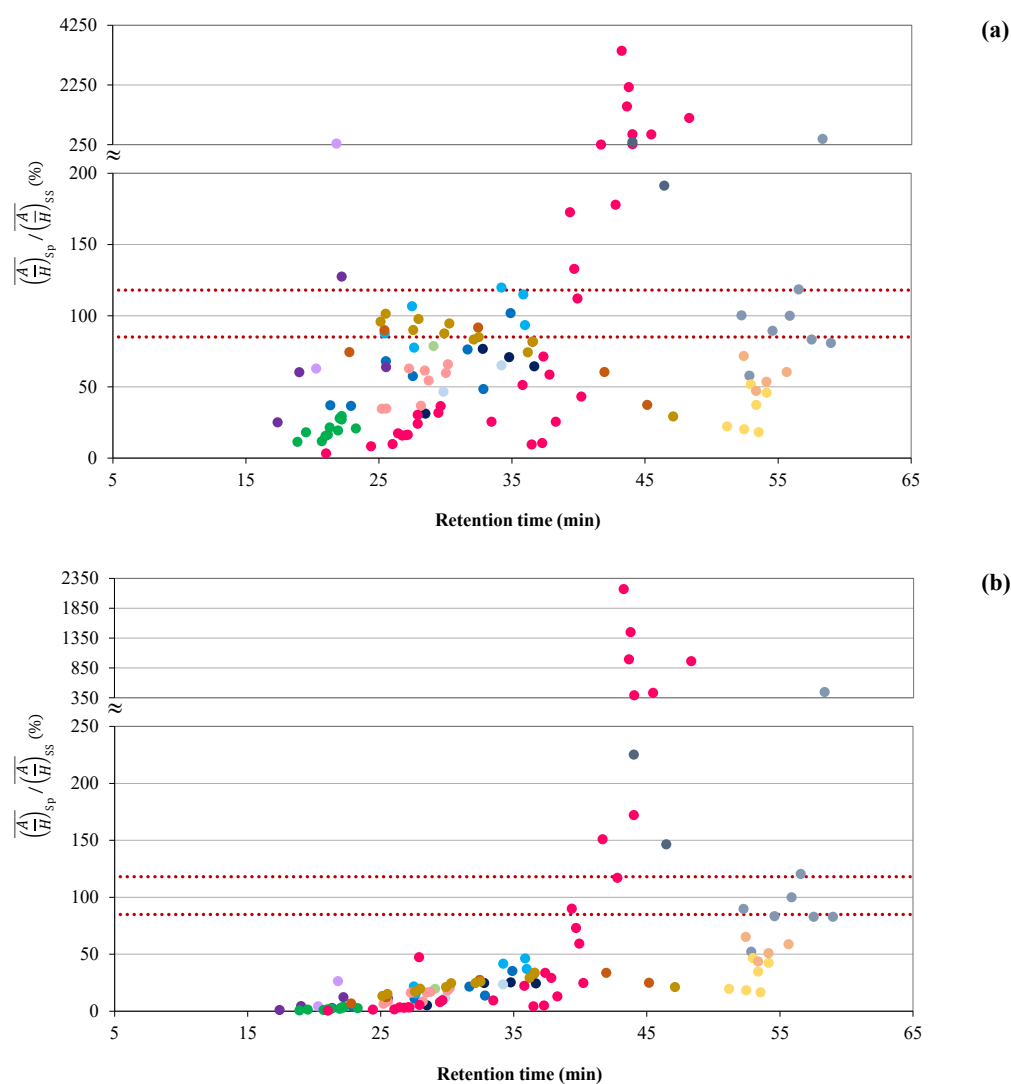


Figure D.4. Assessment of weathering and compositional equivalence of the spill samples 1 and 2 (Sp1 and Sp2, respectively) and the suspected source sample 3 (SS3), using PW-plots with data from the first *DR* comparison trial: (a) Sp1 vs. SS3 and (b) Sp2 vs. SS3. ● *n*-Alkanes; ● Isoprenoids; ● Branched alkanes; ● *n*-Alkylcyclohexanes; ● Decalins; ● Tetralins; ● Adamantanes; ● Diamantanes; ● Sesquiterpanes; ● Alkylbenzenes; ● Alkyltoluenes; ● PAH; ● Tricyclic terpanes; ● Hopanes; ● Steranes; ● Triaromatic steranes; ● FAME; acceptable range for equivalence of compounds' contents in the spill and suspected source samples compared (85% to 118%).

The PW-plots obtained for comparing the pairs Sp1 and Sp2 vs. SS1, Sp1 and Sp2 vs. SS2, and Sp1 and Sp2 vs. SS3, respectively, support the qualitative assessments derived from the visual chromatogram comparison. Sp1 and Sp2 have an analogous composition to SS1 (**Figure D.2**) because $\overline{(A/H)}_{\text{Sp}}/\overline{(A/H)}_{\text{SS}}$ of the most weathering-resistant compounds are between the 85% and 118% criteria, attesting the similar relative amounts in the two samples. The remaining compounds were found in lower abundance in Sp1 and Sp2 compared to SS1, *i.e.*, less than the 85% criterion, indicating weathering. Furthermore, $\overline{(A/H)}_{\text{Sp}}/\overline{(A/H)}_{\text{SS}}$ follow a typical evaporation pattern, as shown by the evaporation curve predicted by the EN 15522-2, demonstrating the occurrence of weathering events, which are, as expected, more prominent in the *in situ* burned spilt oil (Sp2) than the spilt oil collected before the *in situ* burning (Sp1) (CEN, 2023). In contrast, compositional differences between weathering-resistant compounds in Sp1 and SS2 and SS3, as well as between Sp2 and SS2 and SS3 were found and illustrated in the PW-plots shown in **Figures D.3** and **D.4**. These differences are explained not only by some stable compounds being in greater abundance in Sp1 and Sp2 than in SS2 and SS3 (*e.g.*, steranes and hopanes), with $\overline{(A/H)}_{\text{Sp}}/\overline{(A/H)}_{\text{SS}}$ greater than the 118% criterion, but also the less abundant, with $\overline{(A/H)}_{\text{Sp}}/\overline{(A/H)}_{\text{SS}}$ less than the 85% criterion, be both prone to weathering (*e.g.*, adamantanes, sesquiterpanes, polycyclic aromatic hydrocarbons) and stable (*e.g.*, steranes and hopanes) to weathering.

▪ Diagnostic ratio

Table D.3. List of diagnostic ratios and their corresponding *DR* code used for the comparison of the spill samples 1 and 2 (Sp1 and Sp2) with the suspected source samples 1, 2 and 3 (SS1, SS2 and SS3).

<i>DR</i> code	Diagnostic ratio	Sp1 vs. SS1	Sp1 vs. SS2	Sp1 vs. SS3	Sp2 vs. SS1	Sp2 vs. SS2	Sp2 vs. SS3
Normative ratio (NR)							
<i>DR01</i>	1-M-Adam/1,2-DM-Adam	-	-	-	-	-	-
<i>DR02</i>	1-M-Adam/2-E-Adam	-	-	-	-	-	-
<i>DR03</i>	i-C13/2-M-tetralin	-	-	-	-	-	-
<i>DR04</i>	c-1,3,4-TM-Adam/2-E-Adam	-	-	-	-	-	-
<i>DR05</i>	C6-/C7-Benz	-	-	-	-	-	-
<i>DR06</i>	2-E-Adam/i-C14	-	-	-	-	-	-
<i>DR07</i>	BS1/BS2	-	-	-	-	-	-
<i>DR08</i>	C3-de peak/BS2	-	-	-	-	-	-
<i>DR09</i>	B/2-E-N	-	-	-	-	-	-
<i>DR10</i>	2-E-N/2,6+2,7-DM-N	-	-	-	-	-	-
<i>DR11</i>	BS4/BS5	-	-	-	-	-	-
<i>DR12</i>	Br-alk-169-3/n-C15	-	-	-	-	-	-
<i>DR13</i>	BS5/BS6	-	-	-	-	-	-
<i>DR14</i>	BS8/BS9	-	-	-	-	-	-
<i>DR15</i>	m-/o-C8-Tol	-	-	-	-	-	-
<i>DR16</i>	BS10/Norpri	-	-	-	-	-	-
<i>DR17</i>	Norpri/m-C9-Tol	-	-	-	-	-	-
<i>DR18</i>	C10-Benz/n-C11-CyC6	-	-	-	-	-	-
<i>DR19</i>	n-C17/Pri	●	●	●	○ ⁽¹⁾	○ ⁽¹⁾	○ ⁽¹⁾
<i>DR20</i>	Pri/Phy	●	●	●	○ ⁽¹⁾	○ ⁽¹⁾	○ ⁽¹⁾
<i>DR21</i>	n-C18/Phy	●	●	●	○ ⁽¹⁾	○ ⁽¹⁾	○ ⁽¹⁾
<i>DR22</i>	4-M-Dbt/1-M-Dbt	●	●	●	○ ⁽¹⁾	○ ⁽¹⁾	○ ⁽¹⁾
<i>DR23</i>	Br-alk-225-3/n-C19	●	●	●	○ ⁽¹⁾	○ ⁽¹⁾	○ ⁽¹⁾
<i>DR24</i>	2-M-Phe/1-M-Phe	●	●	●	○ ⁽¹⁾	○ ⁽¹⁾	○ ⁽¹⁾
<i>DR25</i>	FAME C16:0/C18:0	○ ⁽²⁾	○ ⁽²⁾	○ ⁽²⁾	○ ⁽²⁾	○ ⁽²⁾	○ ⁽²⁾
<i>DR26</i>	C2-dbt_s/C2-phe_s	●	●	●	○ ⁽¹⁾	○ ⁽¹⁾	○ ⁽¹⁾
<i>DR27</i>	2-M-FI/4-M-Py	●	○ ⁽²⁾	○ ⁽²⁾	○ ⁽¹⁾	○ ^(1; 2)	○ ^(1; 2)
<i>DR28</i>	C15-/C17-Benz	-	-	-	-	-	-
<i>DR29</i>	BaF/4-M-Py	●	●	●	○ ⁽¹⁾	○ ⁽¹⁾	○ ⁽¹⁾

- Normative ratio to be determined for an oil type different from that present in the samples of the current study.

● Normative ratio determined considering the oil type of the samples (heavy fuel oil (Sp1/Sp2 vs. SS1); heavy fuel oil and crude oil (Sp1/Sp2 vs. SS2/SS3)).

○ Normative ratio not determined considering the oil type of the samples (heavy fuel oil (Sp1/Sp2 vs. SS1); heavy fuel oil and crude oil (Sp1/Sp2 vs. SS2/SS3)).

(1) *DR* not determined because at least one of the compounds that define the ratio was weathered in the Sp; weathering assessed by the sample pair known to have equivalent composition (Sp1/Sp2 vs. SS1).

(2) *DR* not determined because at least one of the compounds that define the ratio is absent or shows the chromatographic signal with $S/N < 5$ in one of both Sp and SS.

Table D.3 (cont.).

DR code	Diagnostic ratio	Sp1 vs. SS1	Sp1 vs. SS2	Sp1 vs. SS3	Sp2 vs. SS1	Sp2 vs. SS2	Sp2 vs. SS3
Normative ratio (NR) (cont.)							
DR30	Retene/29bb	-	○ (2)	○ (2)	-	○ (2)	○ (2)
DR31	2-M-Py/4-M-Py	●	●	●	○ (1)	○ (1)	○ (1)
DR32	1-M-Py/4-M-Py	●	●	●	○ (1)	○ (1)	○ (1)
DR33	C23Tr/C24Tr	-	-	-	-	-	-
DR34	27bb/29bb	●	●	●	○ (1)	○ (1)	○ (1)
DR35	27Ts/30ab	●	●	●	●	●	●
DR36	SC26/RC26+SC27 TA	●	●	●	●	●	●
DR37	27Tm/30ab	●	●	●	●	●	●
DR38	28ab/30ab	○ (2)	○ (2)	○ (2)	○ (2)	○ (2)	○ (2)
DR39	SC28/RC26+SC27 TA	●	●	●	●	●	●
DR40	29ab/30ab	●	●	●	●	●	●
DR41	30O/30ab	○ (2)	○ (2)	○ (2)	○ (2)	○ (2)	○ (2)
DR42	RC28/RC26+SC27 TA	●	●	●	●	●	●
DR43	31abS/30ab	●	●	●	●	●	●
DR44	30G/30ab	●	●	●	●	●	●
Informative ratio (IR)							
DR45	De/1-M-Adam	□ (1)	□ (1)	□ (1)	□ (1; 3)	□ (1; 3)	□ (1; 3)
DR46	1-M-Adam/2-M-Adam	□ (1)	□ (1)	□ (1)	□ (1; 3)	□ (1; 3)	□ (1; 3)
DR47	1,3,5-TM-Adam/tr-1,4-DM-Adam	□ (1)	□ (1)	□ (1)	□ (1; 3)	□ (1; 3)	□ (1; 3)
DR48	1,3,5-TM-Adam/1,3,6-TM-Adam	□ (1)	□ (1)	□ (1)	□ (1; 3)	□ (1; 3)	□ (1; 3)
DR49	C1-de _s /C2-de _s	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)
DR50	Tetralin/2-M-Tetralin	□ (1)	□ (1)	□ (1)	□ (1; 3)	□ (1; 3)	□ (1; 3)
DR51	1,2,5,7-TeM-Adam/2-E-Adam	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)
DR52	1,2,5,7-TeM-Adam/BS10	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)
DR53	m-C6-Tol/BS10	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)
DR54	m-/o-C6-Tol	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)
DR55	C7-/C10-Benz	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)
DR56	BS3/BS5	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)
DR57	1,6-DM-N/1,3+1,7-DM-N	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)
DR58	ANY/1,2-DM-N	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)	□ (1)

- Normative ratio to be determined for an oil type different from that present in the samples of the current study.

● Normative ratio determined considering the oil type of the samples (heavy fuel oil (Sp1/Sp2 vs. SS1); heavy fuel oil and crude oil (Sp1/Sp2 vs. SS2/SS3)).

○ Normative ratio not determined considering the oil type of the samples (heavy fuel oil (Sp1/Sp2 vs. SS1); heavy fuel oil and crude oil (Sp1/Sp2 vs. SS2/SS3)).

□ Informative ratio not determined.

(1) DR not determined because at least one of the compounds that define the ratio was weathered in the Sp; weathering assessed by the sample pair known to have equivalent composition (Sp1/Sp2 vs. SS1).

(2) DR not determined because at least one of the compounds that define the ratio is absent or shows the chromatographic signal with $S/N < 5$ in one of both Sp and SS.

(3) DR not determined because the chromatographic signal of at least one of the compounds that define the ratio has not been accurately quantified in one of both Sp and SS.

Table D.3 (cont.).

DR code	Diagnostic ratio	Sp1 vs. SS1	Sp1 vs. SS2	Sp1 vs. SS3	Sp2 vs. SS1	Sp2 vs. SS2	Sp2 vs. SS3
Informative ratio (IR) (cont.)							
DR59	Diam/4-M-Diam	☐ (1)	☐ (1; 2)	☐ (1; 2)	☐ (1; 2)	☐ (1; 2)	☐ (1; 2)
DR60	FAME C12:0/C16:0	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)
DR61	1,3,7-TM-N/1,3,6-TM-N	☐ (1)	☐ (1)	☐ (1)	☐ (1)	☐ (1)	☐ (1)
DR62	BS8/BS10	☐ (1)	☐ (1)	☐ (1)	☐ (1)	☐ (1)	☐ (1)
DR63	8H-A/8H-Phe	■	■	☐ (2)	☐ (1)	☐ (1)	☐ (1; 2)
DR64	1-M-F/8H-Phe	■	■	☐ (2)	☐ (1)	☐ (1)	☐ (1; 2)
DR65	FAME C14:0/C16:0	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)
DR66	FAME C16:1/C16:0	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)
DR67	1-E-Phe/1,7-DM-Phe	■	■	■	☐ (1)	☐ (1)	☐ (1)
DR68	C3-dbt _s /C3-phe _s	■	■	■	☐ (1)	☐ (1)	☐ (1)
DR69	FAME C18:2/C18:0	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)
DR70	FAME C18:1+C18:3/C18:0	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)
DR71	C21Tr/C23Tr	■	■	☐ (2)	☐ (1)	☐ (1)	☐ (1; 2)
DR72	C23Tr/phy-tol	■	■	■	☐ (1)	☐ (1)	☐ (1)
DR73	FAME C20:0/C18:0	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)
DR74	C20TA/C21TA	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)
DR75	C21TA/RC26+SC27 TA	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)	☐ (2)
DR76	C28(22S)/30ab	■	■	☐ (2)	☐ (1)	☐ (1)	☐ (1; 2)
DR77	BaPy/BePy	☐ (3)	☐ (2; 3)	☐ (2; 3)	☐ (1)	☐ (1; 3)	☐ (1; 3)
DR78	29aaS/29aaR	■	■	■	☐ (1)	☐ (1)	☐ (1)
Normative ratios determined (of 44)		20	19	19	8	8	8
Informative ratios determined (of 34)		8	8	4	0	0	0
Total of diagnostic ratios determined (of 78)		28	27	23	8	8	8

■ Informative ratio determined.

☐ Informative ratio not determined.

(1) DR not determined because at least one of the compounds that define the ratio was weathered in the Sp; weathering assessed by the sample pair known to have equivalent composition (Sp1/Sp2 vs. SS1).

(2) DR not determined because at least one of the compounds that define the ratio is absent or shows the chromatographic signal with $S/N < 5$ in one of both Sp and SS.

(3) DR not determined because the chromatographic signal of at least one of the compounds that define the ratio has not been accurately quantified in one of both Sp and SS.

D.3. Detailed results

▪ Assessment of Sp and SS oil patterns equivalence

Tables D.4 to D.21 and Figures D.5 to D.10 present the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ confidence intervals obtained for each of the three *DR* comparison trials performed by the three approaches applying the Nordtest and EN 15522-2 scenarios.

Table D.4. First trial of confidence limits of the difference between the *DR* means $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% (*P2.5* and *P97.5*) and 98% (*P1* and *P99*), for the comparison of *DR* observed in the spill sample 1 (Sp1) and in the suspected source sample 1 (SS1, known to be the origin of the spill), applying the *DR* comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp1} = n_{SS1} = 3$					EN 15522-2 scenario: A/B and $n_{Sp1} = n_{SS1} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	<i>P2.5 - P97.5</i>	<i>P1 - P99</i>	<i>P2.5 - P97.5</i>	<i>P1 - P99</i>	$SC_{LL} - SC_{UL}$	<i>P2.5 - P97.5</i>	<i>P1 - P99</i>	<i>P2.5 - P97.5</i>	<i>P1 - P99</i>	$SC_{LL} - SC_{UL}$
DR19	-0.0340 - 0.0341	-0.0557 - 0.0522	-0.0182 - 0.0210	-0.0251 - 0.0278	-0.105 - 0.107	-0.743 - 0.706	-1.26 - 1.17	-0.609 - 0.655	-1.00 - 1.05	-0.415 - 0.460
DR20	-0.0151 - 0.0142	-0.0221 - 0.0252	-0.0104 - 0.0059	-0.0132 - 0.0088	-0.0657 - 0.0612	-0.0595 - 0.0642	-0.0909 - 0.118	-0.0591 - 0.0442	-0.0910 - 0.0761	-0.123 - 0.109
DR21	-0.0150 - 0.0292	-0.0328 - 0.0442	-0.0063 - 0.0224	-0.0124 - 0.0285	-0.0924 - 0.109	-0.260 - 0.442	-0.532 - 0.676	-0.200 - 0.403	-0.386 - 0.589	-0.254 - 0.458
DR22	-0.0171 - 0.0151	-0.0272 - 0.0299	-0.0111 - 0.0073	-0.0143 - 0.0105	-0.115 - 0.111	-0.572 - 0.530	-0.915 - 1.06	-0.535 - 0.429	-0.834 - 0.728	-0.648 - 0.542
DR23	-0.0125 - 0.0017	-0.0169 - 0.0065	-0.0123 - 0.0008	-0.0164 - 0.0049	-0.0735 - 0.0620	-0.0535 - 0.0125	-0.0743 - 0.0350	-0.112 - 0.0684	-0.247 - 0.204	-0.153 - 0.110
DR24	-0.0231 - 0.0285	-0.0448 - 0.0435	-0.0120 - 0.0214	-0.0191 - 0.0285	-0.0816 - 0.0909	-0.218 - 0.227	-0.443 - 0.403	-0.521 - 0.584	-1.35 - 1.41	-0.194 - 0.256
DR26	-0.0071 - 0.0104	-0.0136 - 0.0148	-0.0062 - 0.0105	-0.0114 - 0.0157	-0.0081 - 0.0125	-0.0112 - 0.0139	-0.0211 - 0.0202	-0.0325 - 0.0376	-0.0853 - 0.0904	-0.0086 - 0.0136
DR27	-0.0253 - 0.0182	-0.0389 - 0.0347	-0.0154 - 0.0072	-0.0194 - 0.0112	-0.0209 - 0.0127	-0.0401 - 0.0318	-0.0661 - 0.0635	-0.0330 - 0.0224	-0.0501 - 0.0395	-0.0244 - 0.0138
DR29	-0.0201 - 0.0113	-0.0274 - 0.0263	-0.0169 - 0.0030	-0.0212 - 0.0073	-0.0401 - 0.0263	-0.0396 - 0.0296	-0.0547 - 0.0645	-0.0401 - 0.0163	-0.0576 - 0.0337	-0.0554 - 0.0316
DR31	-0.0316 - 0.0353	-0.0571 - 0.0637	-0.0174 - 0.0204	-0.0241 - 0.0271	-0.0680 - 0.0710	-0.156 - 0.172	-0.290 - 0.330	-0.136 - 0.148	-0.223 - 0.235	-0.132 - 0.144
DR32	-0.0114 - 0.0297	-0.0209 - 0.0486	-0.0107 - 0.0229	-0.0211 - 0.0333	-0.0591 - 0.0714	-0.0539 - 0.123	-0.100 - 0.214	-0.190 - 0.233	-0.509 - 0.552	-0.101 - 0.144
DR34	-0.0173 - 0.0185	-0.0244 - 0.0347	-0.0170 - 0.0126	-0.0262 - 0.0217	-0.0716 - 0.0671	-0.0810 - 0.0933	-0.121 - 0.176	-0.221 - 0.203	-0.540 - 0.522	-0.146 - 0.128
DR35	-0.0068 - 0.0127	-0.0111 - 0.0216	-0.0049 - 0.0082	-0.0077 - 0.0110	-0.0190 - 0.0224	-0.0119 - 0.0220	-0.0199 - 0.0393	-0.0126 - 0.0173	-0.0219 - 0.0265	-0.0220 - 0.0266
DR36	-0.0214 - 0.0392	-0.0324 - 0.0674	-0.0220 - 0.0298	-0.0380 - 0.0458	-0.0447 - 0.0525	-0.0631 - 0.112	-0.0980 - 0.192	-0.211 - 0.229	-0.542 - 0.560	-0.0655 - 0.0833
DR37	-0.0068 - 0.0062	-0.0143 - 0.0084	-0.0025 - 0.0050	-0.0037 - 0.0063	-0.0136 - 0.0161	-0.0118 - 0.0090	-0.0258 - 0.0125	-0.0072 - 0.0104	-0.0127 - 0.0158	-0.0150 - 0.0181
DR39	-0.0180 - 0.0398	-0.0298 - 0.0664	-0.0110 - 0.0238	-0.0185 - 0.0313	-0.0613 - 0.0742	-0.0881 - 0.183	-0.150 - 0.307	-0.0845 - 0.132	-0.151 - 0.199	-0.107 - 0.155
DR40	-0.0182 - 0.0306	-0.0292 - 0.0520	-0.0113 - 0.0169	-0.0162 - 0.0218	-0.0414 - 0.0469	-0.0488 - 0.0819	-0.0852 - 0.144	-0.0510 - 0.0628	-0.0862 - 0.0981	-0.0586 - 0.0704
DR42	-0.0190 - 0.0224	-0.0275 - 0.0417	-0.0153 - 0.0111	-0.0209 - 0.0168	-0.0628 - 0.0586	-0.0708 - 0.0920	-0.104 - 0.179	-0.0749 - 0.0617	-0.117 - 0.104	-0.114 - 0.101

Table D.4 (cont.).

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{sp1} = n_{ss1} = 3$					EN 15522-2 scenario: A/B and $n_{sp1} = n_{ss1} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR43	-0.0108 - 0.0080	-0.0184 - 0.0137	-0.0063 - 0.0040	-0.0081 - 0.0058	-0.0303 - 0.0280	-0.0219 - 0.0167	-0.0413 - 0.0303	-0.0173 - 0.0137	-0.0269 - 0.0233	-0.0387 - 0.0351
DR44	-0.0073 - 0.0245	-0.0132 - 0.0401	-0.0079 - 0.0191	-0.0162 - 0.0275	-0.0232 - 0.0345	-0.0157 - 0.0469	-0.0274 - 0.0791	-0.0683 - 0.0861	-0.184 - 0.202	-0.0274 - 0.0453
DR63	-0.0192 - 0.0009	-0.0260 - 0.0091	-0.0153 - -0.0035	-0.0174 - -0.0015	-0.0682 - 0.0494	-0.0655 - 0.0109	-0.0969 - 0.0499	-0.0613 - 0.0053	-0.0819 - 0.0259	-0.129 - 0.0734
DR64	-0.0107 - 0.0121	-0.0204 - 0.0194	-0.0052 - 0.0076	-0.0075 - 0.0099	-0.0899 - 0.0923	-0.118 - 0.120	-0.225 - 0.201	-0.0897 - 0.110	-0.151 - 0.171	-0.251 - 0.271
DR67	-0.0305 - 0.0251	-0.0576 - 0.0384	-0.0220 - 0.0245	-0.0364 - 0.0389	-0.0665 - 0.0691	-0.143 - 0.119	-0.267 - 0.188	-0.314 - 0.325	-0.795 - 0.805	-0.126 - 0.137
DR68	-0.0054 - 0.0049	-0.0081 - 0.0082	-0.0032 - 0.0026	-0.0042 - 0.0036	-0.0101 - 0.0095	-0.0076 - 0.0072	-0.0118 - 0.0125	-0.0067 - 0.0060	-0.0107 - 0.0099	-0.0109 - 0.0102
DR71	-0.0068 - 0.0052	-0.0116 - 0.0085	-0.0040 - 0.0033	-0.0052 - 0.0046	-0.0110 - 0.0103	-0.0103 - 0.0076	-0.0175 - 0.0127	-0.0085 - 0.0077	-0.0135 - 0.0127	-0.0119 - 0.0112
DR72	-0.0081 - 0.0208	-0.0214 - 0.0269	0.0002 - 0.0169	-0.0027 - 0.0198	-0.0654 - 0.0825	-0.0612 - 0.105	-0.141 - 0.144	-0.0328 - 0.110	-0.0769 - 0.154	-0.119 - 0.195
DR76	-0.0093 - 0.0166	-0.0191 - 0.0276	-0.0039 - 0.0114	-0.0066 - 0.0141	-0.0076 - 0.0152	-0.0150 - 0.0241	-0.0319 - 0.0450	-0.0127 - 0.0217	-0.0234 - 0.0323	-0.0079 - 0.0169
DR78	-0.0587 - 0.0287	-0.102 - 0.0494	-0.0325 - 0.0135	-0.0406 - 0.0216	-0.0720 - 0.0530	-0.255 - 0.126	-0.488 - 0.240	-0.173 - 0.111	-0.261 - 0.199	-0.144 - 0.0817
τ (%)	0	0	7.1	3.6	0	0	0	0	0	0

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table D.5. Second trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 1 (Sp1) and in the suspected source sample 1 (SS1, known to be the origin of the spill), applying and the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp1} = n_{SS1} = 3$					EN 15522-2 scenario: A/B and $n_{Sp1} = n_{SS1} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR19	-0.0234 - 0.0134	-0.0355 - 0.0234	-0.0212 - 0.0124	-0.0315 - 0.0228	-0.111 - 0.102	-0.461 - 0.315	-0.688 - 0.537	-1.09 - 0.944	-2.62 - 2.48	-0.516 - 0.368
DR20	-0.0240 - 0.0141	-0.0340 - 0.0268	-0.0185 - 0.0072	-0.0239 - 0.0126	-0.0687 - 0.0574	-0.0935 - 0.0648	-0.136 - 0.127	-0.0879 - 0.0508	-0.131 - 0.0937	-0.133 - 0.0961
DR21	-0.0131 - 0.0179	-0.0212 - 0.0278	-0.0070 - 0.0106	-0.0100 - 0.0137	-0.0979 - 0.102	-0.197 - 0.274	-0.320 - 0.460	-0.179 - 0.223	-0.303 - 0.348	-0.324 - 0.369
DR22	-0.0260 - 0.0322	-0.0445 - 0.0548	-0.0138 - 0.0180	-0.0194 - 0.0236	-0.109 - 0.114	-0.777 - 0.908	-1.29 - 1.49	-0.690 - 0.789	-1.15 - 1.25	-0.499 - 0.598
DR23	-0.0143 - 0.0049	-0.0203 - 0.0099	-0.0104 - 0.0011	-0.0124 - 0.0032	-0.0719 - 0.0627	-0.0617 - 0.0255	-0.0900 - 0.0490	-0.0576 - 0.0234	-0.0826 - 0.0484	-0.147 - 0.112
DR24	-0.0225 - 0.0409	-0.0401 - 0.0636	-0.0097 - 0.0251	-0.0158 - 0.0312	-0.0774 - 0.0929	-0.198 - 0.307	-0.349 - 0.466	-0.165 - 0.265	-0.298 - 0.397	-0.167 - 0.267
DR26	-0.0050 - 0.0019	-0.0066 - 0.0042	-0.0042 - 0.0005	-0.0052 - 0.0015	-0.0123 - 0.0086	-0.0066 - 0.0034	-0.0089 - 0.0071	-0.0067 - 0.0023	-0.0095 - 0.0051	-0.0135 - 0.0092
DR27	-0.0247 - 0.0221	-0.0397 - 0.0396	-0.0149 - 0.0106	-0.0194 - 0.0150	-0.0208 - 0.0164	-0.0402 - 0.0386	-0.0672 - 0.0759	-0.0351 - 0.0293	-0.0551 - 0.0493	-0.0244 - 0.0185
DR29	-0.0257 - 0.0280	-0.0428 - 0.0436	-0.0139 - 0.0176	-0.0194 - 0.0231	-0.0317 - 0.0353	-0.0554 - 0.0604	-0.0910 - 0.101	-0.0486 - 0.0549	-0.0806 - 0.0869	-0.0408 - 0.0471
DR31	-0.0428 - 0.0452	-0.0702 - 0.0764	-0.0242 - 0.0247	-0.0327 - 0.0333	-0.0699 - 0.0705	-0.214 - 0.238	-0.379 - 0.473	-0.183 - 0.186	-0.297 - 0.300	-0.139 - 0.142
DR32	-0.0269 - 0.0445	-0.0479 - 0.0671	-0.0163 - 0.0324	-0.0267 - 0.0428	-0.0564 - 0.0725	-0.117 - 0.190	-0.205 - 0.305	-0.111 - 0.167	-0.197 - 0.253	-0.0914 - 0.147
DR34	-0.0293 - 0.0392	-0.0486 - 0.0589	-0.0175 - 0.0274	-0.0270 - 0.0369	-0.0643 - 0.0743	-0.141 - 0.193	-0.232 - 0.294	-0.410 - 0.450	-1.06 - 1.10	-0.117 - 0.157
DR35	-0.0129 - 0.0087	-0.0183 - 0.0155	-0.0084 - 0.0036	-0.0105 - 0.0057	-0.0235 - 0.0187	-0.0210 - 0.0166	-0.0302 - 0.0308	-0.0191 - 0.0125	-0.0289 - 0.0223	-0.0281 - 0.0215
DR36	-0.0104 - 0.0251	-0.0183 - 0.0389	-0.0102 - 0.0211	-0.0199 - 0.0308	-0.0421 - 0.0530	-0.0331 - 0.0669	-0.0595 - 0.106	-0.116 - 0.141	-0.309 - 0.334	-0.0596 - 0.0845
DR37	-0.0129 - 0.0064	-0.0203 - 0.0108	-0.0078 - 0.0030	-0.0097 - 0.0049	-0.0176 - 0.0127	-0.0196 - 0.0105	-0.0327 - 0.0178	-0.0160 - 0.0099	-0.0240 - 0.0179	-0.0201 - 0.0139
DR39	-0.0305 - 0.0139	-0.0450 - 0.0263	-0.0205 - 0.0049	-0.0250 - 0.0094	-0.0758 - 0.0602	-0.135 - 0.0735	-0.207 - 0.140	-0.120 - 0.0615	-0.177 - 0.118	-0.162 - 0.103
DR40	-0.0158 - 0.0157	-0.0242 - 0.0269	-0.0118 - 0.0096	-0.0164 - 0.0142	-0.0446 - 0.0424	-0.0411 - 0.0418	-0.0637 - 0.0715	-0.0395 - 0.0351	-0.0626 - 0.0581	-0.0653 - 0.0609
DR42	-0.0335 - 0.0142	-0.0487 - 0.0292	-0.0263 - 0.0065	-0.0334 - 0.0135	-0.0705 - 0.0506	-0.126 - 0.0601	-0.201 - 0.111	-0.283 - 0.221	-0.662 - 0.600	-0.138 - 0.0757
DR43	-0.0229 - 0.0151	-0.0380 - 0.0236	-0.0188 - 0.0148	-0.0292 - 0.0252	-0.0317 - 0.0277	-0.0468 - 0.0293	-0.0836 - 0.0459	-0.101 - 0.0949	-0.249 - 0.243	-0.0410 - 0.0344
DR44	-0.0148 - 0.0130	-0.0241 - 0.0200	-0.0080 - 0.0076	-0.0107 - 0.0103	-0.0287 - 0.0283	-0.0297 - 0.0247	-0.0510 - 0.0382	-0.0236 - 0.0229	-0.0380 - 0.0373	-0.0361 - 0.0354
DR63	-0.0038 - 0.0242	-0.0092 - 0.0366	0.0002 - 0.0158	-0.0025 - 0.0185	-0.0520 - 0.0680	-0.0192 - 0.0874	-0.0412 - 0.137	-0.0206 - 0.0696	-0.0485 - 0.0975	-0.0805 - 0.130
DR64	-0.0301 - 0.0533	-0.0545 - 0.0831	-0.0121 - 0.0341	-0.0201 - 0.0422	-0.0783 - 0.100	-0.314 - 0.458	-0.576 - 0.684	-0.245 - 0.412	-0.448 - 0.615	-0.163 - 0.331
DR67	-0.0352 - 0.0184	-0.0553 - 0.0325	-0.0306 - 0.0182	-0.0457 - 0.0333	-0.0732 - 0.0608	-0.163 - 0.0865	-0.262 - 0.156	-0.354 - 0.308	-0.851 - 0.805	-0.152 - 0.105
DR68	-0.0029 - 0.0024	-0.0043 - 0.0041	-0.0022 - 0.0014	-0.0029 - 0.0022	-0.0103 - 0.0095	-0.0041 - 0.0034	-0.0061 - 0.0059	-0.0038 - 0.0030	-0.0060 - 0.0051	-0.0111 - 0.0102
DR72	-0.0080 - 0.0077	-0.0143 - 0.0107	-0.0035 - 0.0054	-0.0051 - 0.0069	-0.0097 - 0.0115	-0.0121 - 0.0108	-0.0222 - 0.0151	-0.0088 - 0.0109	-0.0149 - 0.0171	-0.0104 - 0.0125
DR76	-0.0289 - 0.0229	-0.0415 - 0.0396	-0.0199 - 0.0099	-0.0251 - 0.0151	-0.0795 - 0.0694	-0.162 - 0.134	-0.246 - 0.225	-0.152 - 0.106	-0.232 - 0.185	-0.182 - 0.136
DR78	-0.0050 - 0.0088	-0.0108 - 0.0119	-0.0036 - 0.0090	-0.0076 - 0.0129	-0.0083 - 0.0137	-0.0084 - 0.0121	-0.0180 - 0.0165	-0.0239 - 0.0302	-0.0645 - 0.0708	-0.0088 - 0.0151
τ (%)	0	0	3.6	0	0	0	0	0	0	0

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table D.6. Third trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 1 (Sp1) and in the suspected source sample 1 (SS1, known to be the origin of the spill), applying the DR comparison trial and the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp1} = n_{SS1} = 3$					EN 15522-2 scenario: A/B and $n_{Sp1} = n_{SS1} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR19	-0.0265 - 0.0129	-0.0361 - 0.0260	-0.0213 - 0.0044	-0.0268 - 0.0099	-0.114 - 0.0971	-0.489 - 0.307	-0.675 - 0.613	-0.483 - 0.204	-0.695 - 0.417	-0.569 - 0.291
DR20	-0.0222 - 0.0102	-0.0298 - 0.0247	-0.0234 - 0.0084	-0.0333 - 0.0183	-0.0710 - 0.0560	-0.0829 - 0.0526	-0.113 - 0.126	-0.217 - 0.167	-0.506 - 0.456	-0.141 - 0.0912
DR21	-0.0214 - 0.0120	-0.0275 - 0.0265	-0.0170 - 0.0022	-0.0204 - 0.0055	-0.107 - 0.0918	-0.285 - 0.211	-0.379 - 0.456	-0.304 - 0.128	-0.438 - 0.262	-0.429 - 0.253
DR22	-0.0139 - 0.0060	-0.0246 - 0.0099	-0.0121 - 0.0079	-0.0182 - 0.0140	-0.112 - 0.108	-0.372 - 0.168	-0.692 - 0.276	-0.820 - 0.729	-1.99 - 1.89	-0.561 - 0.471
DR23	-0.0272 - 0.0260	-0.0397 - 0.0462	-0.0264 - 0.0218	-0.0413 - 0.0367	-0.0686 - 0.0639	-0.120 - 0.117	-0.178 - 0.207	-0.327 - 0.309	-0.804 - 0.787	-0.135 - 0.117
DR24	-0.0503 - 0.0277	-0.0854 - 0.0497	-0.0295 - 0.0163	-0.0393 - 0.0261	-0.0902 - 0.0770	-0.375 - 0.230	-0.632 - 0.444	-0.275 - 0.195	-0.420 - 0.340	-0.248 - 0.168
DR26	-0.0035 - 0.0003	-0.0046 - 0.0015	-0.0027 - -0.0006	-0.0031 - -0.0002	-0.0120 - 0.0087	-0.0046 - 0.0009	-0.0062 - 0.0028	-0.0042 - 0.0004	-0.0056 - 0.0018	-0.0131 - 0.0093
DR27	-0.0266 - 0.0246	-0.0495 - 0.0474	-0.0157 - 0.0124	-0.0206 - 0.0173	-0.0230 - 0.0197	-0.0487 - 0.0465	-0.100 - 0.104	-0.0394 - 0.0348	-0.0623 - 0.0577	-0.0275 - 0.0229
DR29	-0.0431 - 0.0288	-0.0750 - 0.0588	-0.0283 - 0.0135	-0.0356 - 0.0208	-0.0430 - 0.0282	-0.100 - 0.0716	-0.213 - 0.181	-0.0850 - 0.0584	-0.129 - 0.103	-0.0611 - 0.0344
DR31	-0.0276 - 0.0243	-0.0633 - 0.0339	-0.0178 - 0.0292	-0.0324 - 0.0437	-0.0646 - 0.0759	-0.158 - 0.114	-0.369 - 0.172	-0.320 - 0.367	-0.837 - 0.883	-0.118 - 0.164
DR32	-0.0165 - 0.0178	-0.0281 - 0.0306	-0.0089 - 0.0112	-0.0131 - 0.0155	-0.0641 - 0.0664	-0.0761 - 0.0780	-0.134 - 0.138	-0.0539 - 0.0620	-0.0898 - 0.0979	-0.118 - 0.126
DR34	-0.0301 - 0.0235	-0.0470 - 0.0485	-0.0199 - 0.0085	-0.0248 - 0.0135	-0.0749 - 0.0636	-0.148 - 0.134	-0.304 - 0.303	-0.128 - 0.0833	-0.193 - 0.149	-0.159 - 0.115
DR35	-0.0120 - 0.0110	-0.0177 - 0.0217	-0.0094 - 0.0045	-0.0124 - 0.0075	-0.0241 - 0.0192	-0.0203 - 0.0210	-0.0319 - 0.0408	-0.0197 - 0.0128	-0.0297 - 0.0228	-0.0291 - 0.0222
DR36	-0.0386 - 0.0438	-0.0674 - 0.0696	-0.0178 - 0.0283	-0.0258 - 0.0364	-0.0409 - 0.0515	-0.119 - 0.116	-0.212 - 0.185	-0.0858 - 0.109	-0.146 - 0.170	-0.0573 - 0.0808
DR37	-0.0254 - 0.0145	-0.0410 - 0.0308	-0.0178 - 0.0051	-0.0218 - 0.0091	-0.0231 - 0.0104	-0.0407 - 0.0263	-0.0783 - 0.0605	-0.0362 - 0.0198	-0.0535 - 0.0372	-0.0272 - 0.0109
DR39	-0.0294 - 0.0293	-0.0522 - 0.0459	-0.0151 - 0.0214	-0.0229 - 0.0292	-0.0668 - 0.0731	-0.165 - 0.137	-0.305 - 0.219	-0.107 - 0.132	-0.181 - 0.206	-0.127 - 0.152
DR40	-0.0254 - 0.0195	-0.0437 - 0.0345	-0.0148 - 0.0128	-0.0206 - 0.0187	-0.0449 - 0.0429	-0.0669 - 0.0544	-0.116 - 0.0965	-0.145 - 0.141	-0.361 - 0.357	-0.0659 - 0.0619
DR42	-0.0376 - 0.0301	-0.0556 - 0.0552	-0.0257 - 0.0169	-0.0348 - 0.0260	-0.0655 - 0.0567	-0.150 - 0.120	-0.235 - 0.210	-0.347 - 0.319	-0.848 - 0.819	-0.123 - 0.0943
DR43	-0.0176 - 0.0171	-0.0243 - 0.0361	-0.0193 - 0.0115	-0.0288 - 0.0210	-0.0339 - 0.0261	-0.0324 - 0.0396	-0.0477 - 0.0867	-0.0962 - 0.0836	-0.231 - 0.219	-0.0445 - 0.0319
DR44	-0.0127 - 0.0229	-0.0235 - 0.0377	-0.0120 - 0.0179	-0.0212 - 0.0272	-0.0254 - 0.0313	-0.0252 - 0.0462	-0.0503 - 0.0793	-0.0802 - 0.0897	-0.208 - 0.217	-0.0308 - 0.0403
DR63	-0.0275 - 0.0411	-0.0485 - 0.0642	-0.0127 - 0.0273	-0.0197 - 0.0343	-0.0506 - 0.0651	-0.104 - 0.140	-0.182 - 0.221	-0.0890 - 0.131	-0.157 - 0.199	-0.0776 - 0.120
DR64	-0.0112 - 0.0320	-0.0249 - 0.0458	-0.0032 - 0.0248	-0.0092 - 0.0308	-0.0748 - 0.0964	-0.112 - 0.239	-0.224 - 0.344	-0.0814 - 0.224	-0.176 - 0.318	-0.149 - 0.291
DR67	-0.0333 - 0.0442	-0.0514 - 0.0801	-0.0249 - 0.0235	-0.0352 - 0.0338	-0.0702 - 0.0688	-0.150 - 0.244	-0.245 - 0.448	-0.462 - 0.458	-1.15 - 1.15	-0.140 - 0.136
DR68	-0.0020 - 0.0002	-0.0027 - 0.0008	-0.0016 - -0.0001	-0.0019 - 0.0002	-0.0106 - 0.0089	-0.0026 - 0.0005	-0.0036 - 0.0015	-0.0024 - 0.0004	-0.0032 - 0.0013	-0.0115 - 0.0095
DR72	-0.0128 - 0.0097	-0.0206 - 0.0170	-0.0088 - 0.0049	-0.0117 - 0.0078	-0.0123 - 0.0084	-0.0182 - 0.0152	-0.0307 - 0.0268	-0.0414 - 0.0369	-0.100 - 0.0958	-0.0134 - 0.0089
DR76	-0.0344 - 0.0430	-0.0545 - 0.0753	-0.0242 - 0.0276	-0.0352 - 0.0387	-0.0709 - 0.0743	-0.186 - 0.225	-0.296 - 0.398	-0.177 - 0.191	-0.291 - 0.304	-0.144 - 0.158
DR78	-0.0063 - 0.0088	-0.0116 - 0.0144	-0.0033 - 0.0048	-0.0048 - 0.0062	-0.0109 - 0.0124	-0.0098 - 0.0133	-0.0194 - 0.0228	-0.0083 - 0.0101	-0.0140 - 0.0158	-0.0118 - 0.0136
τ (%)	0	0	7.1	3.6	0	0	0	0	0	0

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

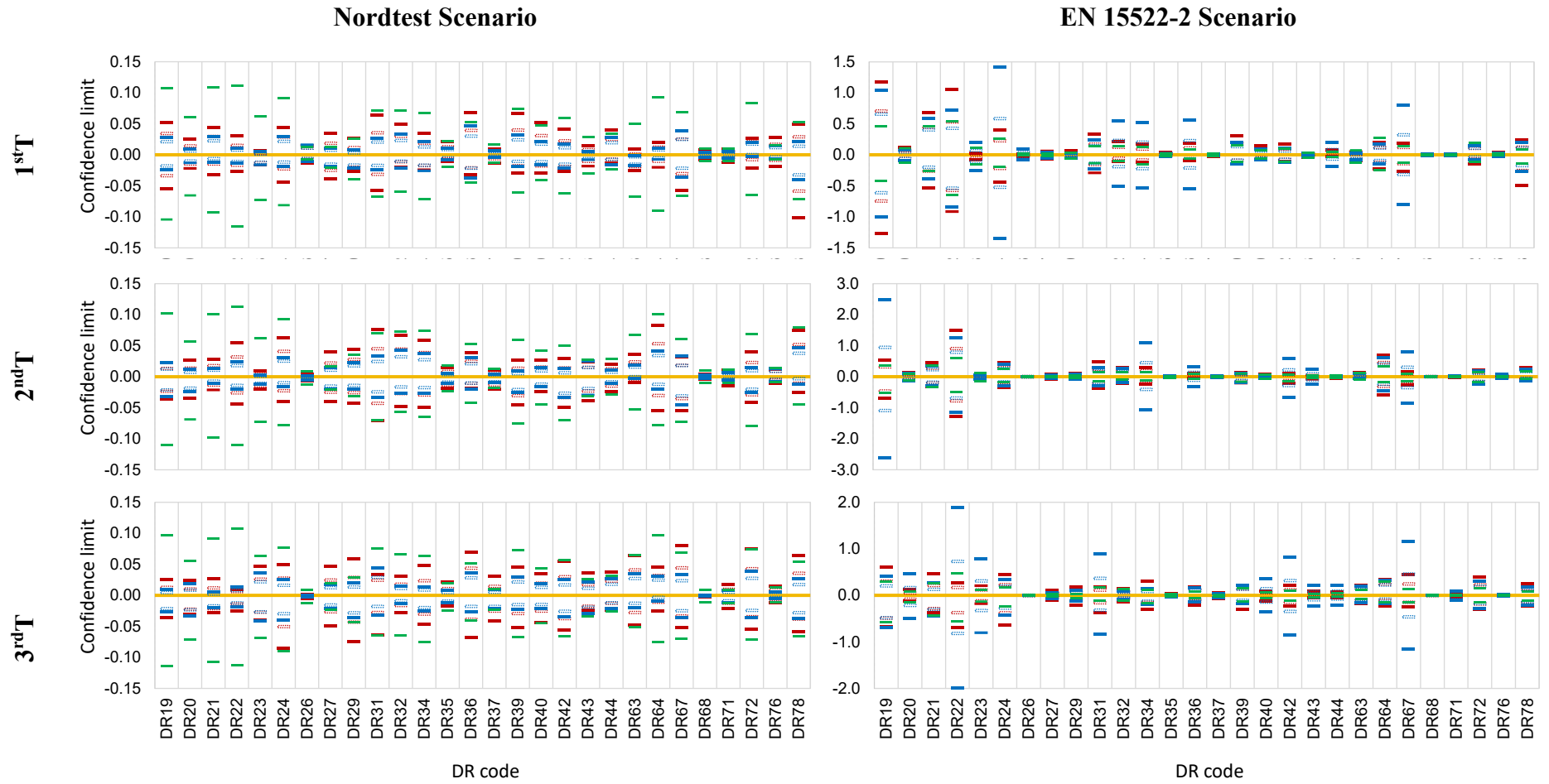


Figure D.5. Confidence limits of the difference between DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach, and by the S-t and MCM approaches considering 95% and 98% confidence levels, for the comparison of DR observed in the spill sample 1 (Sp1) and in the suspected source sample 1 (SS1, known to be the origin of the spill), applying the experimental data obtained for the three DR comparison trials (1stT, 2ndT and 3rdT) and the DR comparison conditions represented by the Nordtest scenario ($A/(A+B)$ ratio format and triplicate injections) and EN 15522-2 scenario (A/B ratio format and duplicate injections). $\cdots$ $P2.5$ and $P97.5$ of MCM; $\cdots$ $P2.5$ and $P97.5$ of S-t; $-$ $P1$ and $P99$ of MCM; $-$ $P1$ and $P99$ of S-t; $-$ SC_{LL} and SC_{UL} ; $-$ $(\overline{DR}_{Sp} - \overline{DR}_{SS}) = 0$.

Table D.7. First trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 1 (Sp1) and in the suspected source sample 2 (SS2, known not to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp1} = n_{SS2} = 3$					EN 15522-2 scenario: A/B and $n_{Sp1} = n_{SS2} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR19	-0.115 - -0.0593	-0.132 - -0.0429	-0.103 - -0.0712	-0.109 - -0.0657	-0.199 - 0.0250	-3.24 - -1.38	-3.77 - -0.815	-3.15 - -1.52	-3.65 - -1.01	-2.93 - -1.73
DR20	-0.114 - -0.0845	-0.123 - -0.0763	-0.107 - -0.0914	-0.110 - -0.0886	-0.170 - -0.0291	-0.483 - -0.331	-0.541 - -0.288	-0.467 - -0.342	-0.506 - -0.303	-0.548 - -0.260
DR21	-0.170 - -0.127	-0.189 - -0.116	-0.161 - -0.133	-0.167 - -0.127	-0.258 - -0.0355	-4.85 - -3.18	-5.42 - -2.58	-6.16 - -1.86	-9.38 - 1.37	-4.65 - -3.37
DR22	-0.0537 - -0.0159	-0.0704 - -0.0081	-0.0426 - -0.0197	-0.0475 - -0.0148	-0.147 - 0.0842	-2.14 - -0.394	-3.20 - -0.0592	-3.02 - 0.984	-6.04 - 4.00	-1.68 - -0.357
DR23	0.129 - 0.184	0.116 - 0.204	0.128 - 0.180	0.111 - 0.197	0.0974 - 0.211	0.373 - 0.519	0.335 - 0.575	0.230 - 0.651	-0.0868 - 0.968	0.342 - 0.540
DR24	-0.0011 - 0.0392	-0.0175 - 0.0501	0.0085 - 0.0313	0.0045 - 0.0353	-0.0653 - 0.105	-0.0521 - 0.283	-0.214 - 0.372	-0.0101 - 0.269	-0.0966 - 0.356	-0.0881 - 0.347
DR26	-0.274 - -0.251	-0.282 - -0.245	-0.273 - -0.252	-0.280 - -0.246	-0.292 - -0.234	-0.460 - -0.398	-0.480 - -0.380	-0.514 - -0.343	-0.642 - -0.215	-0.470 - -0.387
DR29	-0.204 - -0.144	-0.219 - -0.119	-0.197 - -0.160	-0.205 - -0.153	-0.224 - -0.134	-0.480 - -0.282	-0.530 - -0.196	-0.639 - -0.157	-1.00 - 0.206	-0.468 - -0.327
DR31	0.180 - 0.242	0.152 - 0.262	0.195 - 0.229	0.189 - 0.235	0.157 - 0.267	0.450 - 0.697	0.310 - 0.762	0.269 - 0.912	-0.215 - 1.39	0.493 - 0.687
DR32	0.0837 - 0.119	0.0702 - 0.130	0.0867 - 0.119	0.0767 - 0.129	0.0445 - 0.161	0.240 - 0.358	0.190 - 0.402	0.154 - 0.458	-0.0739 - 0.686	0.204 - 0.408
DR34	0.0526 - 0.106	0.0403 - 0.133	0.0503 - 0.0998	0.0349 - 0.115	0.0111 - 0.139	0.172 - 0.374	0.128 - 0.482	-0.0133 - 0.523	-0.417 - 0.927	0.136 - 0.374
DR35	-0.0065 - 0.0103	-0.0101 - 0.0184	-0.0074 - 0.0085	-0.0123 - 0.0134	-0.0202 - 0.0213	-0.0110 - 0.0187	-0.0181 - 0.0353	-0.0388 - 0.0403	-0.0982 - 0.0998	-0.0236 - 0.0252
DR36	0.0400 - 0.0630	0.0312 - 0.0683	0.0467 - 0.0588	0.0446 - 0.0610	0.0076 - 0.0979	0.0805 - 0.142	0.0556 - 0.158	0.0907 - 0.140	0.0756 - 0.155	0.0482 - 0.182
DR37	-0.109 - -0.0805	-0.115 - -0.0676	-0.105 - -0.0879	-0.108 - -0.0843	-0.118 - -0.0747	-0.157 - -0.103	-0.170 - -0.0746	-0.198 - -0.0719	-0.294 - 0.0232	-0.161 - -0.109
DR39	-0.271 - -0.220	-0.287 - -0.204	-0.262 - -0.229	-0.269 - -0.222	-0.331 - -0.160	-2.20 - -1.47	-2.52 - -1.27	-2.79 - -0.806	-4.28 - 0.687	-2.06 - -1.54
DR40	-0.115 - -0.0668	-0.124 - -0.0419	-0.109 - -0.0829	-0.114 - -0.0783	-0.147 - -0.0450	-0.296 - -0.143	-0.329 - -0.0500	-0.303 - -0.176	-0.342 - -0.137	-0.321 - -0.158
DR42	-0.271 - -0.234	-0.279 - -0.216	-0.266 - -0.245	-0.269 - -0.242	-0.334 - -0.177	-1.59 - -1.23	-1.68 - -1.03	-1.92 - -0.971	-2.64 - -0.256	-1.65 - -1.24
DR43	-0.103 - -0.0677	-0.111 - -0.0499	-0.0999 - -0.0772	-0.105 - -0.0724	-0.124 - -0.0532	-0.193 - -0.108	-0.213 - -0.0600	-0.267 - -0.0506	-0.430 - 0.112	-0.207 - -0.111
DR44	0.125 - 0.132	0.124 - 0.135	0.127 - 0.131	0.126 - 0.131	0.109 - 0.149	0.171 - 0.184	0.167 - 0.189	0.172 - 0.182	0.168 - 0.186	0.152 - 0.202
DR63	-0.319 - -0.284	-0.326 - -0.267	-0.315 - -0.294	-0.320 - -0.289	-0.384 - -0.225	-2.07 - -1.58	-2.17 - -1.35	-2.48 - -1.24	-3.41 - -0.313	-2.09 - -1.63
DR64	-0.348 - -0.333	-0.357 - -0.329	-0.346 - -0.332	-0.351 - -0.327	-0.454 - -0.224	-114 - -81.5	-120 - -66.4	-142 - -57.8	-206 - 5.87	-107 - -92.9
DR67	0.0361 - 0.124	0.0101 - 0.159	0.0554 - 0.101	0.0473 - 0.109	0.0160 - 0.141	0.0823 - 0.429	-0.0368 - 0.561	0.114 - 0.399	0.0254 - 0.487	0.142 - 0.370
DR68	-0.304 - -0.282	-0.310 - -0.273	-0.304 - -0.283	-0.310 - -0.277	-0.324 - -0.263	-0.525 - -0.461	-0.541 - -0.437	-0.585 - -0.406	-0.719 - -0.271	-0.540 - -0.450
DR71	-0.0135 - 0.0047	-0.0212 - 0.0093	-0.0094 - 0.0029	-0.0121 - 0.0055	-0.0141 - 0.0076	-0.0193 - 0.0075	-0.0321 - 0.0140	-0.0159 - 0.0082	-0.0233 - 0.0157	-0.0156 - 0.0079
DR72	0.141 - 0.183	0.127 - 0.198	0.148 - 0.175	0.142 - 0.181	0.0984 - 0.225	0.462 - 0.628	0.393 - 0.675	0.480 - 0.620	0.436 - 0.664	0.429 - 0.671
DR76	-0.0180 - 0.0047	-0.0317 - 0.0084	-0.0114 - 0.0033	-0.0146 - 0.0064	-0.0160 - 0.0079	-0.0275 - 0.0075	-0.0494 - 0.0137	-0.0194 - 0.0096	-0.0283 - 0.0186	-0.0179 - 0.0082
DR78	-0.0768 - 0.0033	-0.103 - 0.0314	-0.0596 - -0.0147	-0.0674 - -0.0069	-0.102 - 0.0273	-0.308 - 0.0486	-0.443 - 0.186	-0.277 - 0.0209	-0.369 - 0.113	-0.248 - -0.0082
τ (%)	81.5	81.5	88.9	88.9	74.1	81.5	77.8	74.1	40.7	85.2

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table D.8. Second trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 1 (Sp1) and in the suspected source sample 2 (SS2, known not to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp1} = n_{SS2} = 3$					EN 15522-2 scenario: A/B and $n_{Sp1} = n_{SS2} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR19	-0.112 - -0.0643	-0.126 - -0.0522	-0.100 - -0.0734	-0.105 - -0.0687	-0.199 - 0.0252	-3.22 - -1.52	-3.84 - -1.12	-4.52 - -0.0627	-7.88 - 3.29	-2.89 - -1.70
DR20	-0.120 - -0.0812	-0.130 - -0.0681	-0.114 - -0.0881	-0.119 - -0.0826	-0.171 - -0.0313	-0.492 - -0.311	-0.549 - -0.248	-0.484 - -0.325	-0.533 - -0.277	-0.546 - -0.263
DR21	-0.166 - -0.139	-0.172 - -0.129	-0.163 - -0.145	-0.166 - -0.141	-0.264 - -0.0431	-4.41 - -3.61	-4.68 - -3.35	-5.10 - -2.93	-6.74 - -1.30	-4.65 - -3.39
DR22	-0.0615 - -0.0141	-0.0787 - -0.0007	-0.0506 - -0.0237	-0.0553 - -0.0190	-0.151 - 0.0771	-2.00 - -0.251	-2.53 - 0.300	-1.89 - -0.332	-2.37 - 0.151	-1.74 - -0.481
DR23	0.145 - 0.176	0.134 - 0.183	0.150 - 0.172	0.146 - 0.176	0.105 - 0.217	0.398 - 0.499	0.362 - 0.523	0.406 - 0.498	0.377 - 0.527	0.355 - 0.549
DR24	-0.0148 - 0.0642	-0.0386 - 0.0867	-0.0015 - 0.0513	-0.0128 - 0.0625	-0.0591 - 0.109	-0.166 - 0.428	-0.372 - 0.571	-0.109 - 0.417	-0.271 - 0.580	-0.0558 - 0.364
DR26	-0.271 - -0.248	-0.277 - -0.240	-0.271 - -0.250	-0.278 - -0.243	-0.289 - -0.232	-0.452 - -0.389	-0.469 - -0.367	-0.508 - -0.336	-0.638 - -0.207	-0.463 - -0.382
DR29	-0.214 - -0.143	-0.239 - -0.125	-0.197 - -0.155	-0.204 - -0.148	-0.222 - -0.130	-0.526 - -0.297	-0.628 - -0.247	-0.699 - -0.0947	-1.15 - 0.360	-0.469 - -0.325
DR31	0.133 - 0.248	0.0978 - 0.283	0.158 - 0.225	0.146 - 0.236	0.134 - 0.248	0.354 - 0.785	0.208 - 0.985	0.374 - 0.738	0.261 - 0.851	0.454 - 0.658
DR32	0.0728 - 0.138	0.0514 - 0.159	0.0832 - 0.129	0.0734 - 0.139	0.0485 - 0.164	0.183 - 0.446	0.105 - 0.542	-0.0634 - 0.681	-0.623 - 1.24	0.209 - 0.409
DR34	0.0467 - 0.125	0.0236 - 0.144	0.0640 - 0.108	0.0562 - 0.116	0.0226 - 0.150	0.119 - 0.465	0.0245 - 0.563	0.140 - 0.444	0.0453 - 0.538	0.174 - 0.410
DR35	-0.0029 - 0.0170	-0.0074 - 0.0236	0.0002 - 0.0131	-0.0025 - 0.0159	-0.0138 - 0.0271	-0.0067 - 0.0272	-0.0153 - 0.0379	-0.0056 - 0.0239	-0.0147 - 0.0329	-0.0148 - 0.0331
DR36	0.0388 - 0.0555	0.0343 - 0.0608	0.0393 - 0.0544	0.0346 - 0.0591	0.0022 - 0.0915	0.0809 - 0.123	0.0683 - 0.138	0.0450 - 0.157	-0.0397 - 0.242	0.0353 - 0.167
DR37	-0.100 - -0.0836	-0.105 - -0.0787	-0.0969 - -0.0874	-0.0986 - -0.0857	-0.114 - -0.0707	-0.143 - -0.114	-0.152 - -0.106	-0.142 - -0.116	-0.150 - -0.108	-0.155 - -0.103
DR39	-0.289 - -0.228	-0.303 - -0.208	-0.281 - -0.241	-0.289 - -0.233	-0.347 - -0.175	-2.43 - -1.49	-2.71 - -1.22	-3.21 - -0.708	-5.09 - 1.17	-2.22 - -1.69
DR40	-0.121 - -0.0743	-0.133 - -0.0597	-0.112 - -0.0843	-0.117 - -0.0794	-0.149 - -0.0481	-0.313 - -0.165	-0.353 - -0.120	-0.448 - -0.0344	-0.759 - 0.277	-0.321 - -0.161
DR42	-0.284 - -0.249	-0.295 - -0.238	-0.279 - -0.255	-0.284 - -0.250	-0.345 - -0.188	-1.72 - -1.34	-1.84 - -1.23	-2.05 - -1.00	-2.84 - -0.209	-1.74 - -1.32
DR43	-0.0848 - -0.0693	-0.0884 - -0.0644	-0.0818 - -0.0731	-0.0834 - -0.0716	-0.112 - -0.0425	-0.154 - -0.120	-0.163 - -0.109	-0.153 - -0.123	-0.162 - -0.114	-0.185 - -0.0909
DR44	0.113 - 0.138	0.104 - 0.143	0.119 - 0.133	0.116 - 0.136	0.106 - 0.146	0.147 - 0.192	0.131 - 0.202	0.152 - 0.191	0.139 - 0.204	0.148 - 0.195
DR63	-0.298 - -0.262	-0.307 - -0.251	-0.293 - -0.270	-0.298 - -0.265	-0.361 - -0.201	-1.98 - -1.50	-2.13 - -1.37	-2.36 - -1.11	-3.29 - -0.172	-1.96 - -1.51
DR64	-0.374 - -0.325	-0.396 - -0.315	-0.368 - -0.324	-0.382 - -0.310	-0.460 - -0.232	-106 - -76.7	-115 - -67.8	-131 - -51.0	-191 - 9.07	-97.5 - -84.2
DR67	0.0430 - 0.101	0.0216 - 0.115	0.0481 - 0.101	0.0317 - 0.117	0.0132 - 0.136	0.117 - 0.326	0.0142 - 0.376	-0.0354 - 0.509	-0.445 - 0.919	0.127 - 0.347
DR68	-0.301 - -0.276	-0.307 - -0.268	-0.301 - -0.278	-0.308 - -0.271	-0.319 - -0.259	-0.520 - -0.448	-0.540 - -0.422	-0.588 - -0.385	-0.740 - -0.233	-0.531 - -0.442
DR71	-0.0139 - 0.0087	-0.0215 - 0.0138	-0.0092 - 0.0058	-0.0124 - 0.0090	-0.0125 - 0.0090	-0.0203 - 0.0129	-0.0323 - 0.0204	-0.0166 - 0.0125	-0.0256 - 0.0215	-0.0137 - 0.0096
DR72	0.145 - 0.192	0.131 - 0.205	0.156 - 0.183	0.152 - 0.187	0.107 - 0.232	0.463 - 0.666	0.401 - 0.726	0.475 - 0.649	0.422 - 0.703	0.444 - 0.681
DR76	-0.0145 - 0.0040	-0.0214 - 0.0081	-0.0098 - 0.0007	-0.0116 - 0.0026	-0.0160 - 0.0070	-0.0204 - 0.0070	-0.0304 - 0.0130	-0.0172 - 0.0064	-0.0245 - 0.0137	-0.0179 - 0.0072
DR78	-0.0490 - 0.0202	-0.0707 - 0.0394	-0.0375 - 0.0108	-0.0478 - 0.0211	-0.0777 - 0.0510	-0.205 - 0.0880	-0.317 - 0.156	-0.461 - 0.369	-1.09 - 0.993	-0.166 - 0.0730
τ (%)	81.5	81.5	85.2	81.5	74.1	81.5	77.8	74.1	48.1	81.5

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table D.9. Third trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 1 (Sp1) and in the suspected source sample 2 (SS2, known not to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp1} = n_{SS2} = 3$					EN 15522-2 scenario: A/B and $n_{Sp1} = n_{SS2} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR19	-0.116 - -0.0768	-0.128 - -0.0653	-0.110 - -0.0839	-0.115 - -0.0783	-0.209 - 0.0149	-3.15 - -1.92	-3.56 - -1.56	-3.06 - -2.00	-3.39 - -1.67	-3.13 - -1.93
DR20	-0.121 - -0.0784	-0.133 - -0.0639	-0.113 - -0.0879	-0.117 - -0.0835	-0.170 - -0.0304	-0.515 - -0.297	-0.593 - -0.218	-0.500 - -0.311	-0.559 - -0.252	-0.548 - -0.263
DR21	-0.177 - -0.142	-0.187 - -0.132	-0.170 - -0.150	-0.173 - -0.146	-0.270 - -0.0500	-5.11 - -3.23	-5.95 - -2.83	-6.47 - -1.57	-10.2 - 2.12	-4.64 - -3.40
DR22	-0.0682 - -0.0331	-0.0813 - -0.0173	-0.0617 - -0.0409	-0.0654 - -0.0373	-0.165 - 0.0622	-2.10 - -0.711	-2.50 - 0.0198	-3.33 - 0.395	-6.13 - 3.20	-2.08 - -0.853
DR23	0.138 - 0.184	0.125 - 0.198	0.140 - 0.180	0.128 - 0.193	0.105 - 0.215	0.377 - 0.508	0.338 - 0.551	0.276 - 0.607	0.0268 - 0.855	0.347 - 0.535
DR24	-0.0131 - 0.0585	-0.0448 - 0.0804	0.0076 - 0.0498	-0.0015 - 0.0588	-0.0525 - 0.110	-0.133 - 0.400	-0.352 - 0.636	-0.459 - 0.786	-1.39 - 1.72	-0.0301 - 0.357
DR26	-0.258 - -0.253	-0.260 - -0.250	-0.258 - -0.254	-0.259 - -0.253	-0.284 - -0.228	-0.417 - -0.403	-0.420 - -0.397	-0.430 - -0.393	-0.457 - -0.366	-0.451 - -0.372
DR29	-0.226 - -0.149	-0.249 - -0.112	-0.212 - -0.170	-0.219 - -0.163	-0.239 - -0.143	-0.594 - -0.329	-0.717 - -0.220	-0.560 - -0.352	-0.624 - -0.288	-0.535 - -0.378
DR31	0.158 - 0.220	0.124 - 0.239	0.174 - 0.213	0.166 - 0.221	0.137 - 0.251	0.399 - 0.671	0.226 - 0.737	0.223 - 0.912	-0.295 - 1.43	0.465 - 0.671
DR32	0.0843 - 0.102	0.0789 - 0.109	0.0852 - 0.100	0.0806 - 0.105	0.0339 - 0.152	0.242 - 0.320	0.219 - 0.351	0.183 - 0.372	0.0419 - 0.513	0.175 - 0.381
DR34	0.0604 - 0.117	0.0406 - 0.142	0.0708 - 0.103	0.0653 - 0.108	0.0239 - 0.150	0.178 - 0.438	0.0466 - 0.600	0.184 - 0.391	0.120 - 0.455	0.172 - 0.403
DR35	-0.0009 - 0.0252	-0.0117 - 0.0334	0.0040 - 0.0194	0.0007 - 0.0227	-0.0090 - 0.0324	-0.0058 - 0.0394	-0.0255 - 0.0563	-0.0013 - 0.0335	-0.0121 - 0.0443	-0.0082 - 0.0404
DR36	0.0024 - 0.0603	-0.0263 - 0.0737	0.0162 - 0.0546	0.0080 - 0.0628	-0.0087 - 0.0795	-0.0173 - 0.143	-0.101 - 0.182	-0.132 - 0.284	-0.445 - 0.597	0.0111 - 0.140
DR37	-0.105 - -0.0670	-0.118 - -0.0510	-0.0974 - -0.0767	-0.101 - -0.0730	-0.109 - -0.0646	-0.157 - -0.0880	-0.190 - -0.0569	-0.151 - -0.0962	-0.168 - -0.0791	-0.151 - -0.0966
DR39	-0.260 - -0.222	-0.274 - -0.207	-0.251 - -0.231	-0.255 - -0.227	-0.328 - -0.154	-2.07 - -1.60	-2.19 - -1.38	-2.46 - -1.28	-3.36 - -0.384	-2.14 - -1.60
DR40	-0.128 - -0.0704	-0.153 - -0.0566	-0.110 - -0.0793	-0.116 - -0.0739	-0.145 - -0.0444	-0.338 - -0.161	-0.426 - -0.116	-0.307 - -0.159	-0.353 - -0.113	-0.313 - -0.153
DR42	-0.286 - -0.233	-0.306 - -0.216	-0.273 - -0.246	-0.278 - -0.241	-0.339 - -0.181	-1.75 - -1.22	-1.92 - -1.03	-2.17 - -0.832	-3.18 - 0.175	-1.71 - -1.29
DR43	-0.106 - -0.0402	-0.125 - -0.0123	-0.0976 - -0.0579	-0.106 - -0.0494	-0.113 - -0.0426	-0.206 - -0.0502	-0.263 - 0.0249	-0.201 - -0.0770	-0.240 - -0.0384	-0.187 - -0.0917
DR44	0.110 - 0.147	0.0961 - 0.163	0.111 - 0.142	0.102 - 0.152	0.107 - 0.146	0.140 - 0.214	0.109 - 0.248	0.0864 - 0.259	-0.0432 - 0.388	0.149 - 0.196
DR63	-0.301 - -0.226	-0.323 - -0.196	-0.290 - -0.240	-0.301 - -0.230	-0.342 - -0.188	-1.76 - -1.02	-1.93 - -0.664	-2.47 - -0.402	-4.02 - 1.15	-1.63 - -1.23
DR64	-0.382 - -0.362	-0.391 - -0.358	-0.380 - -0.360	-0.386 - -0.354	-0.482 - -0.258	-85.5 - -65.9	-94.6 - -62.2	-102 - -46.4	-143 - -4.96	-79.4 - -68.6
DR67	0.0192 - 0.115	-0.0114 - 0.150	0.0406 - 0.0910	0.0318 - 0.0998	0.0009 - 0.131	0.0197 - 0.469	-0.151 - 0.684	0.0587 - 0.400	-0.0471 - 0.506	0.108 - 0.351
DR68	-0.299 - -0.283	-0.305 - -0.279	-0.298 - -0.283	-0.302 - -0.278	-0.320 - -0.260	-0.513 - -0.466	-0.532 - -0.454	-0.552 - -0.423	-0.650 - -0.325	-0.532 - -0.443
DR71	-0.0105 - 0.0005	-0.0135 - 0.0051	-0.0091 - -0.0023	-0.0105 - -0.0009	-0.0163 - 0.0049	-0.0135 - 0.0028	-0.0182 - 0.0104	-0.0132 - -0.0001	-0.0172 - 0.0039	-0.0181 - 0.0048
DR72	0.133 - 0.187	0.111 - 0.201	0.148 - 0.177	0.143 - 0.182	0.101 - 0.224	0.391 - 0.636	0.288 - 0.710	0.220 - 0.830	-0.238 - 1.29	0.411 - 0.640
DR76	-0.0154 - 0.0024	-0.0241 - 0.0081	-0.0118 - -0.0002	-0.0143 - 0.0022	-0.0181 - 0.0061	-0.0220 - 0.0054	-0.0373 - 0.0150	-0.0188 - 0.0043	-0.0259 - 0.0114	-0.0205 - 0.0060
DR78	-0.0661 - -0.0073	-0.0812 - 0.0221	-0.0572 - -0.0251	-0.0628 - -0.0196	-0.104 - 0.0213	-0.236 - 0.0107	-0.303 - 0.149	-0.237 - -0.0325	-0.300 - 0.0306	-0.248 - -0.0214
τ (%)	85.2	74.1	100.0	92.6	70.4	77.8	66.7	81.5	48.1	85.2

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

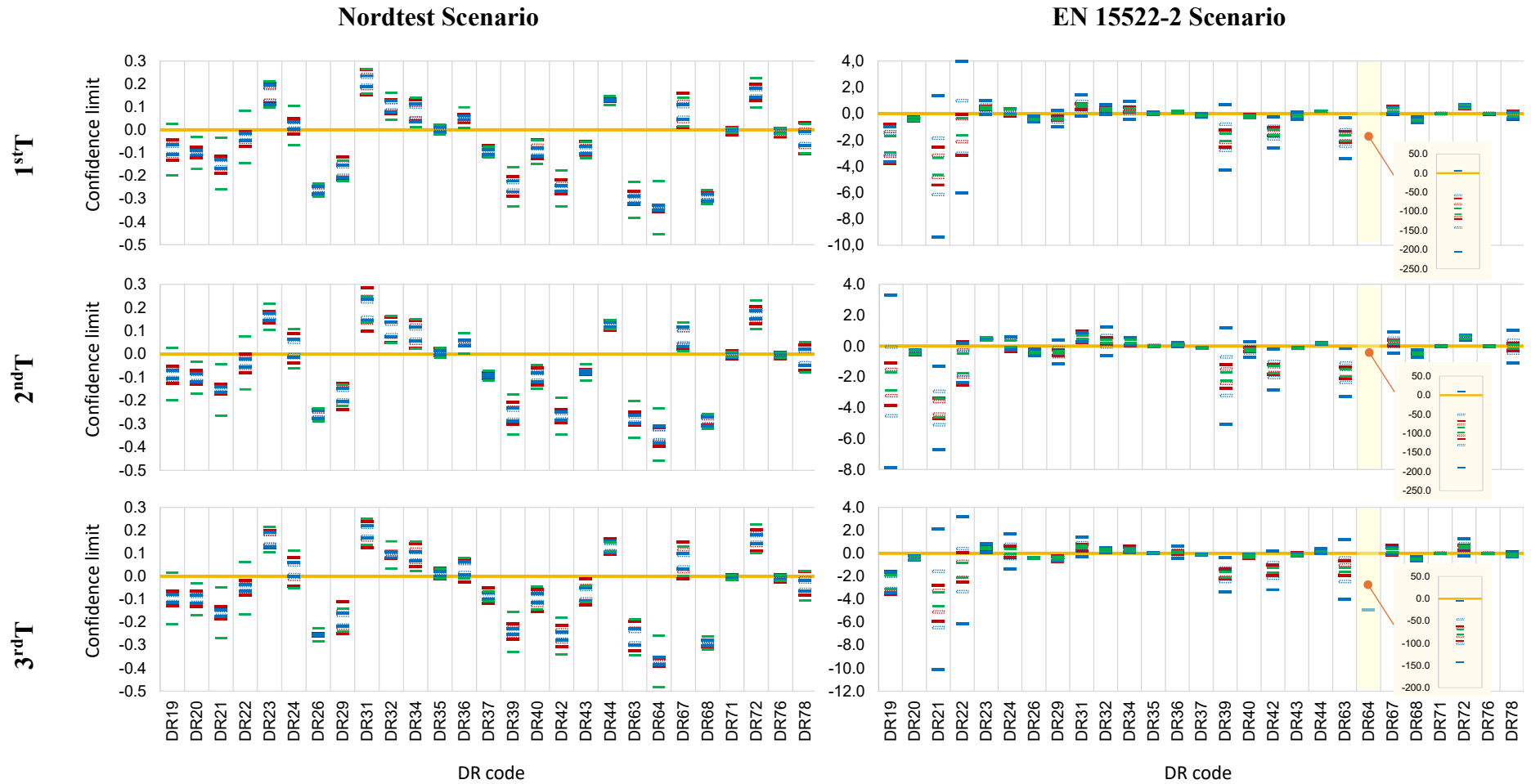


Figure D.6. Confidence limits of the difference between DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach, and by the S-t and MCM approaches considering 95% and 98% confidence levels, for the comparison of DR observed in the spill sample 1 (Sp1) and in the suspected source sample 2 (SS2, known not to be the origin of the spill), applying the experimental data obtained for the three DR comparison trials (1stT, 2ndT and 3rdT) and the DR comparison conditions represented by the Nordtest scenario ($A/(A+B)$ ratio format and triplicate injections) and EN 15522-2 scenario (A/B ratio format and duplicate injections). $P_{2.5}$ and $P_{97.5}$ of MCM; $P_{2.5}$ and $P_{97.5}$ of S-t; — P_1 and P_{99} of MCM; — P_1 and P_{99} of S-t; — SC_{LL} and SC_{UL} ; — $(\overline{DR}_{Sp} - \overline{DR}_{SS}) = 0$.

Table D.10. First trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 1 (Sp1) and in the suspected source sample 3 (SS3, known not to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp1} = n_{SS3} = 3$					EN 15522-2 scenario: A/B and $n_{Sp1} = n_{SS3} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR19	0.0635 - 0.122	0.0453 - 0.138	0.0768 - 0.110	0.0710 - 0.116	-0.0062 - 0.193	0.653 - 1.70	0.370 - 2.07	-0.198 - 2.50	-2.23 - 4.54	0.795 - 1.51
DR20	-0.196 - -0.165	-0.203 - -0.153	-0.191 - -0.173	-0.194 - -0.170	-0.258 - -0.106	-1.00 - -0.787	-1.06 - -0.706	-1.20 - -0.613	-1.64 - -0.172	-1.08 - -0.727
DR21	-0.0948 - -0.0409	-0.114 - -0.0248	-0.0813 - -0.0519	-0.0864 - -0.0468	-0.172 - 0.0391	-1.76 - -0.561	-2.15 - -0.202	-1.65 - -0.616	-1.96 - -0.298	-1.57 - -0.689
DR22	-0.0390 - -0.0007	-0.0566 - 0.0071	-0.0285 - -0.0046	-0.0336 - 0.0005	-0.131 - 0.0978	-1.45 - 0.0710	-2.27 - 0.332	-2.31 - 1.32	-5.04 - 4.05	-1.12 - 0.129
DR23	0.0745 - 0.109	0.0658 - 0.122	0.0736 - 0.107	0.0631 - 0.118	0.0295 - 0.152	0.232 - 0.347	0.204 - 0.387	0.121 - 0.451	-0.126 - 0.698	0.176 - 0.396
DR24	0.0315 - 0.0611	0.0185 - 0.0693	0.0391 - 0.0550	0.0363 - 0.0578	-0.0362 - 0.130	0.163 - 0.404	0.0562 - 0.486	0.191 - 0.384	0.131 - 0.444	0.0810 - 0.494
DR26	-0.227 - -0.215	-0.230 - -0.212	-0.226 - -0.216	-0.230 - -0.212	-0.247 - -0.195	-0.353 - -0.325	-0.361 - -0.316	-0.377 - -0.301	-0.434 - -0.244	-0.374 - -0.304
DR29	-0.508 - -0.471	-0.520 - -0.458	-0.500 - -0.480	-0.504 - -0.476	-0.557 - -0.423	-2.52 - -2.15	-2.72 - -2.06	-2.84 - -1.79	-3.63 - -1.00	-2.52 - -2.11
DR31	0.148 - 0.218	0.114 - 0.234	0.169 - 0.210	0.162 - 0.217	0.133 - 0.246	0.383 - 0.646	0.228 - 0.692	0.427 - 0.662	0.354 - 0.735	0.444 - 0.645
DR32	0.0536 - 0.113	0.0281 - 0.128	0.0589 - 0.114	0.0421 - 0.130	0.0266 - 0.146	0.148 - 0.345	0.0422 - 0.391	-0.0010 - 0.527	-0.398 - 0.924	0.158 - 0.368
DR34	0.0209 - 0.0811	0.0049 - 0.102	0.0215 - 0.0772	0.0042 - 0.0944	-0.0164 - 0.115	0.0565 - 0.299	-0.0108 - 0.376	-0.152 - 0.503	-0.645 - 0.995	0.0507 - 0.300
DR35	-0.0120 - 0.0137	-0.0198 - 0.0231	-0.0070 - 0.0076	-0.0096 - 0.0101	-0.0205 - 0.0210	-0.0207 - 0.0238	-0.0371 - 0.0417	-0.0187 - 0.0195	-0.0306 - 0.0313	-0.0240 - 0.0248
DR36	0.0815 - 0.0942	0.0774 - 0.0982	0.0825 - 0.0936	0.0791 - 0.0971	0.0454 - 0.131	0.164 - 0.201	0.153 - 0.214	0.136 - 0.230	0.0664 - 0.300	0.121 - 0.245
DR37	-0.0772 - -0.0553	-0.0878 - -0.0504	-0.0715 - -0.0570	-0.0746 - -0.0539	-0.0836 - -0.0448	-0.111 - -0.0714	-0.130 - -0.0632	-0.137 - -0.0363	-0.213 - 0.0394	-0.109 - -0.0640
DR39	-0.0077 - 0.0658	-0.0344 - 0.0835	0.0079 - 0.0546	-0.0020 - 0.0645	-0.0348 - 0.0973	-0.0654 - 0.253	-0.203 - 0.323	-0.277 - 0.500	-0.861 - 1.08	-0.0137 - 0.237
DR40	-0.0532 - 0.0071	-0.0704 - 0.0309	-0.0419 - -0.0076	-0.0478 - -0.0016	-0.0708 - 0.0213	-0.137 - 0.0347	-0.198 - 0.105	-0.128 - 0.0179	-0.173 - 0.0631	-0.124 - 0.0137
DR42	0.0458 - 0.0744	0.0377 - 0.0842	0.0513 - 0.0669	0.0485 - 0.0696	0.0026 - 0.116	0.119 - 0.224	0.0880 - 0.265	0.124 - 0.209	0.0971 - 0.235	0.0711 - 0.261
DR43	-0.0578 - -0.0104	-0.0767 - 0.0005	-0.0524 - -0.0112	-0.0652 - 0.0016	-0.0631 - -0.0005	-0.111 - -0.0100	-0.156 - 0.0127	-0.181 - 0.0752	-0.374 - 0.268	-0.0933 - -0.0124
DR44	0.147 - 0.158	0.143 - 0.162	0.149 - 0.156	0.147 - 0.157	0.134 - 0.171	0.195 - 0.213	0.189 - 0.219	0.197 - 0.211	0.192 - 0.216	0.181 - 0.227
DR67	0.0747 - 0.129	0.0494 - 0.141	0.0825 - 0.128	0.0683 - 0.143	0.0450 - 0.166	0.188 - 0.436	0.0791 - 0.493	0.0195 - 0.641	-0.448 - 1.11	0.222 - 0.439
DR68	-0.242 - -0.228	-0.248 - -0.225	-0.239 - -0.230	-0.241 - -0.228	-0.261 - -0.208	-0.381 - -0.349	-0.393 - -0.342	-0.403 - -0.323	-0.464 - -0.262	-0.399 - -0.327
DR72	0.427 - 0.454	0.415 - 0.458	0.435 - 0.451	0.433 - 0.453	0.400 - 0.487	0.973 - 1.09	0.914 - 1.11	0.888 - 1.19	0.657 - 1.43	0.955 - 1.13
DR78	-0.0805 - -0.0166	-0.0969 - 0.0068	-0.0695 - -0.0332	-0.0758 - -0.0269	-0.117 - 0.0141	-0.308 - -0.0285	-0.392 - 0.0855	-0.301 - -0.0615	-0.375 - 0.0126	-0.305 - -0.0578
τ (%)	87.0	73.9	95.7	82.6	60.9	82.6	69.6	65.2	47.8	82.6

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table D.11. Second trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 1 (Sp1) and in the suspected source sample 3 (SS3, known not to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp1} = n_{SS3} = 3$					EN 15522-2 scenario: A/B and $n_{Sp1} = n_{SS3} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR19	0.0662 - 0.124	0.0504 - 0.142	0.0781 - 0.112	0.0722 - 0.118	-0.0044 - 0.194	0.717 - 1.61	0.485 - 1.86	0.764 - 1.55	0.521 - 1.79	0.802 - 1.51
DR20	-0.215 - -0.156	-0.232 - -0.137	-0.203 - -0.169	-0.209 - -0.163	-0.261 - -0.110	-1.16 - -0.710	-1.36 - -0.601	-1.51 - -0.324	-2.40 - 0.569	-1.09 - -0.740
DR21	-0.0939 - -0.0508	-0.105 - -0.0377	-0.0849 - -0.0607	-0.0891 - -0.0565	-0.178 - 0.0321	-1.73 - -0.723	-2.14 - -0.472	-2.48 - 0.101	-4.41 - 2.04	-1.62 - -0.756
DR22	-0.0491 - -0.0099	-0.0691 - -0.0008	-0.0398 - -0.0145	-0.0452 - -0.0091	-0.141 - 0.0864	-1.41 - -0.192	-1.91 - 0.135	-2.36 - 0.840	-4.78 - 3.25	-1.37 - -0.157
DR23	0.0755 - 0.0978	0.0688 - 0.104	0.0802 - 0.0932	0.0779 - 0.0955	0.0258 - 0.148	0.229 - 0.316	0.202 - 0.339	0.233 - 0.313	0.209 - 0.338	0.164 - 0.382
DR24	0.0188 - 0.0802	-0.0001 - 0.0996	0.0321 - 0.0663	0.0261 - 0.0723	-0.0330 - 0.131	0.0738 - 0.502	-0.0636 - 0.632	0.100 - 0.480	-0.0172 - 0.597	0.0894 - 0.491
DR26	-0.222 - -0.215	-0.224 - -0.213	-0.221 - -0.217	-0.222 - -0.216	-0.244 - -0.193	-0.340 - -0.328	-0.343 - -0.324	-0.339 - -0.329	-0.342 - -0.326	-0.369 - -0.300
DR29	-0.513 - -0.469	-0.526 - -0.453	-0.506 - -0.476	-0.513 - -0.469	-0.559 - -0.423	-2.56 - -2.27	-2.67 - -2.19	-2.78 - -2.02	-3.36 - -1.44	-2.61 - -2.19
DR31	0.0948 - 0.190	0.0653 - 0.225	0.116 - 0.169	0.107 - 0.178	0.0824 - 0.203	0.258 - 0.669	0.130 - 0.889	0.279 - 0.614	0.175 - 0.718	0.337 - 0.556
DR32	0.0418 - 0.118	0.0144 - 0.140	0.0606 - 0.105	0.0528 - 0.113	0.0238 - 0.142	0.0928 - 0.398	-0.0131 - 0.515	0.114 - 0.387	0.0296 - 0.471	0.147 - 0.354
DR34	0.0251 - 0.0992	0.0013 - 0.119	0.0402 - 0.0877	0.0300 - 0.0978	-0.0012 - 0.129	0.0583 - 0.397	-0.0368 - 0.501	-0.211 - 0.661	-0.867 - 1.32	0.102 - 0.348
DR35	-0.0168 - 0.0123	-0.0260 - 0.0210	-0.0111 - 0.0062	-0.0141 - 0.0092	-0.0235 - 0.0186	-0.0289 - 0.0208	-0.0456 - 0.0349	-0.0262 - 0.0194	-0.0404 - 0.0336	-0.0282 - 0.0214
DR36	0.0668 - 0.102	0.0562 - 0.113	0.0679 - 0.101	0.0576 - 0.112	0.0425 - 0.127	0.133 - 0.213	0.107 - 0.237	0.0628 - 0.284	-0.103 - 0.450	0.112 - 0.234
DR37	-0.0769 - -0.0508	-0.0864 - -0.0449	-0.0713 - -0.0546	-0.0749 - -0.0510	-0.0824 - -0.0436	-0.110 - -0.0650	-0.130 - -0.0556	-0.143 - -0.0272	-0.230 - 0.0597	-0.108 - -0.0622
DR39	-0.0065 - 0.0491	-0.0210 - 0.0673	0.0046 - 0.0374	-0.0012 - 0.0432	-0.0449 - 0.0869	-0.0441 - 0.199	-0.108 - 0.278	-0.0351 - 0.185	-0.103 - 0.253	-0.0498 - 0.200
DR40	-0.0496 - 0.0018	-0.0673 - 0.0154	-0.0399 - -0.0047	-0.0474 - 0.0028	-0.0672 - 0.0227	-0.125 - 0.0149	-0.176 - 0.0484	-0.113 - 0.0161	-0.153 - 0.0561	-0.115 - 0.0179
DR42	0.0346 - 0.0793	0.0230 - 0.0945	0.0407 - 0.0699	0.0345 - 0.0761	-0.0007 - 0.111	0.0860 - 0.232	0.0478 - 0.283	0.0902 - 0.217	0.0508 - 0.257	0.0600 - 0.248
DR43	-0.0358 - -0.0072	-0.0430 - 0.0021	-0.0316 - -0.0131	-0.0355 - -0.0092	-0.0534 - 0.0088	-0.0648 - -0.0062	-0.0811 - 0.0134	-0.113 - 0.0389	-0.227 - 0.153	-0.0770 - 0.0031
DR44	0.139 - 0.161	0.130 - 0.166	0.144 - 0.158	0.141 - 0.161	0.133 - 0.169	0.177 - 0.218	0.160 - 0.227	0.146 - 0.254	0.0649 - 0.335	0.178 - 0.222
DR67	0.0692 - 0.116	0.0515 - 0.127	0.0799 - 0.110	0.0734 - 0.117	0.0352 - 0.155	0.201 - 0.361	0.131 - 0.396	0.0876 - 0.497	-0.220 - 0.805	0.186 - 0.399
DR68	-0.242 - -0.226	-0.247 - -0.223	-0.241 - -0.226	-0.245 - -0.222	-0.260 - -0.207	-0.382 - -0.344	-0.397 - -0.335	-0.414 - -0.308	-0.494 - -0.229	-0.397 - -0.325
DR72	0.417 - 0.455	0.406 - 0.467	0.425 - 0.446	0.421 - 0.450	0.392 - 0.479	0.945 - 1.11	0.907 - 1.18	0.799 - 1.24	0.465 - 1.58	0.935 - 1.11
DR78	-0.0828 - -0.0122	-0.106 - 0.0060	-0.0697 - -0.0215	-0.0800 - -0.0112	-0.112 - 0.0210	-0.358 - -0.0182	-0.491 - 0.0573	-0.628 - 0.294	-1.32 - 0.987	-0.295 - -0.0392
τ (%)	87.0	73.9	95.7	87.0	52.2	87.0	60.9	65.2	43.5	82.6

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table D.12. Third trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 1 (Sp1) and in the suspected source sample 3 (SS3, known not to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp1} = n_{SS3} = 3$					EN 15522-2 scenario: A/B and $n_{Sp1} = n_{SS3} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR19	0.0562 - 0.115	0.0382 - 0.131	0.0687 - 0.102	0.0628 - 0.108	-0.0135 - 0.184	0.603 - 1.47	0.343 - 1.77	0.643 - 1.40	0.410 - 1.63	0.671 - 1.37
DR20	-0.208 - -0.162	-0.217 - -0.143	-0.201 - -0.175	-0.206 - -0.170	-0.264 - -0.112	-1.09 - -0.771	-1.17 - -0.652	-1.36 - -0.527	-1.99 - 0.0994	-1.12 - -0.763
DR21	-0.0928 - -0.0718	-0.0970 - -0.0618	-0.0935 - -0.0739	-0.0995 - -0.0679	-0.188 - 0.0209	-1.47 - -1.15	-1.53 - -0.991	-1.76 - -0.923	-2.39 - -0.292	-1.77 - -0.914
DR22	-0.0489 - -0.0275	-0.0617 - -0.0225	-0.0467 - -0.0262	-0.0531 - -0.0199	-0.149 - 0.0760	-1.30 - -0.693	-1.63 - -0.534	-1.78 - -0.125	-3.03 - 1.12	-1.53 - -0.374
DR23	0.0555 - 0.115	0.0304 - 0.127	0.0640 - 0.115	0.0483 - 0.131	0.0296 - 0.149	0.154 - 0.354	0.0476 - 0.393	0.0294 - 0.519	-0.339 - 0.888	0.168 - 0.380
DR24	-0.0044 - 0.0812	-0.0478 - 0.103	0.0237 - 0.0687	0.0158 - 0.0766	-0.0337 - 0.126	-0.0941 - 0.509	-0.368 - 0.759	0.0106 - 0.494	-0.139 - 0.643	0.0648 - 0.439
DR26	-0.221 - -0.214	-0.224 - -0.212	-0.220 - -0.215	-0.221 - -0.214	-0.243 - -0.192	-0.340 - -0.324	-0.348 - -0.320	-0.353 - -0.309	-0.385 - -0.277	-0.365 - -0.297
DR29	-0.531 - -0.461	-0.547 - -0.425	-0.521 - -0.482	-0.528 - -0.476	-0.572 - -0.432	-3.17 - -2.25	-3.50 - -1.95	-3.87 - -1.54	-5.63 - 0.214	-2.94 - -2.47
DR31	0.105 - 0.160	0.0732 - 0.173	0.119 - 0.156	0.112 - 0.164	0.0768 - 0.199	0.278 - 0.534	0.122 - 0.584	0.0983 - 0.781	-0.415 - 1.29	0.328 - 0.552
DR32	0.0351 - 0.0885	0.0129 - 0.1000	0.0404 - 0.0894	0.0253 - 0.105	0.0042 - 0.126	0.0910 - 0.284	-0.0048 - 0.328	-0.0526 - 0.459	-0.437 - 0.843	0.0949 - 0.311
DR34	0.0066 - 0.0895	-0.0301 - 0.117	0.0244 - 0.0747	0.0137 - 0.0854	-0.0159 - 0.115	-0.0226 - 0.353	-0.274 - 0.506	0.0334 - 0.316	-0.0541 - 0.404	0.0513 - 0.298
DR35	-0.0259 - 0.0104	-0.0438 - 0.0188	-0.0216 - 0.0108	-0.0316 - 0.0208	-0.0273 - 0.0165	-0.0457 - 0.0184	-0.0832 - 0.0334	-0.0904 - 0.0752	-0.215 - 0.200	-0.0336 - 0.0183
DR36	0.0396 - 0.0945	0.0097 - 0.105	0.0460 - 0.0967	0.0303 - 0.112	0.0298 - 0.113	0.0571 - 0.205	-0.0199 - 0.235	-0.0576 - 0.348	-0.362 - 0.652	0.0853 - 0.205
DR37	-0.0913 - -0.0404	-0.112 - -0.0214	-0.0806 - -0.0520	-0.0856 - -0.0469	-0.0872 - -0.0453	-0.140 - -0.0468	-0.187 - -0.0111	-0.131 - -0.0529	-0.155 - -0.0287	-0.117 - -0.0669
DR39	0.0031 - 0.0619	-0.0208 - 0.0755	0.0173 - 0.0551	0.0092 - 0.0632	-0.0314 - 0.104	-0.0182 - 0.244	-0.151 - 0.304	0.0217 - 0.249	-0.0486 - 0.320	0.0043 - 0.267
DR40	-0.0488 - -0.0077	-0.0640 - 0.0051	-0.0443 - -0.0095	-0.0551 - 0.0013	-0.0726 - 0.0188	-0.117 - -0.0084	-0.158 - 0.0286	-0.193 - 0.0749	-0.395 - 0.276	-0.127 - 0.0087
DR42	0.0297 - 0.0699	0.0160 - 0.0824	0.0397 - 0.0615	0.0359 - 0.0653	-0.0067 - 0.108	0.0688 - 0.213	0.0179 - 0.260	0.0843 - 0.206	0.0465 - 0.244	0.0479 - 0.243
DR43	-0.0448 - -0.0046	-0.0540 - 0.0163	-0.0412 - -0.0158	-0.0466 - -0.0104	-0.0603 - 0.0032	-0.0806 - 0.0031	-0.107 - 0.0502	-0.0823 - -0.0130	-0.104 - 0.0085	-0.0888 - -0.0065
DR44	0.134 - 0.170	0.123 - 0.185	0.135 - 0.165	0.126 - 0.174	0.132 - 0.168	0.168 - 0.238	0.142 - 0.269	0.115 - 0.284	-0.0126 - 0.411	0.177 - 0.221
DR67	0.0561 - 0.136	0.0315 - 0.170	0.0685 - 0.118	0.0580 - 0.128	0.0301 - 0.156	0.145 - 0.528	0.0159 - 0.713	-0.137 - 0.757	-0.809 - 1.43	0.194 - 0.426
DR68	-0.237 - -0.223	-0.240 - -0.219	-0.236 - -0.224	-0.240 - -0.220	-0.256 - -0.204	-0.369 - -0.337	-0.379 - -0.325	-0.398 - -0.307	-0.467 - -0.239	-0.388 - -0.318
DR72	0.400 - 0.441	0.383 - 0.450	0.405 - 0.441	0.394 - 0.452	0.380 - 0.466	0.854 - 1.07	0.769 - 1.12	0.692 - 1.26	0.269 - 1.68	0.891 - 1.06
DR78	-0.114 - -0.0421	-0.140 - -0.0194	-0.100 - -0.0548	-0.110 - -0.0450	-0.143 - -0.0125	-0.457 - -0.114	-0.615 - -0.0168	-0.702 - 0.158	-1.35 - 0.804	-0.395 - -0.149
τ (%)	91.3	73.9	95.7	91.3	56.5	78.3	65.2	73.9	30.4	91.3

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

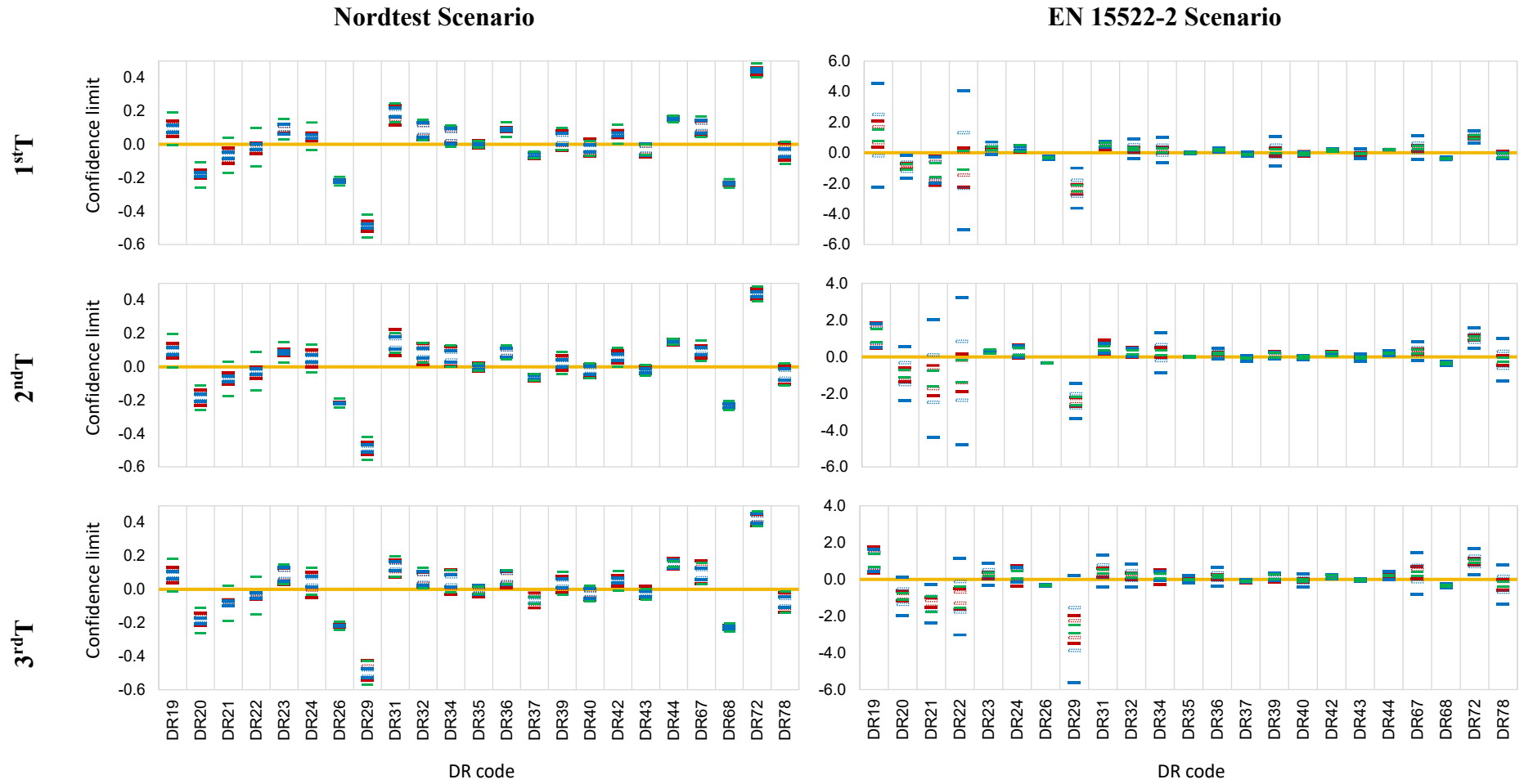


Figure D.7. Confidence limits of the difference between DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach, and by the S-t and MCM approaches considering 95% and 98% confidence levels, for the comparison of DR observed in the spill sample 1 (Sp1) and in the suspected source sample 3 (SS3, known not to be the origin of the spill), applying the experimental data obtained for the three DR comparison trials (1stT, 2ndT and 3rdT) and the DR comparison conditions represented by the Nordtest scenario ($A/(A+B)$ ratio format and triplicate injections) and EN 15522-2 scenario (A/B ratio format and duplicate injections). $\cdots$ $P2.5$ and $P97.5$ of MCM; $\cdots$ $P2.5$ and $P97.5$ of S-t; $-$ $P1$ and $P99$ of MCM; $-$ $P1$ and $P99$ of S-t; $-$ SC_{LL} and SC_{UL} ; $-$ ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) = 0.

Table D.13. First trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 1 (SS1, known to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp2} = n_{SS1} = 3$					EN 15522-2 scenario: A/B and $n_{Sp2} = n_{SS1} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR35	-0.0258 - 0.0002	-0.0365 - 0.0063	-0.0240 - 0.0006	-0.0316 - 0.0082	-0.0314 - 0.0080	-0.0397 - 0.0038	-0.0578 - 0.0140	-0.0753 - 0.0436	-0.165 - 0.133	-0.0388 - 0.0072
DR36	-0.0295 - 0.0430	-0.0425 - 0.0782	-0.0221 - 0.0221	-0.0316 - 0.0316	-0.0483 - 0.0483	-0.0832 - 0.127	-0.123 - 0.226	-0.0862 - 0.0859	-0.139 - 0.139	-0.0739 - 0.0736
DR37	-0.0213 - 0.0027	-0.0315 - 0.0092	-0.0161 - -0.0003	-0.0194 - 0.0031	-0.0223 - 0.0060	-0.0306 - 0.0062	-0.0459 - 0.0163	-0.0576 - 0.0374	-0.129 - 0.109	-0.0259 - 0.0056
DR39	-0.0235 - 0.0638	-0.0425 - 0.102	-0.0094 - 0.0377	-0.0176 - 0.0460	-0.0541 - 0.0825	-0.114 - 0.305	-0.199 - 0.502	-0.117 - 0.226	-0.224 - 0.333	-0.0790 - 0.188
DR40	-0.0393 - 0.0154	-0.0562 - 0.0329	-0.0275 - 0.0032	-0.0329 - 0.0086	-0.0552 - 0.0309	-0.0950 - 0.0447	-0.137 - 0.0903	-0.0862 - 0.0355	-0.124 - 0.0732	-0.0876 - 0.0369
DR42	-0.0043 - 0.0320	-0.0121 - 0.0501	-0.0013 - 0.0230	-0.0065 - 0.0281	-0.0508 - 0.0725	-0.0224 - 0.120	-0.0512 - 0.189	-0.152 - 0.221	-0.433 - 0.502	-0.0757 - 0.145
DR43	-0.0115 - 0.0084	-0.0177 - 0.0159	-0.0072 - 0.0035	-0.0091 - 0.0054	-0.0310 - 0.0273	-0.0222 - 0.0174	-0.0353 - 0.0334	-0.0192 - 0.0132	-0.0292 - 0.0233	-0.0398 - 0.0338
DR44	-0.0112 - 0.0310	-0.0221 - 0.0486	-0.0034 - 0.0192	-0.0074 - 0.0232	-0.0211 - 0.0369	-0.0243 - 0.0580	-0.0456 - 0.0940	-0.0217 - 0.0468	-0.0428 - 0.0680	-0.0240 - 0.0492
τ (%)	0	0	12.5	0	0	0	0	0	0	0

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table D.14. Second trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 1 (SS1, known to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp2} = n_{SS1} = 3$					EN 15522-2 scenario: A/B and $n_{Sp2} = n_{SS1} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR35	-0.0248 - -0.0038	-0.0334 - 0.0004	-0.0189 - -0.0072	-0.0209 - -0.0052	-0.0334 - 0.0073	-0.0386 - -0.0025	-0.0539 - 0.0056	-0.0330 - -0.0028	-0.0423 - 0.0066	-0.0416 - 0.0059
DR36	-0.0359 - 0.0333	-0.0511 - 0.0615	-0.0284 - 0.0172	-0.0381 - 0.0269	-0.0524 - 0.0412	-0.0940 - 0.103	-0.135 - 0.193	-0.0978 - 0.0729	-0.151 - 0.126	-0.0828 - 0.0579
DR37	-0.0193 - 0.0037	-0.0274 - 0.0098	-0.0137 - -0.0009	-0.0159 - 0.0013	-0.0221 - 0.0075	-0.0282 - 0.0077	-0.0419 - 0.0175	-0.0242 - 0.0061	-0.0336 - 0.0154	-0.0257 - 0.0075
DR39	-0.0226 - 0.0275	-0.0401 - 0.0404	-0.0099 - 0.0178	-0.0148 - 0.0227	-0.0648 - 0.0727	-0.114 - 0.128	-0.207 - 0.197	-0.0862 - 0.117	-0.149 - 0.180	-0.120 - 0.151
DR40	-0.0180 - 0.0087	-0.0269 - 0.0161	-0.0122 - 0.0034	-0.0150 - 0.0061	-0.0477 - 0.0388	-0.0447 - 0.0252	-0.0697 - 0.0449	-0.0402 - 0.0216	-0.0593 - 0.0408	-0.0719 - 0.0533
DR42	-0.0192 - 0.0327	-0.0355 - 0.0485	-0.0106 - 0.0245	-0.0180 - 0.0320	-0.0547 - 0.0687	-0.0848 - 0.125	-0.165 - 0.189	-0.0698 - 0.114	-0.127 - 0.171	-0.0882 - 0.133
DR43	-0.0186 - 0.0191	-0.0326 - 0.0278	-0.0108 - 0.0143	-0.0161 - 0.0196	-0.0282 - 0.0317	-0.0407 - 0.0361	-0.0741 - 0.0528	-0.0961 - 0.102	-0.245 - 0.251	-0.0353 - 0.0409
DR44	-0.0076 - 0.0250	-0.0161 - 0.0374	-0.0037 - 0.0182	-0.0084 - 0.0229	-0.0218 - 0.0362	-0.0175 - 0.0488	-0.0349 - 0.0746	-0.0176 - 0.0406	-0.0355 - 0.0586	-0.0251 - 0.0481
τ (%)	12.5	0	25.0	12.5	0	12.5	0	12.5	0	0

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table D.15. Third trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 1 (SS1, known to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp2} = n_{SS1} = 3$					EN 15522-2 scenario: A/B and $n_{Sp2} = n_{SS1} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR35	-0.0260 - 0.0111	-0.0329 - 0.0326	-0.0241 - 0.0004	-0.0294 - 0.0057	-0.0329 - 0.0092	-0.0401 - 0.0259	-0.0524 - 0.0689	-0.0444 - 0.0117	-0.0618 - 0.0290	-0.0411 - 0.0084
DR36	-0.0393 - 0.0321	-0.0611 - 0.0656	-0.0294 - 0.0144	-0.0387 - 0.0238	-0.0528 - 0.0378	-0.108 - 0.0919	-0.180 - 0.187	-0.0968 - 0.0637	-0.146 - 0.113	-0.0836 - 0.0505
DR37	-0.0308 - 0.0246	-0.0494 - 0.0503	-0.0229 - 0.0140	-0.0307 - 0.0219	-0.0213 - 0.0125	-0.0483 - 0.0438	-0.0896 - 0.0985	-0.0451 - 0.0337	-0.0694 - 0.0581	-0.0249 - 0.0136
DR39	-0.0310 - 0.0493	-0.0550 - 0.0893	-0.0164 - 0.0283	-0.0242 - 0.0362	-0.0642 - 0.0761	-0.165 - 0.261	-0.348 - 0.531	-0.147 - 0.195	-0.253 - 0.301	-0.116 - 0.165
DR40	-0.0159 - 0.0033	-0.0238 - 0.0104	-0.0125 - -0.0006	-0.0150 - 0.0019	-0.0500 - 0.0369	-0.0390 - 0.0125	-0.0633 - 0.0365	-0.0346 - 0.0070	-0.0474 - 0.0198	-0.0769 - 0.0493
DR42	-0.0196 - 0.0708	-0.0380 - 0.119	-0.0084 - 0.0426	-0.0173 - 0.0515	-0.0455 - 0.0797	-0.0934 - 0.288	-0.196 - 0.519	-0.105 - 0.217	-0.205 - 0.317	-0.0573 - 0.170
DR43	-0.0119 - 0.0227	-0.0185 - 0.0433	-0.0150 - 0.0179	-0.0252 - 0.0280	-0.0290 - 0.0318	-0.0236 - 0.0482	-0.0382 - 0.0978	-0.0952 - 0.0999	-0.242 - 0.247	-0.0365 - 0.0412
DR44	-0.0055 - 0.0261	-0.0140 - 0.0412	-0.0061 - 0.0227	-0.0150 - 0.0316	-0.0204 - 0.0370	-0.0132 - 0.0508	-0.0311 - 0.0841	-0.0698 - 0.0962	-0.195 - 0.221	-0.0229 - 0.0494
τ (%)	0	0	12.5	0	0	0	0	0	0	0

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

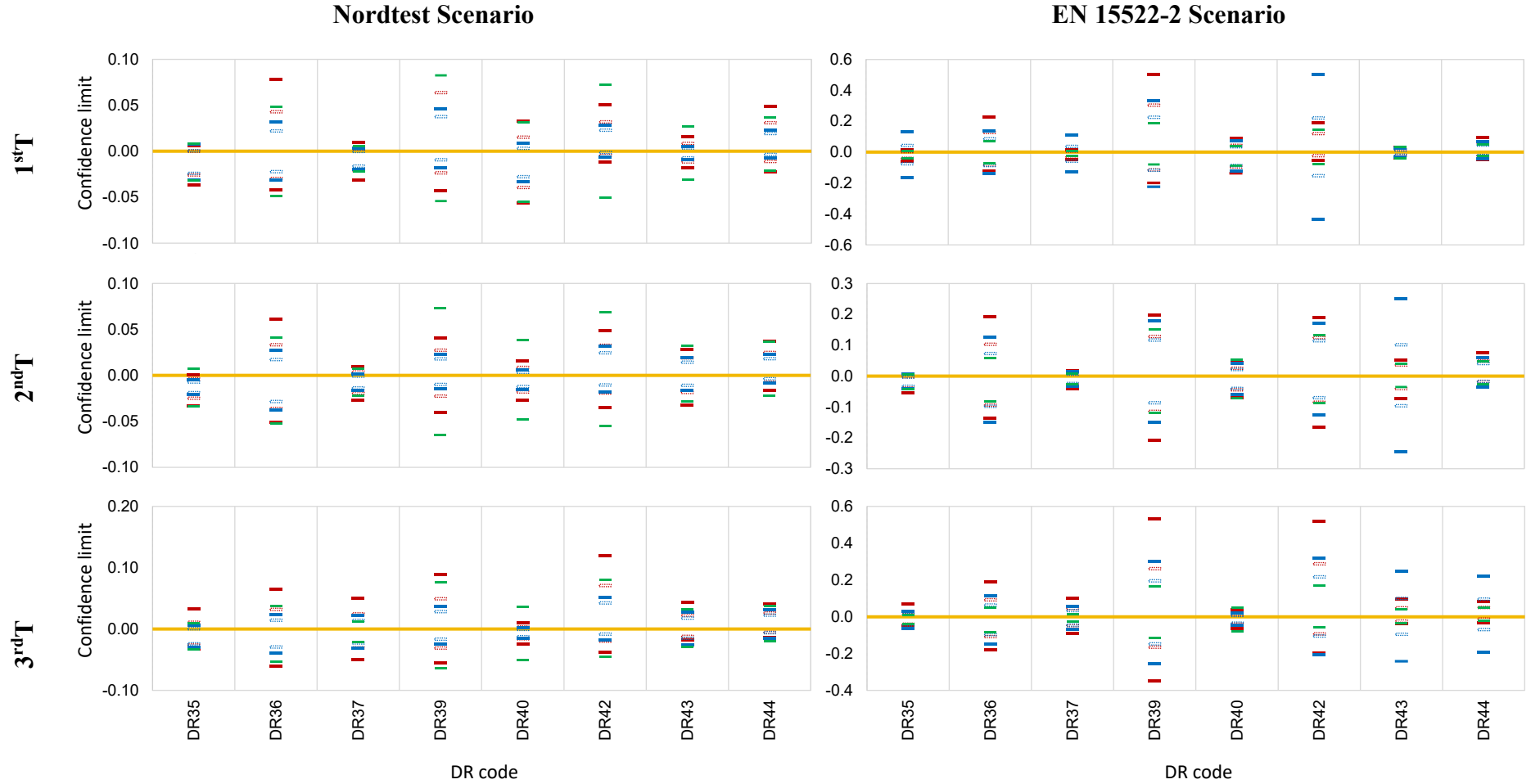


Figure D.8. Confidence limits of the difference between DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach, and by the S-t and MCM approaches considering 95% and 98% confidence levels, for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 1 (SS1, known to be the origin of the spill), applying the experimental data obtained for the three DR comparison trials (1stT, 2ndT and 3rdT) and the DR comparison conditions represented by the Nordtest scenario ($A/(A+B)$ ratio format and triplicate injections) and EN 15522-2 scenario (A/B ratio format and duplicate injections). ••• $P_{2.5}$ and $P_{97.5}$ of MCM; ••• $P_{2.5}$ and $P_{97.5}$ of S-t; — P_1 and P_{99} of MCM; — P_1 and P_{99} of S-t; — SC_{LL} and SC_{UL} ; — $(\overline{DR}_{Sp} - \overline{DR}_{SS}) = 0$.

Table D.16. First trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 2 (SS2, known not to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp2} = n_{SS2} = 3$					EN 15522-2 scenario: A/B and $n_{Sp2} = n_{SS2} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR35	-0.0258 - -0.0021	-0.0360 - 0.0037	-0.0244 - -0.0012	-0.0316 - 0.0060	-0.0326 - 0.0070	-0.0393 - -0.0002	-0.0583 - 0.0091	-0.0735 - 0.0388	-0.158 - 0.123	-0.0405 - 0.0057
DR36	0.0296 - 0.0702	0.0184 - 0.0862	0.0358 - 0.0620	0.0302 - 0.0676	0.0040 - 0.0938	0.0544 - 0.170	0.0243 - 0.229	-0.0400 - 0.252	-0.260 - 0.472	0.0398 - 0.172
DR37	-0.122 - -0.0867	-0.131 - -0.0723	-0.115 - -0.0964	-0.118 - -0.0931	-0.127 - -0.0847	-0.174 - -0.112	-0.190 - -0.0827	-0.172 - -0.122	-0.188 - -0.106	-0.172 - -0.122
DR39	-0.276 - -0.196	-0.297 - -0.167	-0.264 - -0.212	-0.276 - -0.201	-0.324 - -0.152	-2.18 - -1.37	-2.49 - -1.12	-2.84 - -0.699	-4.44 - 0.907	-2.03 - -1.51
DR40	-0.136 - -0.0828	-0.151 - -0.0617	-0.126 - -0.0964	-0.131 - -0.0914	-0.161 - -0.0610	-0.341 - -0.184	-0.382 - -0.105	-0.338 - -0.204	-0.379 - -0.163	-0.350 - -0.191
DR42	-0.256 - -0.224	-0.263 - -0.208	-0.253 - -0.232	-0.257 - -0.228	-0.322 - -0.163	-1.55 - -1.20	-1.62 - -1.02	-1.87 - -0.936	-2.58 - -0.230	-1.62 - -1.19
DR43	-0.104 - -0.0676	-0.111 - -0.0489	-0.101 - -0.0778	-0.106 - -0.0729	-0.125 - -0.0540	-0.193 - -0.108	-0.210 - -0.0624	-0.269 - -0.0508	-0.434 - 0.114	-0.208 - -0.112
DR44	0.118 - 0.143	0.109 - 0.150	0.119 - 0.143	0.112 - 0.150	0.111 - 0.151	0.155 - 0.204	0.136 - 0.217	0.113 - 0.248	0.0124 - 0.349	0.156 - 0.206
τ (%)	100	87.5	100	87.5	87.5	100	87.5	75.0	50.0	87.5

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table D.17. Second trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 2 (SS2, known not to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp2} = n_{SS2} = 3$					EN 15522-2 scenario: A/B and $n_{Sp2} = n_{SS2} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR35	-0.0149 - 0.0044	-0.0226 - 0.0082	-0.0102 - 0.0022	-0.0129 - 0.0049	-0.0237 - 0.0157	-0.0236 - 0.0085	-0.0363 - 0.0148	-0.0194 - 0.0085	-0.0280 - 0.0171	-0.0283 - 0.0175
DR36	0.0096 - 0.0675	-0.0038 - 0.0895	0.0082 - 0.0634	-0.0089 - 0.0805	-0.0081 - 0.0797	0.0079 - 0.169	-0.0270 - 0.241	-0.148 - 0.300	-0.485 - 0.637	0.0122 - 0.140
DR37	-0.107 - -0.0864	-0.113 - -0.0800	-0.103 - -0.0911	-0.105 - -0.0891	-0.118 - -0.0759	-0.152 - -0.117	-0.161 - -0.106	-0.150 - -0.120	-0.159 - -0.110	-0.160 - -0.110
DR39	-0.281 - -0.216	-0.298 - -0.194	-0.267 - -0.231	-0.274 - -0.225	-0.336 - -0.163	-2.39 - -1.45	-2.66 - -1.18	-3.17 - -0.656	-5.06 - 1.24	-2.18 - -1.64
DR40	-0.124 - -0.0806	-0.136 - -0.0686	-0.117 - -0.0867	-0.123 - -0.0803	-0.152 - -0.0517	-0.319 - -0.180	-0.362 - -0.140	-0.446 - -0.0508	-0.743 - 0.246	-0.328 - -0.169
DR42	-0.271 - -0.230	-0.282 - -0.218	-0.262 - -0.238	-0.266 - -0.234	-0.330 - -0.170	-1.67 - -1.28	-1.79 - -1.16	-2.01 - -0.937	-2.82 - -0.131	-1.69 - -1.26
DR43	-0.0807 - -0.0656	-0.0846 - -0.0599	-0.0783 - -0.0692	-0.0799 - -0.0676	-0.109 - -0.0385	-0.147 - -0.114	-0.155 - -0.102	-0.147 - -0.117	-0.157 - -0.107	-0.180 - -0.0844
DR44	0.120 - 0.150	0.113 - 0.162	0.123 - 0.144	0.119 - 0.148	0.113 - 0.154	0.159 - 0.215	0.146 - 0.237	0.105 - 0.262	-0.0123 - 0.379	0.159 - 0.208
τ (%)	87.5	75.0	87.5	75.0	75.0	87.5	75.0	75.0	37.5	87.5

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table D.18. Third trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 2 (SS2, known not to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

<i>DR</i> Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp2} = n_{SS2} = 3$					EN 15522-2 scenario: A/B and $n_{Sp2} = n_{SS2} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
<i>DR35</i>	-0.0158 - 0.0202	-0.0273 - 0.0370	-0.0104 - 0.0099	-0.0139 - 0.0134	-0.0201 - 0.0196	-0.0268 - 0.0356	-0.0541 - 0.0701	-0.0265 - 0.0258	-0.0427 - 0.0420	-0.0235 - 0.0228
<i>DR36</i>	0.0122 - 0.0464	0.0044 - 0.0661	0.0165 - 0.0357	0.0131 - 0.0391	-0.0173 - 0.0696	0.0190 - 0.112	-0.0067 - 0.173	0.0160 - 0.0939	-0.0081 - 0.118	-0.0081 - 0.118
<i>DR37</i>	-0.111 - -0.0612	-0.130 - -0.0411	-0.103 - -0.0708	-0.110 - -0.0640	-0.109 - -0.0643	-0.167 - -0.0793	-0.216 - -0.0387	-0.159 - -0.0877	-0.181 - -0.0657	-0.150 - -0.0961
<i>DR39</i>	-0.260 - -0.190	-0.274 - -0.151	-0.265 - -0.201	-0.285 - -0.181	-0.320 - -0.145	-2.06 - -1.46	-2.21 - -1.06	-2.08 - -1.59	-2.24 - -1.44	-2.11 - -1.56
<i>DR40</i>	-0.122 - -0.0847	-0.142 - -0.0765	-0.118 - -0.0832	-0.128 - -0.0726	-0.150 - -0.0504	-0.325 - -0.193	-0.408 - -0.161	-0.421 - -0.0687	-0.687 - 0.197	-0.324 - -0.166
<i>DR42</i>	-0.259 - -0.189	-0.275 - -0.153	-0.253 - -0.209	-0.263 - -0.199	-0.312 - -0.150	-1.68 - -1.06	-1.95 - -0.775	-2.13 - -0.682	-3.22 - 0.409	-1.63 - -1.19
<i>DR43</i>	-0.100 - -0.0345	-0.119 - -0.0043	-0.0902 - -0.0547	-0.0964 - -0.0485	-0.108 - -0.0369	-0.198 - -0.0411	-0.263 - 0.0403	-0.194 - -0.0670	-0.233 - -0.0277	-0.179 - -0.0824
<i>DR44</i>	0.116 - 0.150	0.105 - 0.166	0.117 - 0.147	0.108 - 0.156	0.112 - 0.152	0.151 - 0.218	0.123 - 0.253	0.0967 - 0.265	-0.0300 - 0.392	0.157 - 0.205
τ (%)	87.5	87.5	87.5	87.5	75.0	87.5	62.5	87.5	37.5	75.0

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

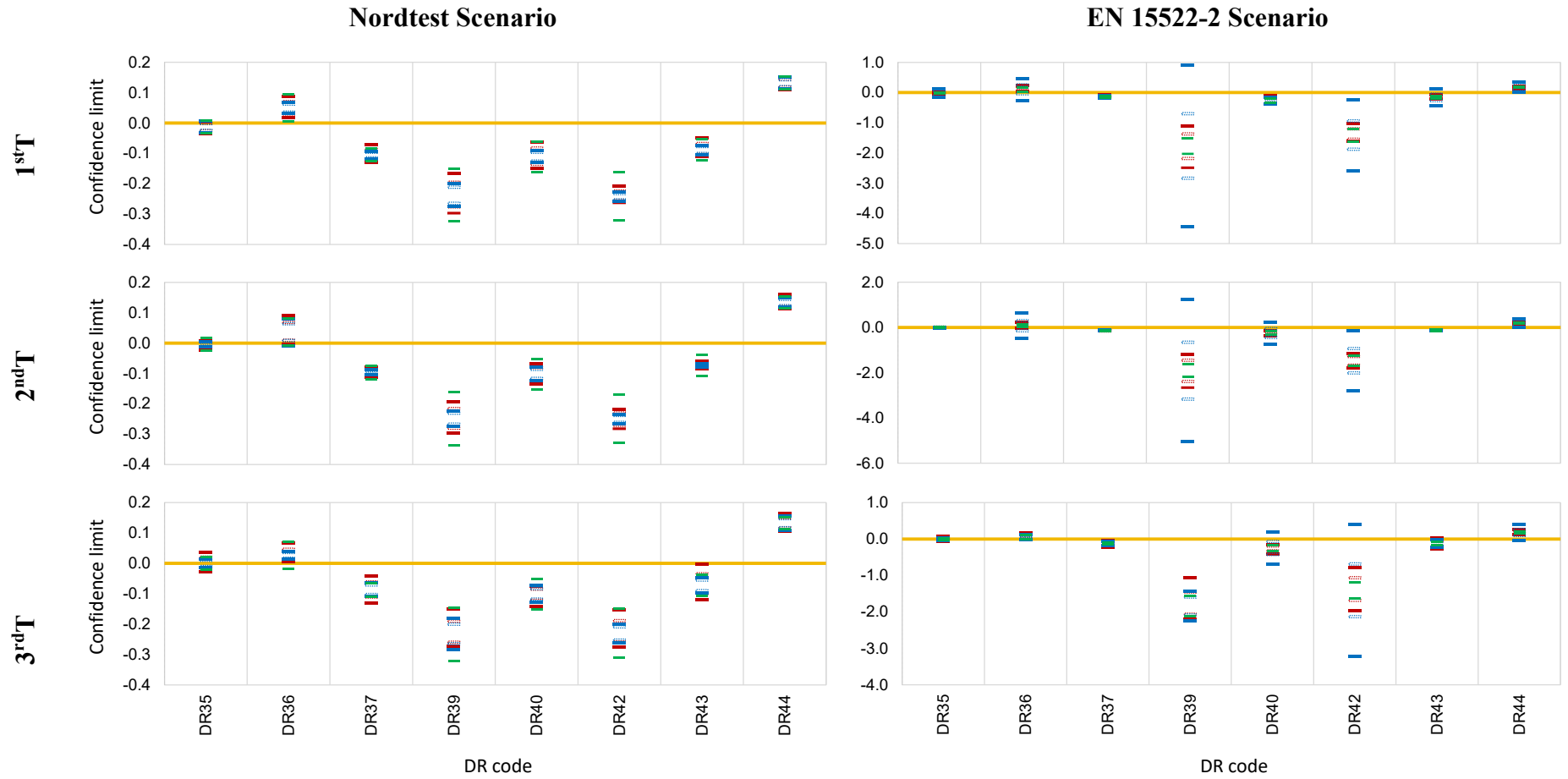


Figure D.9. Confidence limits of the difference between DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach, and by the S-t and MCM approaches considering 95% and 98% confidence levels, for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 2 (SS2, known not to be the origin of the spill), applying the experimental data obtained for the three DR comparison trials (1stT, 2ndT and 3rdT) and the DR comparison conditions represented by the Nordtest scenario ($A/(A+B)$ ratio format and triplicate injections) and EN 15522-2 scenario (A/B ratio format and duplicate injections). ••• $P_{2.5}$ and $P_{97.5}$ of MCM; ••• $P_{2.5}$ and $P_{97.5}$ of S-t; — P_1 and P_{99} of MCM; — P_1 and P_{99} of S-t; — SC_{LL} and SC_{UL} ; — $(\overline{DR}_{Sp} - \overline{DR}_{SS}) = 0$.

Table D.19. First trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 3 (SS3, known not to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp2} = n_{SS3} = 3$					EN 15522-2 scenario: A/B and $n_{Sp2} = n_{SS3} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR35	-0.0303 - 0.0006	-0.0434 - 0.0072	-0.0222 - -0.0040	-0.0254 - -0.0008	-0.0330 - 0.0067	-0.0468 - 0.0048	-0.0707 - 0.0160	-0.0412 - 0.0056	-0.0556 - 0.0201	-0.0409 - 0.0053
DR36	0.0691 - 0.103	0.0618 - 0.119	0.0681 - 0.100	0.0582 - 0.110	0.0417 - 0.127	0.133 - 0.232	0.114 - 0.278	0.0387 - 0.309	-0.165 - 0.513	0.112 - 0.236
DR37	-0.0906 - -0.0604	-0.102 - -0.0540	-0.0822 - -0.0651	-0.0852 - -0.0621	-0.0924 - -0.0549	-0.127 - -0.0771	-0.150 - -0.0658	-0.120 - -0.0767	-0.134 - -0.0632	-0.120 - -0.0765
DR39	-0.0098 - 0.0881	-0.0393 - 0.117	0.0118 - 0.0662	0.0024 - 0.0756	-0.0276 - 0.106	-0.0790 - 0.365	-0.231 - 0.514	-0.0453 - 0.330	-0.161 - 0.445	0.0148 - 0.269
DR40	-0.0734 - -0.0086	-0.0937 - 0.0109	-0.0579 - -0.0214	-0.0642 - -0.0151	-0.0847 - 0.0054	-0.178 - -0.0030	-0.239 - 0.0519	-0.162 - -0.0102	-0.209 - 0.0369	-0.153 - -0.0198
DR42	0.0614 - 0.0841	0.0553 - 0.0917	0.0657 - 0.0783	0.0634 - 0.0805	0.0146 - 0.129	0.171 - 0.251	0.149 - 0.282	0.173 - 0.241	0.152 - 0.262	0.109 - 0.305
DR43	-0.0573 - -0.0108	-0.0754 - 0.0001	-0.0533 - -0.0117	-0.0662 - 0.0011	-0.0638 - -0.0012	-0.110 - -0.0099	-0.159 - 0.0139	-0.183 - 0.0748	-0.377 - 0.269	-0.0944 - -0.0137
DR44	0.140 - 0.167	0.131 - 0.175	0.145 - 0.164	0.142 - 0.167	0.136 - 0.173	0.181 - 0.232	0.163 - 0.246	0.139 - 0.277	0.0352 - 0.380	0.185 - 0.231
τ (%)	75.0	50.0	100	87.5	62.5	75.0	50.0	62.5	37.5	87.5

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table D.20. Second trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 3 (SS3, known not to be the origin of the spill), applying the DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

DR Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp2} = n_{SS3} = 3$					EN 15522-2 scenario: A/B and $n_{Sp2} = n_{SS3} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
DR35	-0.0298 - -0.0005	-0.0428 - 0.0055	-0.0229 - -0.0033	-0.0271 - 0.0008	-0.0334 - 0.0072	-0.0469 - 0.0028	-0.0698 - 0.0128	-0.0403 - 0.0044	-0.0541 - 0.0182	-0.0418 - 0.0058
DR36	0.0422 - 0.111	0.0260 - 0.137	0.0503 - 0.0967	0.0404 - 0.107	0.0322 - 0.115	0.0685 - 0.249	0.0252 - 0.328	-0.0950 - 0.392	-0.461 - 0.758	0.0893 - 0.207
DR37	-0.0836 - -0.0541	-0.0951 - -0.0464	-0.0759 - -0.0598	-0.0787 - -0.0570	-0.0869 - -0.0488	-0.118 - -0.0683	-0.141 - -0.0564	-0.112 - -0.0699	-0.125 - -0.0569	-0.113 - -0.0687
DR39	0.0016 - 0.0628	-0.0174 - 0.0820	0.0154 - 0.0501	0.0094 - 0.0562	-0.0340 - 0.0995	-0.0233 - 0.252	-0.111 - 0.342	0.0008 - 0.239	-0.0729 - 0.312	-0.0082 - 0.248
DR40	-0.0530 - -0.0036	-0.0725 - 0.0071	-0.0422 - -0.0091	-0.0493 - -0.0020	-0.0704 - 0.0191	-0.132 - 0.0013	-0.192 - 0.0278	-0.236 - 0.125	-0.508 - 0.397	-0.121 - 0.0103
DR42	0.0484 - 0.0986	0.0353 - 0.118	0.0584 - 0.0860	0.0536 - 0.0908	0.0150 - 0.129	0.125 - 0.295	0.0771 - 0.360	0.135 - 0.279	0.0898 - 0.324	0.109 - 0.305
DR43	-0.0320 - -0.0035	-0.0397 - 0.0064	-0.0279 - -0.0092	-0.0319 - -0.0052	-0.0500 - 0.0128	-0.0585 - 0.0001	-0.0751 - 0.0207	-0.108 - 0.0460	-0.223 - 0.162	-0.0714 - 0.0096
DR44	0.146 - 0.174	0.139 - 0.184	0.145 - 0.172	0.137 - 0.180	0.140 - 0.177	0.188 - 0.242	0.174 - 0.265	0.137 - 0.287	0.0252 - 0.399	0.189 - 0.235
τ (%)	100	50.0	100	87.5	50.0	50.0	50.0	50.0	37.5	50.0

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

Table D.21. Third trial of confidence limits of the difference between the DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach (SC_{LL} and SC_{UL}), and by the S-t and MCM approaches considering the confidence levels of 95% ($P2.5$ and $P97.5$) and 98% ($P1$ and $P99$), for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 3 (SS3, known not to be the origin of the spill), applying DR comparison conditions represented by the Nordtest and EN 15522-2 scenarios.

<i>DR</i> Code	Nordtest scenario: $A/(A+B)$ and $n_{Sp2} = n_{SS3} = 3$					EN 15522-2 scenario: A/B and $n_{Sp2} = n_{SS3} = 2$				
	MCM		S-t		SC	MCM		S-t		SC
	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$	$P2.5 - P97.5$	$P1 - P99$	$P2.5 - P97.5$	$P1 - P99$	$SC_{LL} - SC_{UL}$
<i>DR35</i>	-0.0378 - 0.0095	-0.0574 - 0.0276	-0.0285 - -0.0012	-0.0332 - 0.0036	-0.0360 - 0.0064	-0.0611 - 0.0209	-0.106 - 0.0570	-0.0568 - 0.0156	-0.0791 - 0.0380	-0.0456 - 0.0045
<i>DR36</i>	0.0437 - 0.0792	0.0348 - 0.0970	0.0470 - 0.0702	0.0421 - 0.0751	0.0179 - 0.0993	0.0798 - 0.170	0.0566 - 0.220	-0.0023 - 0.236	-0.181 - 0.415	0.0590 - 0.174
<i>DR37</i>	-0.0957 - -0.0307	-0.119 - -0.0027	-0.0826 - -0.0461	-0.0890 - -0.0397	-0.0854 - -0.0433	-0.144 - -0.0331	-0.198 - 0.0160	-0.137 - -0.0415	-0.167 - -0.0119	-0.114 - -0.0642
<i>DR39</i>	0.0026 - 0.0819	-0.0219 - 0.116	0.0162 - 0.0618	0.0083 - 0.0698	-0.0288 - 0.107	-0.0227 - 0.354	-0.184 - 0.551	-0.0199 - 0.314	-0.123 - 0.418	0.0153 - 0.279
<i>DR40</i>	-0.0367 - -0.0265	-0.0392 - -0.0208	-0.0358 - -0.0292	-0.0372 - -0.0278	-0.0778 - 0.0128	-0.0820 - -0.0550	-0.0897 - -0.0384	-0.105 - -0.0367	-0.157 - 0.0149	-0.138 - -0.0039
<i>DR42</i>	0.0457 - 0.114	0.0332 - 0.151	0.0486 - 0.0957	0.0385 - 0.106	0.0133 - 0.131	0.116 - 0.391	0.0665 - 0.572	-0.169 - 0.600	-0.748 - 1.18	0.113 - 0.318
<i>DR43</i>	-0.0393 - 0.0008	-0.0479 - 0.0231	-0.0366 - -0.0098	-0.0423 - -0.0040	-0.0553 - 0.0089	-0.0710 - 0.0120	-0.0918 - 0.0577	-0.0760 - -0.0020	-0.0989 - 0.0208	-0.0807 - 0.0027
<i>DR44</i>	0.141 - 0.173	0.131 - 0.188	0.141 - 0.170	0.132 - 0.178	0.137 - 0.174	0.180 - 0.243	0.162 - 0.274	0.125 - 0.290	0.0007 - 0.414	0.185 - 0.230
τ (%)	75.0	62.5	100	97.5	50.0	62.5	50.0	50.0	25.0	75.0

Blue background – Confidence interval that does not include the zero (non-equivalent DR).

τ - Percentage of confidence intervals that do not include the zero (non-equivalent DR).

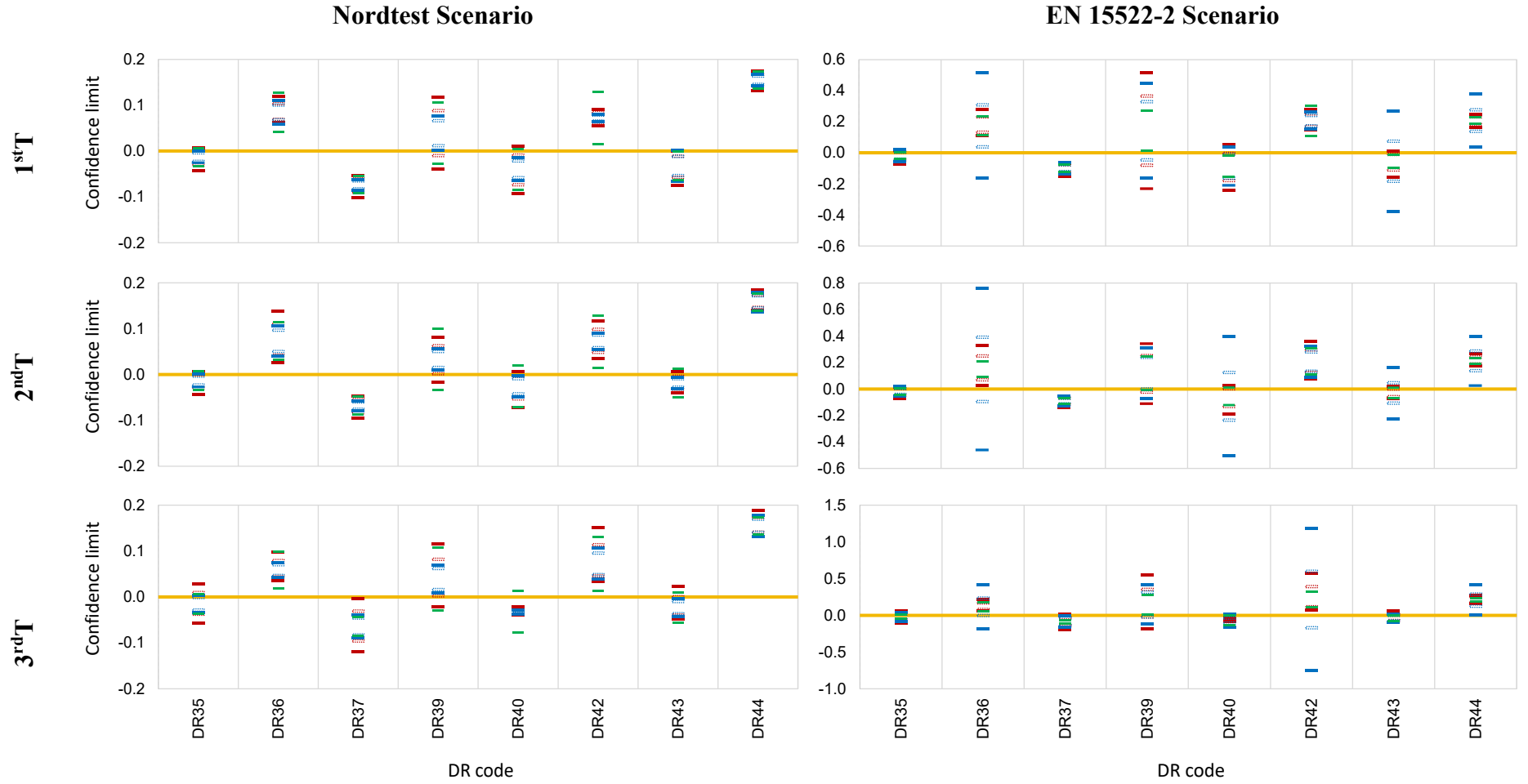


Figure D.10. Confidence limits of the difference between DR means ($\overline{DR}_{Sp} - \overline{DR}_{SS}$) defined by the SC approach, and by the S-t and MCM approaches considering 95% and 98% confidence levels, for the comparison of DR observed in the spill sample 2 (Sp2) and in the suspected source sample 3 (SS3, known not to be the origin of the spill), applying the experimental data obtained for the three DR comparison trials (1stT, 2ndT and 3rdT) and the DR comparison conditions represented by the Nordtest scenario ($A/(A+B)$ ratio format and triplicate injections) and EN 15522-2 scenario (A/B ratio format and duplicate injections). $\cdots$ $P2.5$ and $P97.5$ of MCM; $\cdots$ $P2.5$ and $P97.5$ of S-t; $-$ $P1$ and $P99$ of MCM; $-$ $P1$ and $P99$ of S-t; $-$ SC_{LL} and SC_{UL} ; $-$ $(\overline{DR}_{Sp} - \overline{DR}_{SS}) = 0$.

▪ **Probabilities of true and false compositional equivalence claim**

Tables D.22 and **D.23** presents the probabilities of true (δ) and false (ε) compositional equivalence claim estimated in the three trials performed, by the three approaches and for the Nordtest and EN 15522-2 scenarios, as well as their mean values ($\bar{\delta}$ and $\bar{\varepsilon}$) and the relative standard deviations (RSD).

Table D.22. Mean value ($\bar{\delta}$) and relative standard deviation (RSD), based on simulations of three *DR* comparison trials (1stT, 2ndT and 3rdT), of the probability of true compositional equivalence claim estimated for the comparison between the spill samples 1 and 2 (Sp1 and Sp2) and the suspected source sample known to be the origin of the spill (SS1), applying the *DR* comparison conditions represented by the Nordtest and EN15522-2 scenarios and by the SC, MCM and S-t approaches, both considering 95% and 98% confidence levels.

Sample pair compared	Number of <i>DR</i>	Comparison trial	Nordtest scenario: $A/(A+B)$ and $n_{sp} = n_{ss} = 3$					EN 15522-2 scenario: A/B and $n_{sp} = n_{ss} = 2$				
			MCM		S-t		SC	MCM		S-t		SC
			95%	98%	95%	98%		95%	98%	95%	98%	
Sp1 vs. SS1	28	$\delta_{1^{st}T}$ (%)	83.5	94.1	62.5	78.1	84.9	83.6	93.8	81.2	92.1	70.0
		$\delta_{2^{nd}T}$ (%)	82.8	93.2	60.9	77.0	89.6	83.8	93.8	81.3	92.7	68.4
		$\delta_{3^{rd}T}$ (%)	82.8	93.5	62.5	78.0	85.1	83.0	93.3	80.4	91.7	67.2
		$\bar{\delta}$ (%)	83.0	93.6	62.0	77.7	86.5	83.5	93.6	81.0	92.1	68.5
		RSD (%)	0.45	0.49	1.5	0.79	3.0	0.50	0.27	0.64	0.53	2.1
Sp2 vs. SS1	8	$\delta_{1^{st}T}$ (%)	87.1	95.4	68.5	81.8	86.9	88.3	95.5	86.5	94.8	69.8
		$\delta_{2^{nd}T}$ (%)	86.8	95.1	67.3	81.8	88.5	87.1	95.1	84.2	93.9	68.8
		$\delta_{3^{rd}T}$ (%)	88.0	95.3	76.9	86.7	80.9	87.9	95.6	86.2	94.0	54.8
		$\bar{\delta}$ (%)	87.3	95.3	70.9	83.4	85.4	87.8	95.4	85.6	94.2	64.5
		RSD (%)	0.72	0.19	7.4	3.4	4.7	0.66	0.26	1.4	0.52	13.1

Table D.23. Mean value ($\bar{\varepsilon}$) and relative standard deviation (RSD), based on simulations of three *DR* comparison trials (1stT, 2ndT and 3rdT), of the probability of false compositional equivalence claim estimated for the comparison between the spill samples 1 and 2 (Sp1 and Sp2) and the suspected source samples known not to be the origin of the spill (SS2 and SS3), applying the *DR* comparison conditions represented by the Nordtest and EN15522-2 scenarios and by the SC, MCM and S-t approaches, both considering 95% and 98% confidence levels.

Sample pair compared	Number of <i>DR</i>	Comparison trial	Nordtest scenario: $A/(A+B)$ and $n_{sp} = n_{ss} = 3$					EN 15522-2 scenario: A/B and $n_{sp} = n_{ss} = 2$				
			MCM		S-t		SC	MCM		S-t		SC
			95%	98%	95%	98%		95%	98%	95%	98%	
Sp1 vs. SS2	27	$\varepsilon_{1^{st}T}$ (%)	0.00100 (‡)	0.00200	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00600	0.192	0.912	0.00100 (‡)
		$\varepsilon_{2^{nd}T}$ (%)	0.00100 (‡)	0.00200	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00400	0.0120	0.0540	0.492	0.00100 (‡)
		$\varepsilon_{3^{rd}T}$ (%)	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.0340	0.124	0.626	0.00100 (‡)
		$\bar{\varepsilon}$ (%)	0.00100 (‡)	0.00167	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00200	0.0173	0.0123	0.677	0.00100 (‡)
		RSD (%)	0.000500 (‡)	34.6	0.000500 (‡)	0.000500 (‡)	0.000500 (‡)	86.6	85.1	56.0	31.7	0.000500 (‡)
Sp2 vs. SS2	8	$\varepsilon_{1^{st}T}$ (%)	0.334	0.678	0.484	0.942	0.00100 (‡)	0.318	0.694	1.50	6.60	0.00100 (‡)
		$\varepsilon_{2^{nd}T}$ (%)	0.298	0.562	0.512	1.04	0.00100 (‡)	0.240	0.580	1.34	5.73	0.00100 (‡)
		$\varepsilon_{3^{rd}T}$ (%)	1.56	2.76	2.21	3.82	0.00100 (‡)	2.30	3.93	5.68	13.3	0.00100 (‡)
		$\bar{\varepsilon}$ (%)	0.353	1.33	1.07	1.93	0.00100 (‡)	0.95	1.73	2.84	8.54	0.00100 (‡)
		RSD (%)	90.4	92.8	92.4	84.4	0.000500 (‡)	123	110	86.7	48.4	0.000500 (‡)
Sp1 vs. SS3	23	$\varepsilon_{1^{st}T}$ (%)	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.0340	0.460	0.00100 (‡)
		$\varepsilon_{2^{nd}T}$ (%)	0.00100 (‡)	0.00600	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00400	0.1440	0.574	0.00100 (‡)
		$\varepsilon_{3^{rd}T}$ (%)	0.00100 (‡)	0.00200	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00400	0.0420	0.344	0.00100 (‡)
		$\bar{\varepsilon}$ (%)	0.00100 (‡)	0.00300	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00100 (‡)	0.00300	0.0733	0.459	0.00100 (‡)
		RSD (%)	0.000500 (‡)	88.2	0.000500 (‡)	0.000500 (‡)	0.000500 (‡)	0.000500 (‡)	57.7	83.6	25.0	0.000500 (‡)
Sp2 vs. SS3	8	$\varepsilon_{1^{st}T}$ (%)	0.998	2.10	1.42	2.72	0.00100 (‡)	1.94	3.78	8.17	19.6	0.00100 (‡)
		$\varepsilon_{2^{nd}T}$ (%)	0.872	1.88	1.19	2.40	0.00100 (‡)	1.52	3.45	6.67	23.0	0.00100 (‡)
		$\varepsilon_{3^{rd}T}$ (%)	1.94	3.29	2.76	4.80	0.00100 (‡)	2.96	5.35	10.1	24.8	0.00100 (‡)
		$\bar{\varepsilon}$ (%)	1.27	2.42	1.79	3.31	0.00100 (‡)	2.14	4.19	8.33	22.5	0.00100 (‡)
		RSD (%)	45.9	31.2	47.3	39.4	0.000500 (‡)	34.6	24.2	20.9	11.6	0.000500 (‡)

(‡) For statistical comparison of $\bar{\varepsilon}$ estimated by different approaches, a ε equal to zero was assumed as half of one compositional equivalence claim in 50,000 analysed *DR* sets (*i.e.*, 0.00100%). Additionally, a standard deviation of 0.000500% (RSD of 50.0%) was assumed if the estimated ε in the three trials was zero.

Because the *DR* are correlated to each other, the $\bar{\delta}$ estimated by MCM and S-t varies between P^M and P (with M being the number of *DR* in the *DR* set), *i.e.*, between 23.8% and 95.0% and 56.8% and 98.0% for the comparison of Sp1 with SS1 (28 *DR*), and between 66.3% and 95.0% and 85.1% and 98.0% for the comparison of Sp2 with SS1 (8 *DR*). The exception was observed for the $\bar{\delta}$ obtained by S-t in the comparison of Sp2 and SS1 using the Nordtest scenario with a P of 98% (*i.e.*, 83.4% below 85.1%). This behaviour of the S-t approach, in the aforementioned conditions, was already evidenced when a reduced number of *DR* is compared and is attributed to statistical inconsistencies of the S-t approach (Rocha *et al.*, 2023). As expected, increasing the P , which increases the *DR* difference confidence intervals width, as well as decreasing the number of *DR* in the *DR* set to be compared, result in an increase in δ and ε since it is more likely that all *DR* in the set will be equivalent leading to a compositional equivalence claim. As demonstrated by comparisons with SS3, whose composition was found to be the second more similar to that of Sp1 and Sp2, the ε are also raised by a higher degree of similarity of the oil patterns in the SS that are not the spill source (**Table D.23**). The estimated δ showed reduced variation, with RSD ranging from 0.19% to 13.1% (**Table D.22**). Contrary, the RSD of the ε vary between 0% and 123% as a result of considerably greater variation and taking into account cases in which null ε are observed in all trials, or in one or two out of three trials (**Table D.23**).

D.4. Spreadsheets used to estimate the probability of false compositional equivalence claim by the studied approaches

Available to download using this [weblink](#) 

Files:

- **MCM:** MCM_False_Compositional_Equiv_Claim.xlsx
- **S-t:** S-t_False_Compositional_Equiv_Claim.xlsx
- **SC:** SC_False_Compositional_Equiv_Claim.xlsx

Annex E

List of indicators

This annex summarises the dissemination of the studies conducted as part of this PhD, the training activities provided, and the distinctions received.

In references of the scientific events presentations, the presenting author of the study is underlined.

▪ **International publications**

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N. (2022). Development and validation of statistically sound criteria for the match of unweathered GC-MS fingerprints in oil spill forensics. *Chemosphere*, 289, 133085. DOI: [10.1016/j.chemosphere.2021.133085](https://doi.org/10.1016/j.chemosphere.2021.133085).

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N. (2022). Optimisation of the uncertainty of oil spill identification from replicate comparative analyses: Comparison of standardised and novel identification methods. *Chemosphere*, 308, 136201. DOI: [10.1016/j.chemosphere.2022.136201](https://doi.org/10.1016/j.chemosphere.2022.136201).

Rocha, A.C., Bettencourt da Silva, R.J.N., Palma, C. (2023). Statistically sound comparison of standardized and simulation methods for oil spill source identification in real spill scenarios. *Science of the Total Environment*, 887, 163930. DOI: [10.1016/j.scitotenv.2023.163930](https://doi.org/10.1016/j.scitotenv.2023.163930).

Rocha; A.C., Palma, C., Bettencourt da Silva, R.J.N. (2025). Sound uncertainty-based strategy for oil spill source identification. *Chemometrics and Intelligent Laboratory Systems*, 256, 105275. DOI: [10.1016/j.chemolab.2024.105275](https://doi.org/10.1016/j.chemolab.2024.105275).

▪ **National publications**

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N. (2021). Identificação da origem de derrames petrolíferos com critérios não paramétricos de dados de GC-MS. *Química* 45(162), 209–215. DOI: [10.52590/M3.P697](https://doi.org/10.52590/M3.P697).

▪ **Oral communications**

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N., *Optimisation and evaluation of uncertainty in oil spill source identification by GC-MS*, CQE Days 2020 Spring Meeting, May 28 and 29, 2020, Lisboa, Portugal (virtual meeting).

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N., *Statistically sound identification of oil spills origin: simulation of non-normal diagnostic ratios by the Monte Carlo method*, 10º Encontro da Divisão de Química Analítica da Sociedade Portuguesa de Química: ANALITICA 2020, October 26 to 28, 2020, Lisboa, Portugal (virtual meeting).

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N., *Abordagem alternativa de comparação de razões de diagnóstico para a identificação da origem de derrames de produtos petrolíferos*, 6^{as} Jornadas de Engenharia Hidrográfica/1^{as} Jornadas Luso-Espanholas de Hidrografia, November 3 to 5, 2020, Lisboa, Portugal (in-person meeting).

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N., *Inovação nos critérios e objetividade na identificação da origem de derrames de produtos petrolíferos no meio Marinho*, Ideia2021: Inovação nas Operações Marítimas, January 26 and 27, 2021, Lisboa, Portugal (virtual meeting).

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N., *Desenvolvimento e comparação de métodos de identificação da origem de derrames petrolíferos*, 7^{as} Jornadas de Engenharia Hidrográfica/2^{as} Jornadas Luso-Espanholas de Hidrografia, June 21 to 23, 2022, Lisboa, Portugal (in-person meeting).

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N., *Improving the reliability of oil spill identification by the accurate simulation of diagnostic ratios*, 2nd Chemistry and Biochemistry Students Meeting, June 15, 2022, Lisboa, Portugal (in-person meeting).

Rocha, A.C., Bettencourt da Silva, R.J.N., Palma, C., *Comparison of standardized and novel methods for oil spill source identification in real spill scenarios reproduced in proficiency tests*, Eurachem Workshop – Ensuring reliable and accurate results of analytical processes, May 22 and 23, 2023, Bern, Switzerland (in-person meeting).

▪ **Communications in poster with its oral presentation**

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N., *First assessment of total risks in oil spill source identification*, Eurachem Workshop – Trends & Challenges in Ensuring Quality in Analytical Measurements, May 17 to 21, 2021, Prague, Czech Republic (virtual meeting).

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N., *Total risk assessment in oil spill source identification using normalised methods requirements*, Eurachem Workshop – Quality assurance challenges of measurements from field to laboratory with a focus on ISO/IEC 17025:2017 requirements, May 16 to 18, 2022, Tbilisi, Georgia (virtual meeting).

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N., *Quality assessment of the source identification applied to different spilled oils and performed by distinct methods*, SETAC Europe 33rd Annual Meeting, April 30 to May 5, 2023, Dublin, Ireland (virtual meeting).

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N., *Assessing the accuracy of findings in oil pollution cases using likelihood ratios*, SETAC Europe 34th Annual Meeting, May 5 to 9, 2024, Seville, Spain (in-person meeting).

▪ **Poster communications**

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N., *Quality assessment of the oil spill identification performed by different methods*, CQE Days 2022, May 26 to 27, 2022, Lisboa, Portugal (in-person meeting).

Rocha, A.C., Bettencourt da Silva, R.J.N., Palma, C., *Optimising criteria and uncertainty for oil spill source identification*, Eurachem Workshop – Quality Assurance in Chemical, Medical and Microbiological Laboratories, May 13 to 14, 2024, Vilnius, Lithuania (in-person meeting).

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N., *Statistically sound approach to compare oil patterns and assess the accuracy of the forensic findings*, 8th IAHR Europe Congress, June 4 to 7, 2024, Lisboa, Portugal (in-person meeting).

- **Training provided by the *Escola de Hidrografia e Oceanografia* of the *Instituto Hidrográfico*¹ to officers and sergeants**

Rocha A.C., *Identificação da origem de produto petrolífero derramado*, Chemical Oceanography – Marine Pollution of the Specialisation Course in Hydrography, Escola de Hidrografia e Oceanografia – Instituto Hidrográfico, March 25, 2021, Lisboa, Portugal.

Rocha A.C., *Identificação da origem de produto petrolífero derramado*, Chemical Oceanography – Marine Pollution of the Specialisation Course in Hydrography, Escola de Hidrografia e Oceanografia – Instituto Hidrográfico, September 16, 2022, Lisboa, Portugal.

Rocha A.C., *Identificação da origem de produto petrolífero derramado*, Chemical Oceanography – Marine Pollution of the Specialisation Course in Hydrography, Escola de Hidrografia e Oceanografia – Instituto Hidrográfico, September 5, 2023, Lisboa, Portugal.

- **Training provided by the *Escola da Autoridade Marítima*² to marine casualty pollution investigators and officers of *Polícia Marítima*³, as well as future harbour masters and officers of *Polícia Marítima***

Rocha A.C., *Recolha e análise de amostras de hidrocarbonetos: vertente laboratorial*, ADN05 – Improvement Course in Maritime Authority, Escola da Autoridade Marítima – Base Naval de Lisboa, July 6, 2021, Almada, Portugal.

Rocha A.C., *Recolha e análise de amostras de hidrocarbonetos: vertente laboratorial*, ADN05 – Improvement Course in Maritime Authority, Direção de Combate à Poluição do Mar – Base Naval de Lisboa, June 1, 2022, Almada, Portugal.

Rocha A.C., *Recolha e análise de amostras de hidrocarbonetos: vertente laboratorial*, ADN05 – Improvement Course in Maritime Authority, Escola da Autoridade Marítima – Base Naval de Lisboa, June 1, 2023, Almada, Portugal.

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¹ School of Hydrography and Oceanography of the Hydrographic Institute.

² School of Maritime Authority.

³ Maritime Police.

Rocha A.C., *Identificação da origem de poluição por produto petrolífero: metodologia analítica e Identificação da origem de poluição por produto petrolífero: técnicas de amostragem*, ANQ20 – Improvement Course in Collecting Samples, Direção de Combate à Poluição do Mar – Base Naval de Lisboa, November 21, 2022, Almada, Portugal.

Rocha A.C., *Identificação da origem de poluição por produto petrolífero: metodologia analítica e Identificação da origem de poluição por produto petrolífero: técnicas de amostragem*, ANQ20 – Improvement Course in Collecting Samples, Comando Regional da Polícia Marítima do Norte, February 9, 2023, Leixões, Portugal.

Rocha A.C., *Identificação da origem de poluição por produto petrolífero: metodologia analítica e Identificação da origem de poluição por produto petrolífero: técnicas de amostragem*, ANQ20 – Improvement Course in Collecting Samples, Comando Regional da Polícia Marítima do Norte, February 10, 2023, Leixões, Portugal.

Rocha A.C., *Identificação da origem de poluição por produto petrolífero: metodologia analítica e Identificação da origem de poluição por produto petrolífero: técnicas de amostragem*, ANQ20 – Improvement Course in Collecting Samples, Direção de Combate à Poluição do Mar – Base Naval de Lisboa, February 20, 2024, Almada, Portugal.

Rocha A.C., *Identificação da origem de poluição por produto petrolífero: metodologia analítica e Identificação da origem de poluição por produto petrolífero: técnicas de amostragem*, ANQ20 – Improvement Course in Collecting Samples, Direção de Combate à Poluição do Mar – Base Naval de Lisboa, October 22, 2024, Almada, Portugal.

* * *

Rocha A.C., *Identificação da origem de poluição por produto petrolífero: metodologia analítica e Identificação da origem de poluição por produto petrolífero: técnicas de amostragem*, Training Course for Officers of Polícia Marítima – Pollution Module, Escola da Autoridade Marítima – Base Naval de Lisboa, May 13, 2021, Almada, Portugal.

Rocha A.C., *Identificação da origem de poluição por produto petrolífero: metodologia analítica*, Training Course for Officers of Polícia Marítima – Pollution Module, Escola da Autoridade Marítima – Base Naval de Lisboa, November 27, 2024, Almada, Portugal.

Rocha A.C., *Identificação da origem de poluição por produto petrolífero: técnicas de amostragem*, Training Course for Officers of Polícia Marítima – Pollution Module, Escola da Autoridade Marítima – Base Naval de Lisboa, November 28, 2024, Almada, Portugal.

▪ **Training provided by universities to master's students**

Rocha A.C., *Identificação da origem de derrames de produtos petrolíferos*, Environmental Chemical Analysis of the MSc in Chemistry, Faculdade de Ciências da Universidade de Lisboa⁴, November 20, 2020, Lisboa, Portugal.

Rocha A.C., *Identificação da origem de derrames de produtos petrolíferos*, Environmental Chemical Analysis of the MSc in Chemistry, Faculdade de Ciências da Universidade de Lisboa, November 12, 2021, Lisboa, Portugal.

Rocha A.C., *Identificação da origem de derrames de produtos petrolíferos*, Environmental Chemical Analysis of the MSc in Chemistry, Faculdade de Ciências da Universidade de Lisboa, November 18, 2022, Lisboa, Portugal.

Rocha A.C., *Oil spill source identification*, Environmental Chemical Analysis of the MSc in Chemistry, Faculdade de Ciências da Universidade de Lisboa, October 20, 2023, Lisboa, Portugal.

Rocha A.C., *Oil spill source identification*, Chemical Oceanography of the MSc in Marine Sciences, Faculdade de Ciências da Universidade de Lisboa, April 29, 2024, Lisboa, Portugal.

Rocha A.C., *Identificação da origem de produto petrolífero derramado*, Chemistry and Society of the MSc in Chemistry, Faculdade de Ciências da Universidade do Porto⁵, September 13, 2024, Porto, Portugal.

⁴ Faculty of Sciences of the University of Lisbon.

⁵ Faculty of Sciences of the University of Oporto.

▪ **Other training**

Rocha A.C., *Oil spill source identification: sampling and chemical analysis*, TAIEX Study Visit on Monitoring and Detecting Ship Based Pollution in Marine and Inland Waters – Co-operation with Turkish Coast Guard Command and Direção Geral da Autoridade Marítima/Marinha Portuguesa, Instituto Hidrográfico⁶, November 13, 2024, Lisboa, Portugal.

▪ **Distinctions – Best oral presentation**

Rocha, A.C., Palma, C., Bettencourt da Silva, R.J.N., *Statistically sound identification of oil spills origin: simulation of non-normal diagnostic ratios by the Monte Carlo method*, 10º Encontro da Divisão de Química Analítica da Sociedade Portuguesa de Química: ANALITICA 2020, October 26 to 28, 2020, Lisboa, Portugal (virtual meeting).

⁶ General Directorate of Maritime Authority/ Portuguese Navy, Hydrographic Institute.