First Assessment of Total Risks in Oil Spill Source Identification

A.C. Rocha [1; 2]; C. Palma [1]; R.J.N. Bettencourt da Silva [2]

[1] Division of Chemistry and Marine Pollution, Hydrographic Institute, Lisbon, Portugal
[2] Centre for Structural Chemistry, Faculty of Science of the University of Lisbon, Lisbon, Portugal

Eurachem Prague 2021
17th May - 21st May 2021

Introduction

Chemical analyses of samples taken from oil spills (spill sample and suspected source samples) have been used as evidence in legal proceedings to identify the origin of the spill and holding the offender liable under the law.
Each sample collected is characterized by identifying and quantifying a wide range of hydrocarbons (*fingerprint*) using Gas Chromatography-Mass Spectrometry (GC-MS). The chromatographic data are processed in different ways and the results obtained for the spill and suspected source samples compared. The abundance ratio of specific hydrocarbons, *i.e.*, diagnostic ratios (*DR*), is widely used to assess oil fingerprints' equivalence on two samples. One of the methods used to compare *DR* is the Student's t statistics (S-t). Triplicate determinations of one sample define the limits for the *DR* comparison of the second sample, assuming the equivalence of *DR* if the *DR* estimated from the second sample is within the confidence interval defined [1-3]. To support the compositional equivalence between samples, used to identify the spill source, is necessary the agreement of a set of characteristic *DR* observed for the samples compared [4;5].

The Issues

The Student's t method for *DR* comparison assumes the *DR* probability distribution normality. This approach can lead to a higher risk of false decisions of compositional equivalence between two samples, since the *DR* distributions can deviate from normality. Therefore, the estimation of the risk associated with the compositional equivalence decision between two samples is relevant, leading the chemical analyses to more valuable evidence. No published studies were found in this field.

Research Goals

This work presents an unconventional method, involving simulations by the Monte Carlo Method (MCM), and allows:

- the statistically sound assessment of the *DR* agreement of samples from oil spills that does not assume ratio normality;
- to estimate the risks of true acceptance and false rejection of the compositional equivalence of samples with the same oil.

In addition, the study:

- compares the risks estimated using the MCM and S-t methods;
- presents an alternative methodology for chemical composition comparison, which leads to a lower risk of false decision.

Conclusions

A new method based on simulations by MCM was developed with the objective to compare *DR* obtained for different samples collected in oil spills, and to estimate the total risks of true acceptance/false rejection of compositional equivalence between similar samples.
The MCM was successfully applied in the comparison of three distinct *DR* sets defined from a different number of correlated chromatographic signals.
The probability distributions of the simulated *DR* showed some deviation from normality, as well as wider confidence intervals than those obtained by the conventional S-t method. This leads to higher total risks of true acceptance (lower total risks of false rejection) when MCM is applied.
Since the *DR* sets assessed are not perfectly correlated, the total risks of true acceptance of compositional equivalence between two samples with the same oil were lower than the confidence level studied, regardless the number of *DR* in the set.
The alternative methodology to conclude about the compositional equivalence between two samples increase of total risk of true acceptance above the 98% confidence level for both MCM and S-t methods.
The MCM improves the criteria used in *DR* comparison by adapting to their actual distribution. The accurate modelling of *DR* also allows the reliable assessment of the risk of false decisions on oil patterns equivalence and the evaluation of the reliability of S-t based assessments.

References

[1] Daling, P.S.; Faksness, L.G.; Hansen, A.B.; Stout, S.A. *Environ. Forensics* **2002**, *3*, 263-278.
[2] Wang, Z.; Yang, C.; Fingas, M.; Hollebone, B.; Peng, X.; Hansen, A.B.; Christensen, J.H. *Environ. Sci. Technol.* **2005**, *39*, 8700-8707.
[3] Wang, Z.; Yang, C.; Hollebone, B.; Fingas, M. *Environ. Sci. Technol.* **2006**, *40*, 5636-5646.
[4] Stout, S.A.; Uhler, A.D.; McCarthy, K.J. *Environ. Forensics* **2001**, *2*, 87-98.
[5] Wang, Z.; Fingas, M; Page, D.S. *J. Chromatogr. A* **1999,** *843*, 369-411.

Methodology

The developed method to compare *DR* from two samples, and to estimate the risk of true acceptance and the risk of false rejection of the compositional equivalence between two similar samples, involves the simulation of the probability distributions of *DR,* by the MCM, supported on the experimentally observed correlation and dispersion of chromatographic signals combined in the ratio.

1 Experimental data: GC-MS analysis after solvent extraction of three different oils

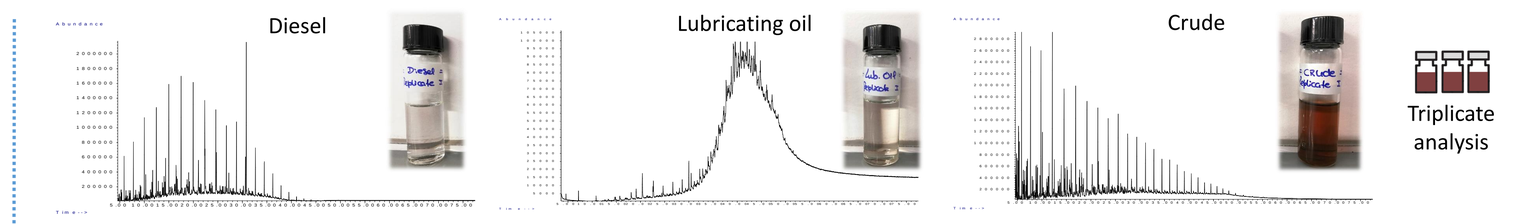

Figure 1 – Total ion chromatograms of the three oils analysed.

2 Simulation by MCM and S-t modelling

$$DR = \frac{A}{(A+B)}$$

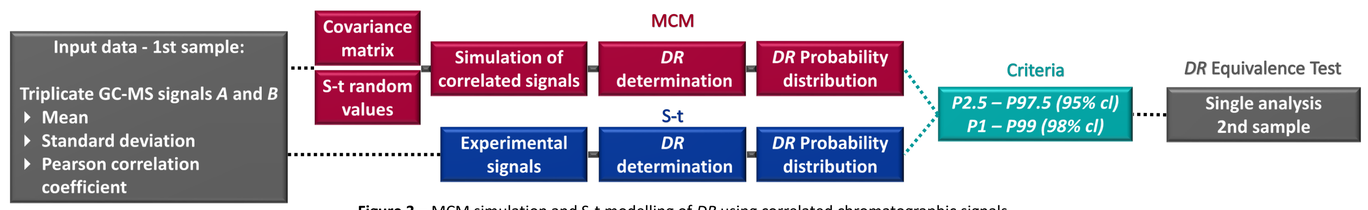

Figure 3 – MCM simulation and S-t modelling of *DR* using correlated chromatographic signals.

3 Total risk estimation: simulation by MCM applied to a 69 *DR* set

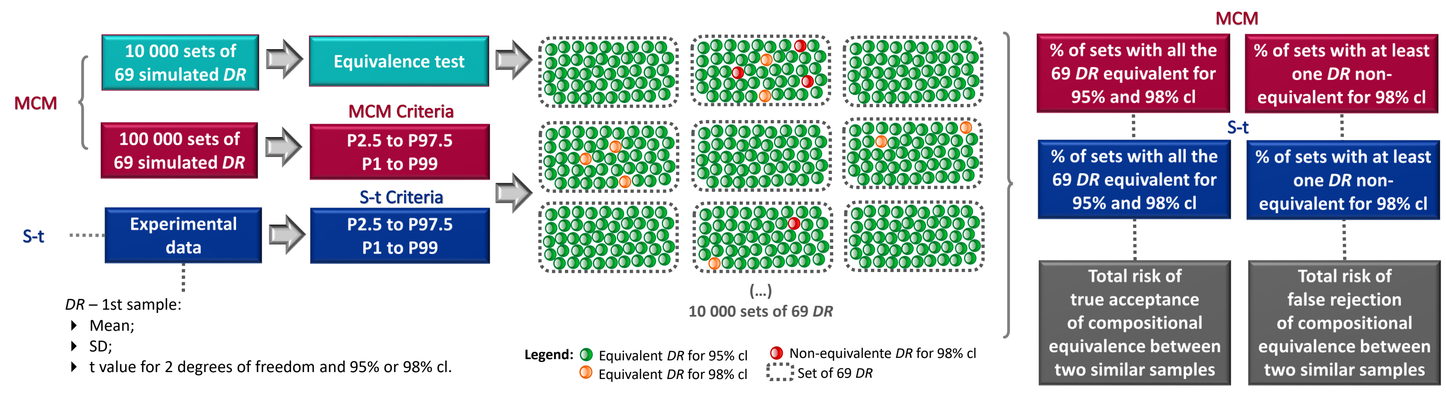

Figure 3 – Estimation of the total risks of true acceptance and false rejection of compositional equivalence between two similar samples using MCM simulation and S-t modelling of *DR*.

4 Alternative method to conclude about the compositional equivalence between two similar samples: comparison between two consecutive simulated sets of 69 *DR*

The data obtained for total risks estimation were used to evaluate the application of the alternative method: 10 000 sets of 69 *DR* assessed.

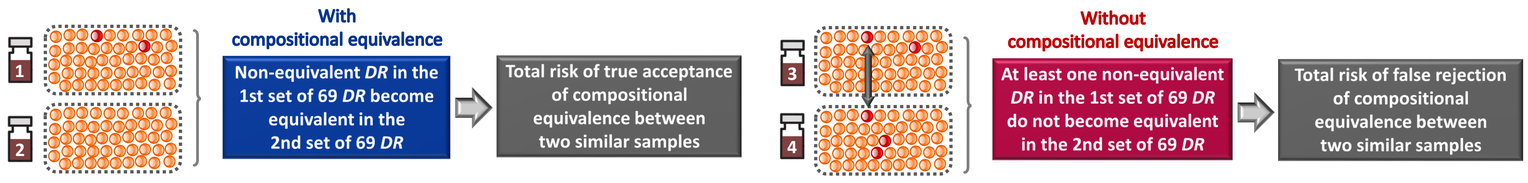

Figure 4 – Alternative method to estimate the total risks of true acceptance and false rejection of compositional equivalence between two similar samples, assessing two consecutive simulated *DR* sets with MCM and S-t approaches.

Results

Diesel

36 chromatographic signals

46 *DR*

Lubricating oil

15 chromatographic signals

13 *DR*

Crude

48 chromatographic signals

58 *DR*

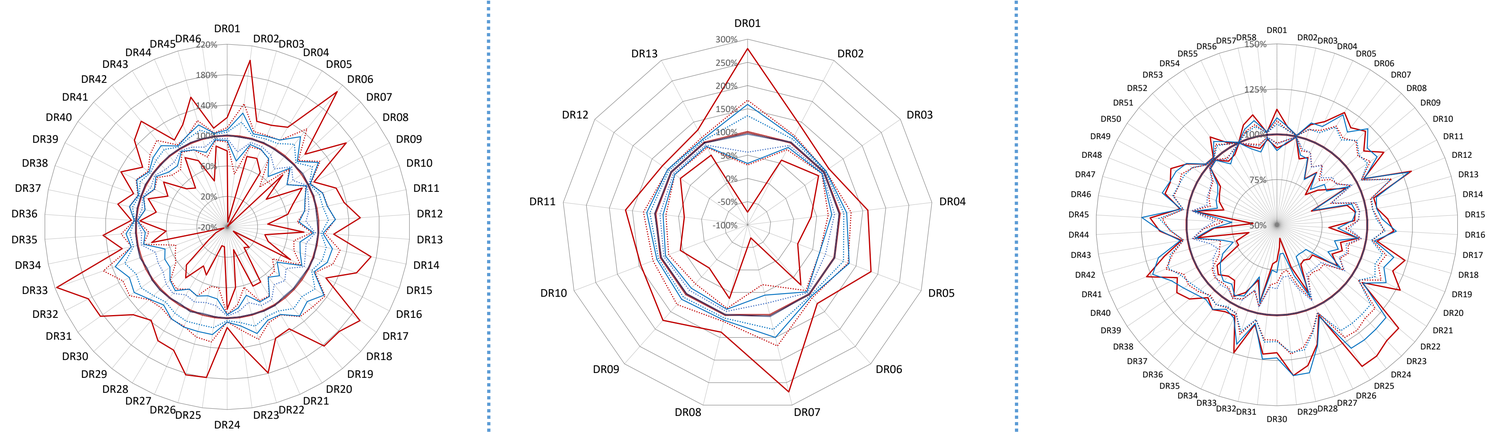

Figure 5 – Percentiles required to define 95% and 98% confidence limits, by the MCM and S-t methods, normalised to the 50th percentile simulated by MCM:
= P50 – MCM; = P50 – S-t; ··· P2.5 and P97.5 – MCM; ··· P2.5 and P97.5 – S-t; — P1 and P99 – MCM; — P1 and P99 – S-t.

Table I - Total risks of compositional equivalence between two similar samples.

	Diesel		Lubricating Oil		Crude	
	True Acceptance (%)	False Rejection (%)	True Acceptance (%)	False Rejection (%)	True Acceptance (%)	False Rejection (%)
MCM (95% cl)	90.7	9.3	90.1	9.9	89.6	10.4
MCM (98% cl)	95.0	5.0	94.3	5.7	95.7	4.3
S-t (95% cl)	81.6	18.4	84.9	15.1	86.7	13.3
S-t (98% cl)	88.0	12.0	91.3	8.7	93.5	6.5
Alternative method						
MCM (98% cl)	99.8	0.2	99.8	0.2	99.8	0.2
S-t (98% cl)	98.7	1.3	98.8	1.2	99.8	0.2

- Different oils were characterized by different *DR* sets: presence of compounds is limited by the oil type;
- Deviations from normality of the *DR* distributions were observed (Figure 5), leading to MCM confidence intervals wider than S-t ones;
- The MCM approach reveals higher total risks of true acceptance of compositional equivalence between two similar oils than the S-t approach;
- The totals risks are similar among the oils analysed, in particular for MCM, besides the oils are characterized by different number and sets of *DR*;
- The alternative method for total risks estimation increases the total risk of true acceptance for both MCM and S-t approaches: values higher than the confidence level assessed (98%).