Eurachem

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Total risk assessment in oil spill source identification using normalised methods requirements

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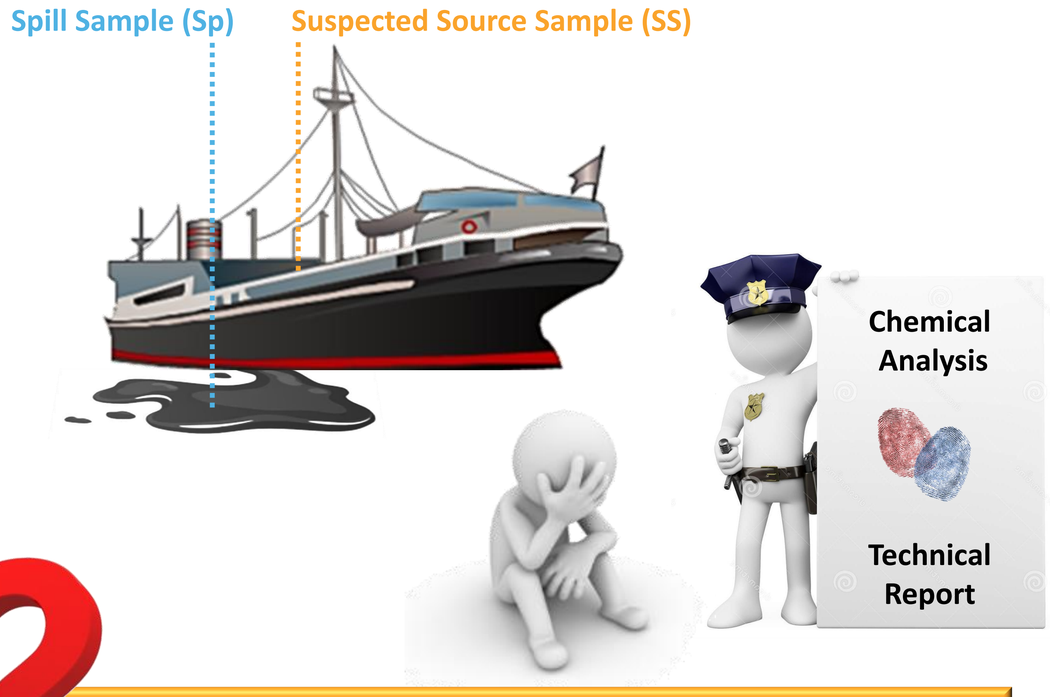
1 Introduction

- Chemical analysis has been a valuable support for forensic investigations in oil spill source identification;
- Ratios between chromatographic signals of specific compounds, *i.e.*, diagnostic ratios (DR), have been widely used to characterize and correlate chemical compositions of oil samples;
- Common methods for DR comparison observed in two samples are based on inadequate assumptions or approximations that lead to a erroneous assessments about the equivalence of sample compositions: student's *t* statistics (S-t) [1] and a single criterion that defines a maximum relative difference of 14% (SC) [2, 3];
- The development of new methods for DR comparison that describe better the reality of the DR probability is essential to ensure identification quality.

2 Aim

- Demonstrate the application of an innovative method for DR comparison based on simulations by the Monte Carlo Method (MCM);
- Compare the MCM method with the S-t and SC methods using normalised methodologies requirements:
  - evaluation of the confidence intervals produced;
  - assessment of the identification quality by the total risk of true acceptance of composition equivalence.



- **How do different data processing conditions impact on the criteria defined by the DR comparison methods?**
- **Does the alternative MCM method lead to better quality identifications compared to the S-t and SC methods?**

3 Methodology

Data set
- Spill and suspected source samples: mixture of crude oil extracts from different geographical areas (Mixcrude extract) [4];
- GC-MS analysis according to acquisition and processing conditions suggested by prEN 15522-2 [3];
- 29 signals quantified to simulate 22 normative ratios [3].

MCM Simulation
- Simulation of chromatographic signals for each sample, supported by dispersion and correlation observed experimentally [4];
- Determination of the DR difference between simulated data ($\overline{DR}_{Sp;i} - \overline{DR}_{SS;i}$).

Total risk Estimate
- Probability of true acceptance of equivalence between sample compositions: % DR sets with all ratios statistically equivalent

Tested conditions
- $n_{Sp} = 3, 5$ and 8, and $n_{SS} = 2$ and 3;
- Ratio formats: *A/(A+B)* and *A/B*.

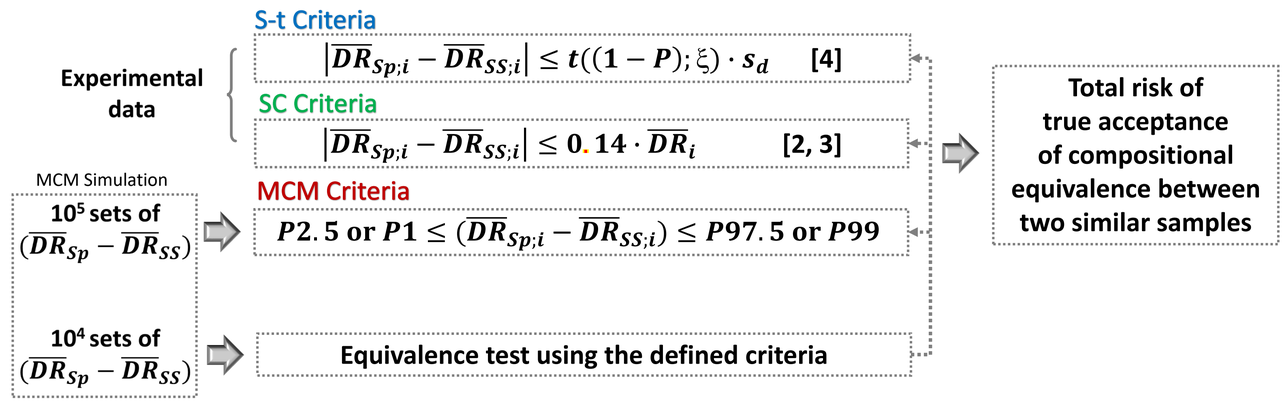


Figure 1. Descriptive scheme of the total risk estimate: *P* – confidence level; ξ - degrees of freedom; s_d – standard deviation of the DR difference; $\overline{DR}_{Sp;i}$ and $\overline{DR}_{SS;i}$ - Mean of DR *i* observed for spill or suspected source samples, respectively; $\overline{DR}_i$ - Mean value of $\overline{DR}_{Sp;i}$ and $\overline{DR}_{SS;i}$; $P\chi$ – χ^{th} percentiles.

4 Results

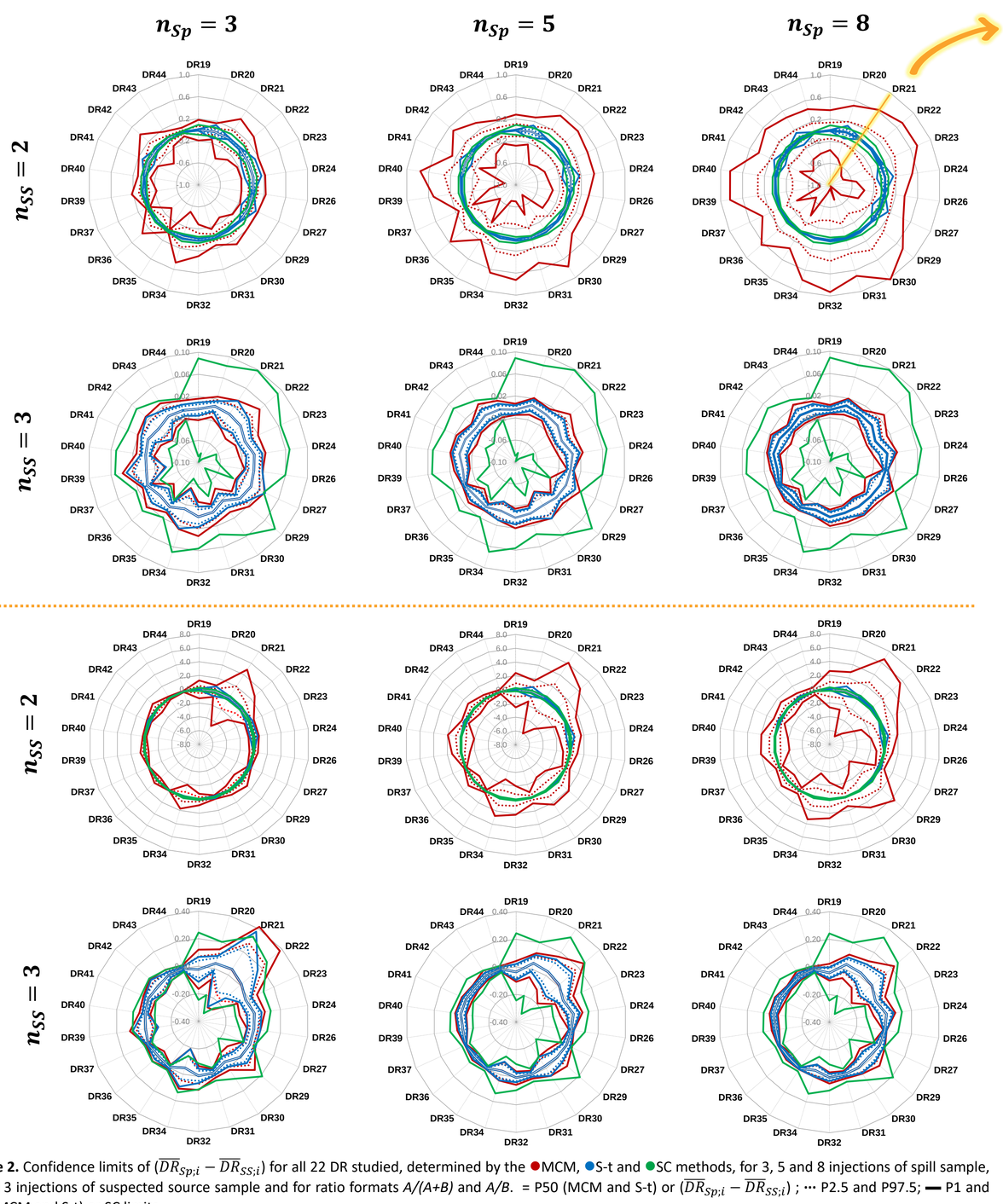
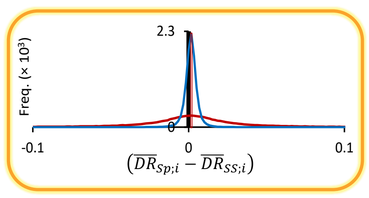


Figure 2. Confidence limits of $(\overline{DR}_{Sp;i} - \overline{DR}_{SS;i})$ for all 22 DR studied, determined by the ●MCM, ●S-t and ●SC methods, for 3, 5 and 8 injections of spill sample, 2 and 3 injections of suspected source sample and for ratio formats *A/(A+B)* and *A/B*. = P50 (MCM and S-t) or $(\overline{DR}_{Sp;i} - \overline{DR}_{SS;i})$; ⋯ P2.5 and P97.5; ▬ P1 and P99 (MCM and S-t) or SC limits.



$n_{SS} = 2$: the confidence intervals defined by the MCM method proved to be broader than those defined by S-t and SC methods and tend to widen with the increase of replicate analysis of the spill sample.

→ **$(\overline{DR}_{Sp;i} - \overline{DR}_{SS;i})$ probability distributions obtained by simulation are flatter than those modeled for S-t.**

$n_{SS} = 3$: the confidence intervals defined by the MCM method revealed to be slightly wider than those defined by the S-t method and tend to narrow with the increase of replicate analyses of the spill sample.

In general, the confidence intervals defined…
- by the S-t methods tend to narrow with the increase of replicate analyses of the spill sample;
- by the SC method do not vary with the increase of replicate analysis of the spill sample and, in general, are wider than those defined by the S-t method.

Total risk of true acceptance of compositional equivalence between two similar samples (%)

n_{Sp}	n_{SS}	A/(A+B) MCM 95% *	A/(A+B) MCM 98% *	A/(A+B) S-t 95% *	A/(A+B) S-t 98% *	A/(A+B) SC	A/B MCM 95% *	A/B MCM 98% *	A/B S-t 95% *	A/B S-t 98% *	A/B SC
3	2	89,3	94,8	29,9	45,2	71,9	89,1	94,5	30,3	45,1	53,0
5	2	88,3	92,8	2,3	5,9	52,8	86,7	91,5	2,3	5,7	31,3
8	2	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	3	76,6	91,0	56,8	76,8	97,8	75,7	90,7	56,0	75,7	95,7
8	3	74,7	90,4	51,4	72,5	98,3	74,5	90,7	51,3	72,3	96,7

* Confidence level

5 Conclusions

- The alternative method for DR comparison developed, based on MCM simulations, was successfully applied to access the compositional equivalence between samples;
- The different conditions for processing data tested impact the confidence limits amplitude defined for MCM, S-t and SC methods, as well as the total risk of the true acceptance of compositional equivalence between samples;
- The probability distributions of $(\overline{DR}_{Sp;i} - \overline{DR}_{SS;i})$ showed deviations from normality revealing a flatter shape, especially when duplicate analysis of suspected source samples are used;
- MCM method prove to be very suitable for oil spill identification: MCM method describes exactly the probability distributions of $(\overline{DR}_{Sp;i} - \overline{DR}_{SS;i})$ leading to better quality identifications using fewer resources (number of analysis and time spent on data acquisition and processing).

References

[1] Daling, P.S.; Faksness, L.G.; Hansen, A.B.; Stout, S.A. *Environ. Forensics* **2002**, *3*, 263-278.
[2] CEN (2012). Brussels Studies Institute. Brussels:Belgium. 138 p. (Ref. CEN/TR 15522-2:2012:E).
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[4] Rocha, A.C.; Palma, C.; Bettencourt da Silva, R.J.N. *Chemosphere* **2022**, *289*, 133085.

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