# EVALUATION OF THE UNCERTAINTY OF COMPLEX SAMPLE PREPARATION - MONTE CARLO BOTTOM-UP APPROACH

**Vanessa Morgado[1, 2], Carla Palma[2], Ricardo Bettencourt da Silva[1]**

[1]Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal
[2]Instituto Hidrográfico, R. Trinas 49, 1249-093 Lisboa, Portugal

Eurachem Prague 2021
17th May - 21st May 2021

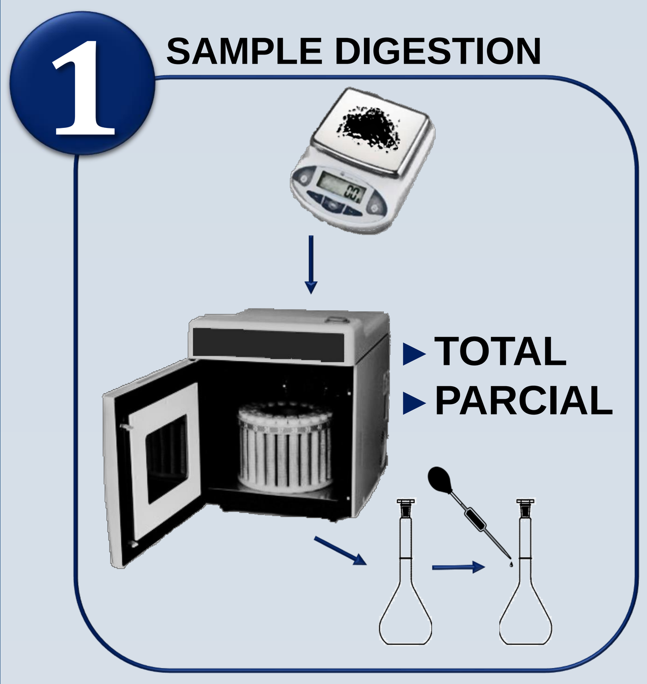
## INTRODUCTION

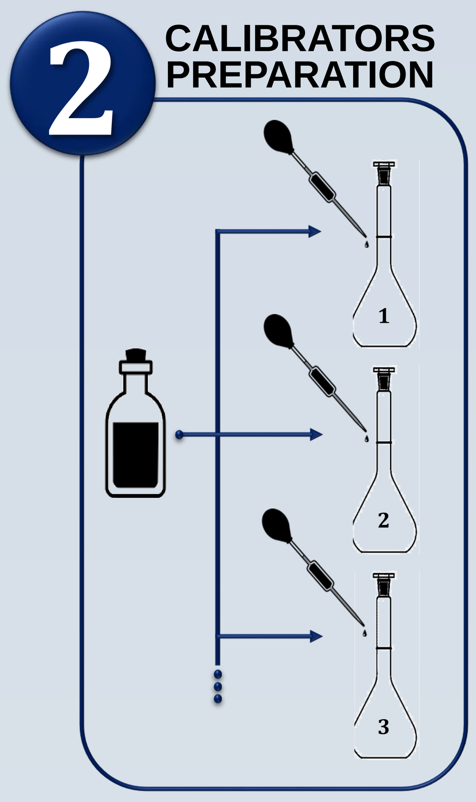
Many chemical analyses involve a complex sample preparation and some, based on an instrumental method of analysis such as spectrometric and chromatographic methods, are affected by matrix effects. The objective interpretation of the results of these analyses, performed in the framework of a research or of a conformity assessment, requires the quantification of the measurement uncertainty. Top-down assessments of the measurement uncertainty are known to involve the oversimplification of the measurement process and a pessimist quantification of the uncertainty [1].

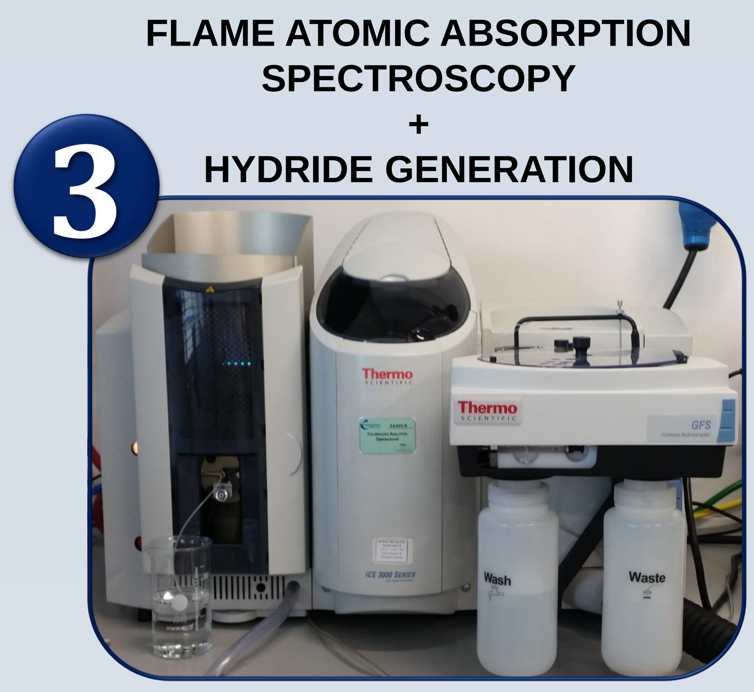
## PURPOSE

This work presents a novel methodology for the bottom-up modelling of the performance of complex analytical operations, such as sample digestion or extraction, by the Monte Carlo simulation of their performance independently of the performance of the other analytical steps [2].

## EXPERIMENTAL




## DATA USAGE

**ANALYSED ITENS**

- Blanck → BK
- Certified Reference Material (CRM)
- Sample A → A1
- Duplicate sample A → A2
- Spiked sample A → AS
- Sample B → B
- Sample C → C*
- Spiked sample C → CS*

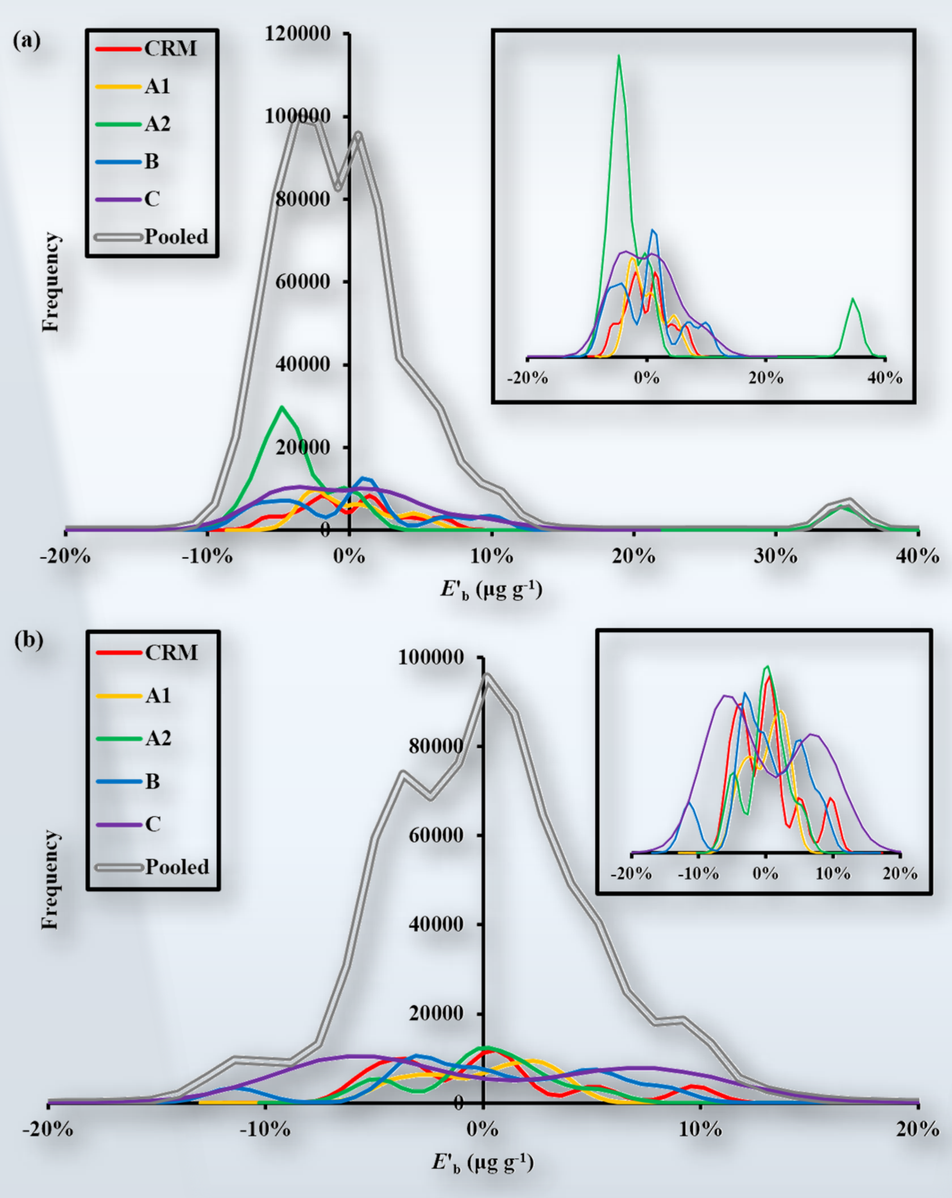
Random effects
Systematic effects

**TOTAL & PARTIAL DIGESTION**

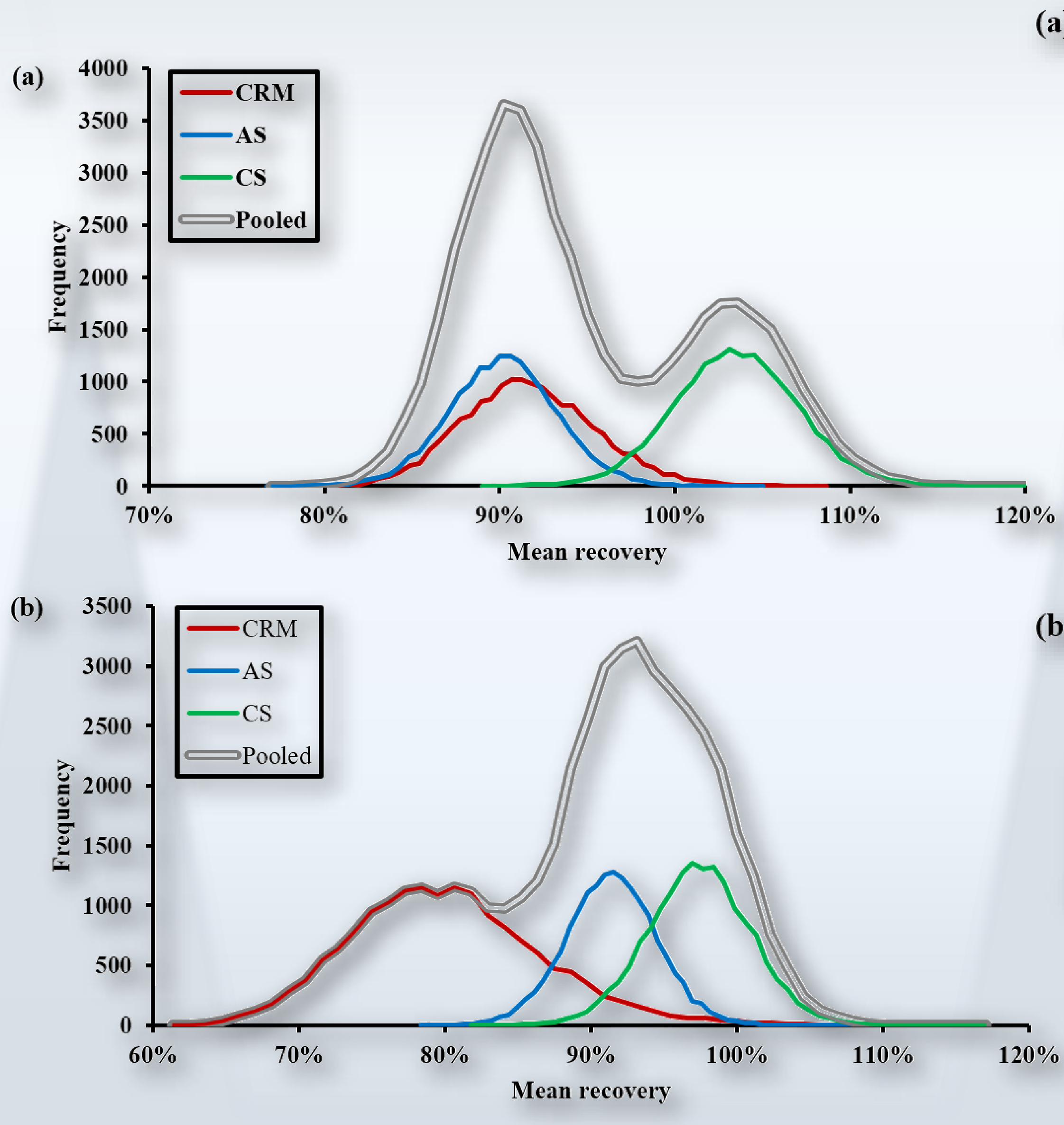

## RESULTS

### SIMULATED DISTRIBUITIONS BY MONTE CARLO METHOD

**BETWEEN-DAYS RANDOM EFFECTS, $E'_b$**

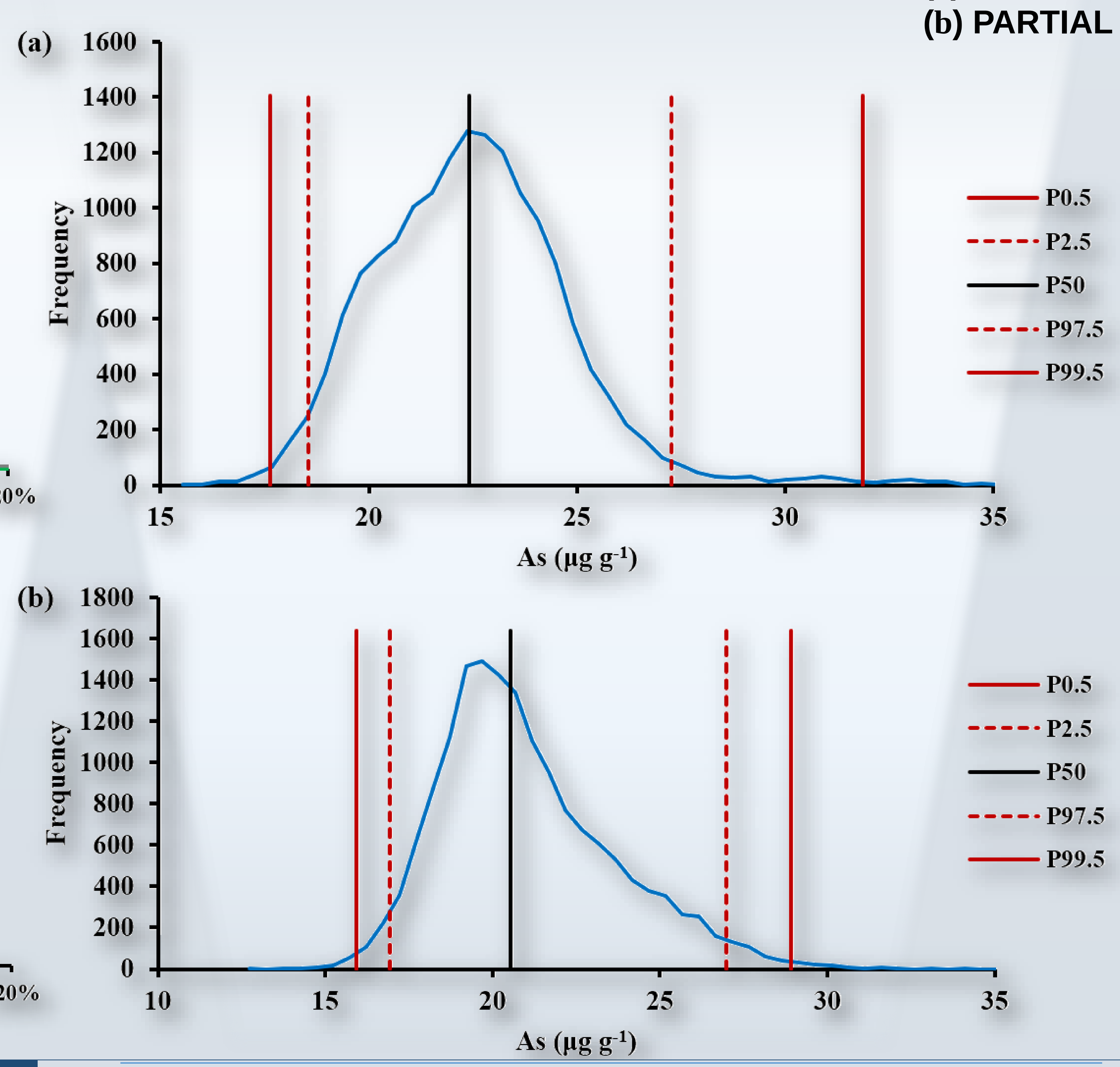



**MEAN RECOVERY, $\bar{R}$**




**MEASURAND, $w$**

(a) TOTAL
(b) PARTIAL




| | Item | Percentiles (µg g-1) P2.5 | P50 | P97.5 | $\eta'_{95}$ (%) | $U'^{tg}_{95}$ (%) |
|---|---|---|---|---|---|---|
| Total As | CRM | 18.5 | 22.4 | 27.4 | 19.7 | 29.5 |
| | A1 | 13.4 | 16.3 | 20.2 | 20.9 | 31.1 |
| | A2 | 13.0 | 15.9 | 19.6 | 20.6 | 31.3 |
| | B | 12.7 | 15.6 | 19.4 | 21.5 | 31.4 |
| | C | 4.8 | 6.4 | 8.5 | 29.3 | 40.5 |
| Partial As | CRM | 17.1 | 20.6 | 27.0 | 24.0 | 29.9 |
| | A1 | 14.5 | 17.5 | 23.0 | 24.3 | 30.7 |
| | A2 | 13.6 | 16.6 | 21.9 | 25.0 | 31.0 |
| | B | 13.0 | 15.9 | 20.9 | 24.8 | 31.3 |
| | C | 3.6 | 5.4 | 7.8 | 38.9 | 43.5 |

$\eta'_{95}$ – Half relative range of 95% confidence level interval: (P97.5-P2.5)/(2P50).
$U'^{tg}_{95}$ – Target relative expanded uncertainty for 95% confidence level: 2(0.125+0.5/P50).

**27% < $U'$ target, c.l. = 95% ($k$ = 2) < 75%**
between 2 mg $kg^{-1}$ and 50 mg $kg^{-1}$

## CONCLUSIONS

- The developed methodology was successfully applied to the determination of total or acid-extractable As (following OSPAR [3] or EPA 3051A [4] methods, respectively), in sediments.
- Random effects were simulated from the analysis of one CRM, and three sediment samples and trueness was assessed from the analysis of the CRM and two spiked samples.
- The evaluated uncertainty is fit for environmental monitoring considering performance criteria defined for Quasimeme proficiency tests [5].
- The developed measurement models were successfully cross-validated by randomly extracting data from the validation set subsequently used to check the compatibility between estimated and reference values for 95% or 99% confidence level. The observed success rate of these assessments is compatible with the confidence level of the tests.

**FUNDING:** This research was funded by Universidade de Lisboa through a PhD Scholarship 2018 and Fundação para a Ciência e Tecnologia (FCT) through projects UIDB/00100/2020 and UIDP/00100/2020.

**REFERENCES:** [1] Silva, R. B., Santos, J. R., Camões, M. F.: A New Terminology for the Approaches to the Quantification of the Measurement Uncertainty. Accred. Qual. Assur. 10, 664-671 (2006) (DOI 10.1007/s00769-005-0071-y). [2] Morgado, V., Palma, C., Silva, R. B.: Monte Carlo Bottom-up Evaluation of Global Instrumental Quantification Uncertainty: Flexible and user-friendly computational tool. Chemosphere 258, 127285 (2020) (DOI 10.1016/j.chemosphere.2020.127285). [3] OSPAR Commission: JAMP Guidelines for Monitoring Contaminants in Sediments, Agreement Ref. no. 2002-16, OSPAR (2015). [4] EPA: Method 3051A – Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils, EPA, USA (2007). [5] Eurachem/CITAC Guide: Setting and Using Target Uncertainty in Chemical Measurement, Eurachem (2015) (ISBN 978-989-98723-7-0).