# Validation of Heavy Metals Determination in Marine Sediments: A comparison of uncertainty evaluation approaches

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## INTRODUCTION

Marine sediments are the major pollution receptor and a potential source of heavy metals in aquatic systems. Sediments must be monitored before their use in beach recharge or other applications. The determination of heavy metals concentrations in sediments can involve a microwave digestion of samples using OSPAR method or the empirical EPA 3050B method before Atomic Absorption Spectrometry quantification. In this context, the analytical procedures must be validated to verify if produced measurements are fit for the intended use.

The validation process involves defining analytical requirements and the metrological assessment of measurements ability to fulfil these requirements, in particular, the ability to produce results with adequately small measurement uncertainty. The estimated measurement uncertainty provides information on result quality [1].

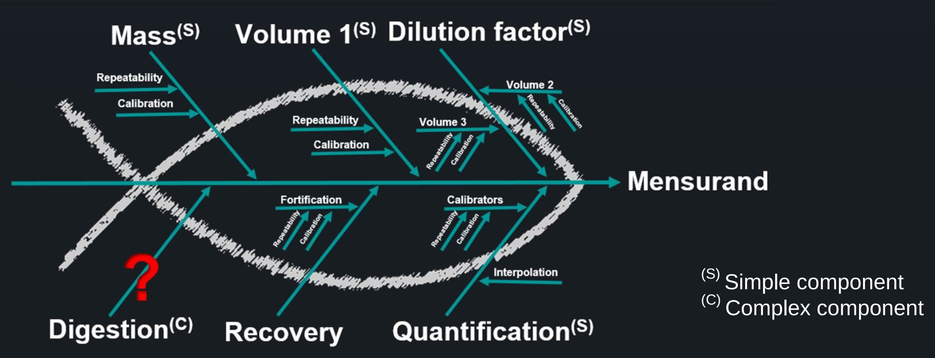
This work performs bottom-up and top-down evaluations of measurements uncertainty for the determination of lead in sediments. Top-down evaluations were performed as described in Eurachem and Nordtest guides.

Since the bottom-up approach is difficult to apply to this complex procedure, the differential approach for measurement uncertainty evaluation was used [2]. The Monte-Carlo Method was used for the combination of uncertainty components of the differential approach.

## APPROACHES

### DIFFERENTIAL

#### SOURCES OF UNCERTAINTY



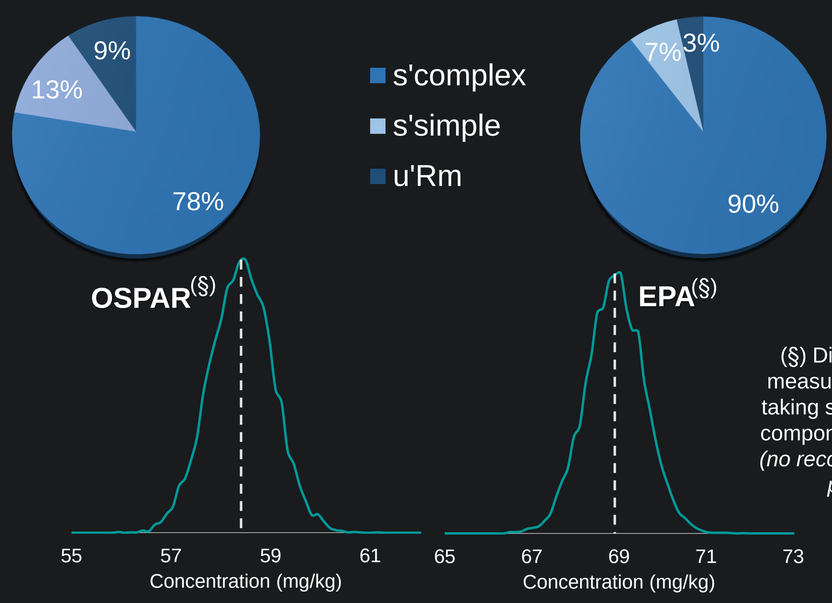

(S) Simple component
(C) Complex component

#### UNCERTAINTY COMPONENTS COMBINATION

$$u' = \sqrt{\left(s'_{simple}\right)^2 + \left(s'_{complex}\right)^2 + \left(u'_{\overline{R}_m}\right)^2}$$

#### RESULTS

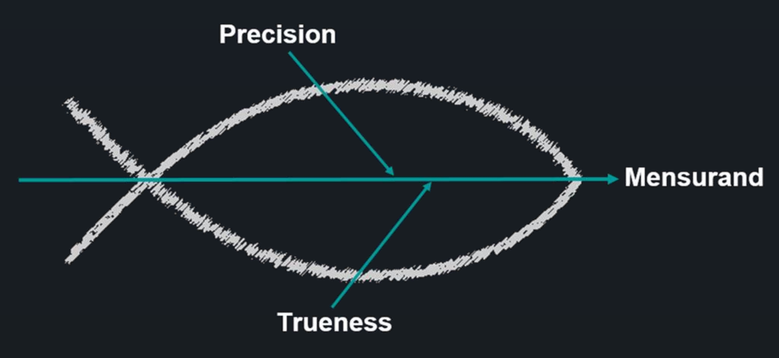
| Digestion | Uncertainty components (%) | | | Result (mg/kg) | U' (%) | Conf. level |
|---|---|---|---|---|---|---|
| | $s'_{complex}$ | $s'_{simple}$ | $u'_{\overline{R}_m}$ | | | |
| OSPAR | 4.49 | 1.83 | 1.57 | (63.8 ± 6.9) | 10.2 | 95% |
| EPA | 6.17 | 1.69 | 1.24 | (70.2 ± 9.7) | 13.0 | |




(§) Distribution of the measured quantity after taking simple uncertainty components into account *(no recovery correction is performed)*

### TOP-DOWN

#### SOURCES OF UNCERTAINTY




#### UNCERTAINTY COMPONENTS COMBINATION

$$u' = \sqrt{\left(u'_{precision}\right)^2 + \left(u'_{trueness}\right)^2}$$

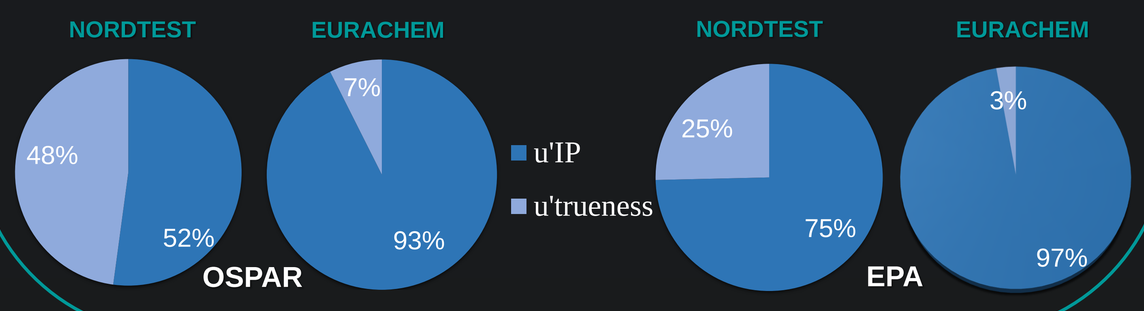
#### RESULTS

**NORDTEST**

| Digestion | Uncertainty components (%) | | Result (mg/kg) | U' (%) | Conf. Level |
|---|---|---|---|---|---|
| | $u'_{IP}$ | $u'_{bias}$ | | | |
| OSPAR | 5.54 | 5.31 | (64 ± 10) | 15.3 | 95 % |
| EPA | 7.28 | 4.24 | (70 ± 12) | 16.8 | |

**EURACHEM**

| Digestion | Uncertainty components (%) | | Result (mg/kg) | U' (%) | Conf. level |
|---|---|---|---|---|---|
| | $u'_{IP}$ | $u'_{\overline{R}_m}$ | | | |
| OSPAR | 5.54 | 1.57 | (68.1 ± 7.8) | 11.5 | 95 % |
| EPA | 7.28 | 1.24 | (74 ± 11) | 14.8 | |




## CONCLUSIONS

- The measurement uncertainty estimated by the differential approach is smaller that estimates performed by top-down approaches.
- The differential approach allowed sample digestion uncertainty estimation.
- The sample digestion uncertainty is the major uncertainty component.
- Monte Carlo Simulations allowed determining the measured quantity distribution estimated by the differential approach.

**REFERENCES**

[1] S. L. R. Ellison, A. Williams (Eds). Eurachem/CITAC guide: *Quantifying Uncertainty in Analytical Measurement*, Third edition, 2012.
[2] R. B. Silva, M. J. Lino, J. R. Santos, M. F. Camões, *Analyst* **125** (2000) 1459-1464.

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