DETERMINATION OF TRACE ELEMENTS IN THE OPEN OCEAN: METHOD VALIDATION

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Introduction

Oceanographic research over the past few decades has unveiled the significance of trace metals in marine biogeochemical cycles. Trace element determination in seawater is analytically dificult, due to the typically very low concentrations and the potential interference of the saline matrix. Determination of trace elements contents in the low ng kg^{-1} level remains a fundamental analytical challenge and a great source of complexity. Although the detection sensitivity of ICP-MS allows the direct measurement of trace elements at sub-ng g^{-1} levels the physical deposition of salts on interface cones and polyatomic interference from the major ions in seawater does not allow a simple analysis. Therefore, sample pre-treatment or matrix elimination prior to sample introduction into the plasma is often inevitable.

Methods

A method based on the application of an automated off-line seaFAST preconcentration system, combined with subsequent HR ICP-MS detection was developed.The preconcentration of the trace elements was achievd on a column integrated into seaFAST containing chelating resin with ethylenediaminetriacetic acid and iminodiacetic acid functional groups. Seven trace elements (Cd, Co, Cu, Mn, Ni, Pb and Zn) were simultaneously and quantitatively preconcentrated from 10 mL of seawater, eluted with 200µL of 1.8 M HNO_3, and determined by HR-ICP-MS using external calibration strategy. The single-step preconcentration removed more than 99.9% of Na, K, Mg and Ca from seawater.

Results

ISO-17025 standard and Eurachem guidelines were followed to perform the validation of the proposed methodology. Accordingly, blanks, selectivity, linearity of the calibration curve, working range, recovery, precision, traceability, limit of detection, limit of quantification and expanded uncertainty were assessed. The estimation of the total uncertainty associated to each measurement result was fundamental tool for sorting the main sources of measurement biases. Preliminary forecast of the uncertainty budgets was used as a strategy to ensure that determination of trace elements in seawater could be achieved with demonstrated traceability to a stated system of reference within less than 10 % expanded uncertainty ($k=2$) respectively.

Summary of the obtained from the validation study results are given in Table 1

Parameter	Value
Recovery, %	90 ± 10
Bias %	1-10
Uncertainty	7-10% (*k=2*)
Repeatability, RSD	~4%
Reproducibility, RSD	~6%
LOD pg kg^{-1}	5 - 100
LOQ, pg kg^{-1}	15 - 300
Blank, pg kg^{-1}	5 - 100

Additional validation of the developed analytical procedure was effectuated by comparison with the values reported in the frame of the organized by the EC JRC Institute for Reference Materials and Measurements IMEP 40 inter-laboratory comparison exercise. Good agreement was obtained also with the reference values of the several CRMs analyzed with the proposed analytical methodology: CASS- 5 NASS-6, from the NRCC Canada.

Table 2. Comparison of obtained results (µg kg^{-1}), k=2 with the IMEP-40 reference values

Element	Reference values IMEP 40	Ext. calibration results (this study)
Cd	0.096 ± 0.013	0.091± 0.007
Co	0.075 ± 0.012)	0.066± 0.005
Cu	0.88 ± 0.15	0.79± 0.08
Mn	2.46 ± 0.15	2.53 ± 0.09
Ni	1.06 ± 0.11	0.963 ± 0.067
Pb	0.097 ± 0.14	0.092 ± 0.008
Zn	4.70 ± 0.50	4.30 ± 0.31

Conclusions

The proposed and validated analytical method based on the combination of sea*FAST* system with HR SF ICP-MS is fit for purpose and can be applied for trace elements ocean monitoring.