21GRD09 MetroPOEM

D7: Report describing the development of one aqueous certified reference material that is certified for the same stable isotope ratios of B, Cd, Li, Ni, Pb and U with lowest possible uncertainties

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Due date of the deliverable: September 2025

Actual submission date of the deliverable: 30/09/2025

Glossary

CCQM	Consultative Committee for Amount of Substance
CIPM	International Committee for Weights and Measures
CRM	Certified reference material
GUM	Guide to the expression of uncertainty in measurement
ICP-MS	(Single-collector) Inductively coupled plasma mass spectrometry
ICP-MS/MS	Inductively coupled plasma tandem mass spectrometry
MC-ICP-MS	Multi-collector inductively coupled plasma mass spectrometry
RM	Reference material
UME	TÜBİTAK National Metrology Institute of Türkiye

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1 Summary

This report is intended to be the 7th deliverable report of the project 21GRD09 MetroPOEM describing the production of UME MetroPOEM CRM, a seawater material certified for the isotope amount ratios of selected elements: B, Cd, Li, Ni, Pb and U. The certified reference material was produced in accordance with the requirements of ISO 17034:2016 standard [1]. The collection of starting material, 250 L of seawater, was conducted at the station UE67, which was located at the edge of German EEZ in the North Sea (55° 25' N; 4° 5' E). The sample was filtered before filling into pre-cleaned 25 L HDPE carboys and acidified using subboiled HNO_3 for the stabilisation. The carboys were sealed and individually packed in clean PE foil, and stored at 4 °C prior to transport to TÜBİTAK UME by Hereon for further processing. After preliminary analysis, the material was spiked with the elements whose mass fractions were below the target levels to obtain the material having suitable concentrations to be measured in standard analytical laboratories. After filling into pre-cleaned 250 mL polypropylene bottles, the whole batch was sterilized with 25 kGy γ-radiation by ^{60}Co source. Between-unit homogeneity and stability during dispatch and storage conditions were assessed in accordance with ISO 33405:2024 standard [2] by 21GRD09 MetroPOEM Project [3] partners in a collaborative manner. The characterisation was conducted by an interlaboratory study where, in addition to the project partners, several expert laboratories were also involved in isotope ratio measurements. Uncertainties of the characterisation measurements were estimated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [4]. Certified values include uncertainties arising from possible inhomogeneity, instability and characterisation measurements. The material is intended to be used for calibration or quality control purposes in laboratories performing isotope ratio measurements.

2 Introduction

Measurement capabilities have become important as water matrices need to be evaluated for compliance with the countries' own quality standards. It is well known that monitoring useful parameters systematically such as contaminants and keeping them under control directly affect the quality of life. Besides, the importance of air and soil quality, water quality is also quite important for Earth. Understanding the dynamics of ocean life has become crucial over the last decade as oceans cover about two-thirds of Earth (70 %), and are the main reservoir of CO_2 with a notable role in the global carbon cycle [5,6]. Countries with coastal borders have to follow well established regulations to help those mechanisms and keep most environmental pollution under control by performing routine analyses. However, as the necessity of monitoring trace elements in seawater is well established, the challenges of these measurements have raised the topic for the last few decades. There is a strong need to improve data quality for the monitoring and reporting of pollution in air, water and soil. In addition, comparability and robustness of measurements are often compromised by lack of suitable traceability chains and appropriate quality controls. Thus, laboratories performing sampling and tests in this field are regulated by respective authorities, and need matrix certified reference materials (CRMs) for appropriate quality controls as well as to ensure long term comparability of the data.

For the determination of either stable or radioactive polluting elements in the environment, fast, sensitive and inexpensive analytical procedures are needed. Many of the measurement principles in chemical analysis are on molar bases and some are isotope selective. Conversion from mass fraction to amount content requires knowledge of isotopic composition. The determination of isotope ratios is highly important in establishing traceability in quantitative elemental analysis by the method of isotope dilution which is widely considered as a primary method. As the isotopic compositions of elements do vary in nature due to several processes, including radioactive decay, biological mass fractionation, cosmic ray spallation and mass-independent fractionation, isotope ratio data plays a fundamental role in earth and environmental sciences. Despite its importance, the SI-traceability of isotope amount ratios is realised only very rarely, and its establishment remains a critical and highly demanding task in all areas concerning the pollutants mentioned above. This situation caused the CCQM to demand a 'traceability exception related to delta scale isotope ratio measurements' from the CIPM [7]. Such delta scale measurements in most cases are based on iRMs without SI-traceable isotopic composition, in other words artefacts. Most iRMs from artefacts containing different isotopes of the same element are inhomogeneous, are running out of stock or are hypothetical materials. Therefore, SI traceable matrix matched reference materials are needed [8].

The project aimed at the production and certification of a new seawater reference material for selected isotopes of environmentally relevant elements covering the mass range of elements while improving our understanding of mass fractionation behaviour across different atomic masses. Because these types of measurements require specific capabilities and only a limited number of institutes can provide reliable absolute isotope ratio data. Combined with constraints in available traceability sources, the range of elements and measurands selected for certification was intentionally kept limited. Seawater is one of the most challenging matrices for ICP techniques as it contains high amount of salt, which requires matrix separation for accurate and reliable measurements. The mass fraction ranges of the target elements and the measurands selected for certification in the seawater reference material are given in Table 1.

Table 1. The mass fraction range of the target elements and the measurands selected for certification in seawater reference material.

Element	*Mass fraction range, µg/kg*	*Measurand, mol/mol*
B	5000 - 6000	$n(^{11}B)/n(^{10}B)$
Li	140 - 170	$n(^{6}Li)/n(^{7}Li)$
Cd	10 - 15	$n(^{114}Cd)/n(^{110}Cd)$ $n(^{114}Cd)/n(^{111}Cd)$
Cr	12 - 18	$n(^{53}Cr)/n(^{52}Cr)$
Ni	10 - 16	$n(^{60}Ni)/n(^{58}Ni)$
Pb	6 - 8	$n(^{204}Pb)/n(^{206}Pb)$ $n(^{207}Pb)/n(^{206}Pb)$ $n(^{208}Pb)/n(^{206}Pb)$
Sb	5 - 10	$n(^{123}Sb)/n(^{121}Sb)$
U	3 - 5	$n(^{234}U)/n(^{238}U)$ $n(^{235}U)/n(^{238}U)$

2.1 Certification of CRM

The certification of CRM was realized under WP4 by the coordination of TÜBİTAK UME in accordance with the requirements of ISO 17034. Isochronous design was used for the stability and homogeneity studies where measurements were carried out by project partners contributing to WP4. Seawater is one of the most challenging matrices due to high salt content and usually requires matrix separation before introduction to instrument. The methods developed in WP2 of this project were used by the project partners in the certification measurements. Due to difficulties encountered during matrix separation, some measurements took longer time than expected. The characterisation of the materials were conducted by an interlaboratory study with participation of external laboratories which are experienced in the field of precise isotopic measurements. The certified values and associated uncertainties are given in Table 2.

Table 2. Certified values and associated uncertainties with its uncertainty components

Parameter	Certified Value, mol/mol	U_{CRM}, mol/mol	Coverage Factor	$U_{CRM,rel}$ %	$u_{char,rel}$ %	$u_{bb,rel}$ %	$u_{lts,rel}$ %	$u_{sts,rel}$ %
$n(^{11}B)/n(^{10}B)$	4.2041	0.0061	2.03	0.15	0.062	0.018	0.024	0.018
$n(^{114}Cd)/n(^{110}Cd)$	2.30378	0.00098	2.03	0.043	0.019	0.0047	0.0059	0.0050
$n(^{114}Cd)/n(^{111}Cd)$	2.24559	0.00084	2.02	0.037	0.015	0.0061	0.0045	0.0079
$n(^{6}Li)/n(^{7}Li)$	0.07972	0.00042	2.20	0.53	0.24	0.0088	0.013	0.0084
$n(^{204}Pb)/n(^{206}Pb)$	0.05502	0.00019	2.13	0.35	0.034	0.060	0.082	0.12
$n(^{207}Pb)/n(^{206}Pb)$	0.8572	0.0025	2.10	0.29	0.016	0.059	0.079	0.095
$n(^{208}Pb)/n(^{206}Pb)$	2.0995	0.0050	2.13	0.23	0.022	0.044	0.056	0.080
$n(^{234}U)/n(^{238}U)$	0.0000626	0.0000012	2.10	1.9	0.89	0.093	0.13	0.083
$n(^{235}U)/n(^{238}U)$	0.007252	0.000012	2.1	0.17	0.077	0.013	0.011	0.016

In addition to the certified parameters, nickel isotope ratio measurements took part in the certification study as an informative value. According to the aforementioned standards and the RM producer quality policies, parameters with limited number of characterisation data may be provided to customers as an informative parameter. Thus, nickel isotope ratio was provided as informative value because of the limited number of characterisation measurements as well as stability and homogeneity tests. One participant managed reporting isotopic ratio values for $n(^{60}Ni)/n(^{58}Ni)$. Despite the inability to cross check the reported value, the value was acknowledged to be an informative parameter as very limited matrix reference materials are available for Ni isotope ratio The data are given in Table 3.

Table 3. The informative value and associated measurement uncertainty for $n(^{60}Ni)/n(^{58}Ni)$ reported by LGC

Measurand	Informative Value, mol/mol	U, mol/mol	U_{rel} %	u_{char_rel} %
$n(^{60}Ni/n(^{58}Ni)$	0.38833	0.00060	0.16	0.076

The details of the whole certification is given in the certification report for the stable isotope ratios in seawater that is given as Annex 1 to this D7 report.

3 Conclusions

During the life time of the project, the majority of the isotope ratios of B, Cd, Li, Pb and U given in Table 1 have successfully been certified within the limits of target uncertainties aimed at the beginning of the project. A collaborative study conducted with the involvement of project partners produced the seawater CRM for isotope ratios of elements having environmental concern. The total number of units produced are 470. Approximately one third of the whole batch is used during the certification studies. The material will be useful for the reliability of the measurements related to tracing the environmental pollutants. Although in the proposed list, Cr

($n(^{53}Cr)/n(^{52}Cr)$) and Sb ($n(^{123}Sb)/n(^{121}Sb)$) could not be certified due to the difficulties encountered during high salt content of matrix separation, and the lack of traceable isotopic standards, respectively. A follow up project can be conducted in the future to certify these elements or other elements in the same material.

The certified reference material can be used as QC material for validation of the methods, including trueness, for measurements of isotope ratios in seawater matrices. The material is suitable for checking the sample preparation processes prior to stable isotopic measurements.

4 References

[1] ISO 17034:2016 General requirements for the competence of reference material producers, 2016

[2] ISO 33405 Reference Materials – Approaches for characterization and assessment of homogeneity and stability, 2024

[3] Annex 2 of the JRP 21GRD09 MetroPOEM “Metrology for the Harmonisation of Measurements of Environmental Pollutants in Europe”

[4] JCGM 100, Evaluation of measurement data — Guide to the expression of uncertainty in measurement, September 2008, BIPM

[5] P.G. Falkowski, The role of phytoplankton photosynthesis in global biogeochemical cycles, Photosynth. Res. 39 (1994) 235–258. doi:10.1007/BF00014586

[6] J.H. Martin, Glacial-Interglacial CO2 Change: The Iron Hypothesis, Paleoceanography. 5 (1990) 1–13.

[7] 104th Meeting of the CIPM (Session I), decision 104/26, 2015,

https://www.bipm.org/documents/20126/34439501/CIPM2015-I-EN.pdf/58ff6e3f-47f5-a230-4194-e2a23667e6da

[8] Willi A. Brand, Tyler B. Coplen, Jochen Vogl, Martin Rosner and Thomas Prohaska, Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report), Pure Appl. Chem. 2014; 86(3): 425–467.

5 Appendix 1 – Certification Report for Stable Isotope Ratios in Seawater (UME MetroPOEM CRM)