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Progress achieved in EURAMET project 21GRD09 MetroPOEM: Metrology for the harmonisation of measurements of environmental pollutants in Europe

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Progress achieved in EURAMET project 21GRD09 MetroPOEM: Metrology for the harmonisation of measurements of environmental pollutants in Europe

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Abstract. The European Green Deal's ambition for zero pollution requires development of highly sensitive techniques to detect ultra-low amounts of pollutants and determine their isotope ratios, where mass spectrometry is a key method. The project bridges the traceability gap between activity and mass measurements – particularly estimation of mass bias – and establishes new tools for pollutant tracing. SI-traceable reference materials and measurement procedures are being developed that significantly reduce measurement uncertainty and detection limits, to enable tracking pollution sources by commonly available mass spectrometers. This project supports strategies described by the European Metrology Network on pollution monitoring and the established EMN on radiation protection. Main areas of work are:

- Development of low-level radionuclide standards for ⁹⁰Sr and a series of actinides,
- Development of SI traceable high-precision analytical methods for isotope ratio determination of Li, B, Cr, Cd, Ni, Sb, Pb, and U in environmental matrices applicable to single and multi-collector ICP-MS systems.
- Generation of two reference materials – seawater and silica – spiked with radionuclides
- Production of certified seawater reference material for isotope ratio to validate analytical methods, support proficiency testing, and ensure quality control in future monitoring.
- Communication of project outcomes include peer reviewed papers, good practice guides, workshops, conference presentations and more.

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1 Introduction

The overall aim of the project is to bridge the gap between radiometric techniques and mass spectrometry for the characterisation and detection of polluting long lived radionuclides and stable elements and element tracers by comparing and linking both techniques, thus significantly improving measurement uncertainties and detection limits.

The specific objectives of the project are:

- To establish and compare the selectivity and detection limits of different types of mass spectrometers for selected radioactive pollutants using isotope reference materials and activity standards. This included assessing relative instrument performance with respect to current measurement challenges and establishing detection limits in relation to regulatory waste criteria levels or environmental regulations.
- To develop measurement methods for isotope ratios that are traceable to the SI by using multi-collector ICP-MS and apply these methods on more commonly available techniques (ICP-MS/MS, ICP-QMS) by providing suitable operating procedures focussing on selected stable polluting elements. This leads to producing recommendations for sample processing, treatment, uncertainty budgets and the quantification of the mass bias.
- To develop two radioactive reference materials with the sample matrix containing radioactive pollutants for use in an inter-laboratory comparison employing techniques used in the first objective, demonstrating the variations in parameters including detection limits, sample preparation requirements, sample introduction methods, total procedural time, and uncertainty budgets.
- To implement and validate the methods for isotope ratio measurements established in second objective by the development of one aqueous certified reference material (CRM) certified for the same stable polluting elements with lowest possible uncertainties using multi-collector instruments, in order to facilitate the calibration of single collector ICP-MS, instrument validation, as well as quality control.
- To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain, standards developing organisations and international organisations and end users.

These objectives are described in detail below.

Further information about the project can be accessed from the project website:

<https://www.npl.co.uk/euramet/metropoem>

2 Work Package 1: Establish and compare the selectivity and detection limits of different mass spectrometers

Mass spectrometry is increasingly being used in the measurement of medium and long-lived radionuclides

(half-lives of approximately 20 years or longer). Approximately 25 radionuclides have up to now been measured using mass spectrometry techniques, including actinides, ^{90}Sr , ^{93}Zr , ^{99}Tc , ^{129}I and ^{135}Cs . The application areas for mass spectrometric measurement of radionuclides include contributing to safe and cost-effective decommissioning through accurate waste characterisation, nuclear forensics to determine the source of contamination, contributing to updated half-life measurements, and environmental radioactivity measurement. Mass spectrometry offers potential advantages over α - and β -particle counting techniques, including short measurement times of several minutes per sample, and the potential to measure several hundred samples each day depending on the instrument type and setup. Some instrument designs are also capable of online separation from interferences (for example through high resolution or collision/reaction cell capabilities), reducing reliance on relatively time-consuming offline chemical separation and further contributing to the high sample throughput.

The increasing application of mass spectrometry for radionuclide measurement needs to be supported with underpinning traceable standards and methods. The aim of WP1 is to develop a series of single and mixed standards of radionuclides relevant to mass spectrometry measurement. These standards are distributed to participating laboratories for measurement by a range of mass spectrometric techniques, as well as radiometric techniques through an inter-laboratory comparison exercise and report.

2.1 Determination of starting materials

Given the range of participating laboratories in the consortium, the first step was to send a survey to all laboratories to understand their measurement capabilities and what radionuclide and activity levels would make sense for the most valuable comparison exercise. It was decided at the start of the project to focus on actinides (^{237}Np , ^{234}U , ^{236}U , U_{nat} , ^{239}Pu , ^{240}Pu , ^{241}Am , $^{239/240}\text{Pu}$), ^{90}Sr and a mixed standard. Questions in the survey included the activity range measurable by each laboratory, the activity levels that would be of interest, interferences to be considered, the carrier the samples should be prepared in, and any national or international regulatory limits that should be considered when selecting the activity concentrations.

As expected, the survey results produced a range of activity levels. It was decided to focus on low-level measurements, which reflected the activity levels expected in environmental samples and the detection limits that needed to be achieved to comply with most regulatory limits. Some participating laboratories did not have the required licence to handle radioactive materials. However, by preparing standards at environmentally relevant levels, the samples could be considered as exempt for shipping purposes and safely sent.

2.2 Sample Preparation

All samples were prepared in dilute sub-boiled nitric acid, which can be directly measured by some mass spectrometry designs. A series of dilutions were performed from standardised single radionuclide standard solutions prepared at NPL and diluted in a dedicated source preparation facility containing calibrated five and six figure balances. For some radionuclides, these same starting standards were used for the preparation of the liquid and solid reference materials in WP3. The starting materials had previously been characterised for impurity levels but were remeasured by NPL with additional measurements being undertaken by CEA. The activity concentrations could be determined from the masses of material and carrier added, along with the characterisation of the standards by NPL with supporting measurements from CEA. Dilution checks were performed using Liquid Scintillation Counting for higher activity samples, and by Inductively Coupled Plasma Tandem Mass Spectrometry (ICP-MS/MS) for lower activity samples. A series of standards were also prepared for long-term homogeneity and stability measurements by ICP-MS/MS.

Materials were dispatched to eighteen participating laboratories. The aim was for all laboratories to receive the same starting activities for each radionuclide and mix of interest, even though not all laboratories were able to receive the same range of radionuclides due to measurement and/or sample handling restrictions. In some specific cases, higher activity starting materials were also requested. In the cases of laboratories receiving samples containing U and Pu isotopes, an export licence was required prior to dispatch, along with acknowledgement of safety and security considerations of handling the samples.

2.3 Sample Measurement and next steps

A range of mass spectrometric techniques are being used to measure the standards prepared, specifically quadrupole ICP-MS, tandem ICP-MS/MS, sector field ICP-MS, multi-collector ICP-MS, thermal ionisation MS, accelerator MS and decay counting techniques (α -spectrometry, liquid scintillation counting and γ -spectrometry). A template was prepared for submission of results from each laboratory. This included the activity levels (and where relevant isotopic ratio values) measured, the uncertainty budget, the measurement technique(s) used and details of any sample preparation. The details submitted through the template will form the basis of data analysis and the production of an interlaboratory comparison report. The report will provide a comprehensive overview of the advantages and limitations of different mass spectrometric techniques for measurement of the same starting materials. This will also support the development of a Good Practice Guide on the Measurement of radionuclides using mass spectrometry, that will be a valuable resource for current and potential future users of this technique.

3 Work Package 2: Advancing stable and long-lived radiogenic isotope ratio measurements of environmental pollutants

Determining isotope ratios in environmental pollutants has become a crucial tool in modern analytical chemistry, providing valuable insights into pollution sources, transformation processes, and environmental fate. Isotope ratio analysis enables researchers to trace the origins of contaminants, differentiate between natural and anthropogenic sources, and assess chemical pathways in various environmental matrices. Recent advancements in mass spectrometry techniques, single and multi-collector inductively coupled plasma mass spectrometry ((MC)-ICP-MS), have significantly improved the precision, sensitivity, and applicability of isotope analysis in environmental studies. Despite these advancements, several challenges remain in ensuring accurate and reproducible isotope ratio measurements. Matrix effects, instrumental mass bias, and sample preparation artifacts can introduce significant uncertainties, necessitating rigorous calibration strategies. A critical limitation in the field is the scarcity of SI-traceable certified reference materials (CRMs) for many non-traditional elements, which hinders method validation, interlaboratory comparability, and the establishment of standardized protocols. The lack of widely available CRMs also complicates the development of accurate mass bias correction models, which are essential for achieving high-precision isotope ratio determinations.

Work Package 2 of the MetroPOEM project is actively advancing the accurate and SI-traceable determination of isotope ratios for non-traditional elements using ICP-MS. New analytical methods are being developed to enable precise and traceable isotope ratio measurements of lithium (Li), boron (B), chromium (Cr), cadmium (Cd), nickel (Ni), antimony (Sb), lead (Pb), and uranium (U), ensuring robust metrological foundations. Analyte/matrix separation techniques are being optimized to improve the accuracy of isotope ratio measurements in complex environmental samples, effectively minimizing matrix-induced biases and interferences. At the same time, instrumental mass fractionation in ICP-MS is being evaluated and modelled by quantifying variations in instrumental isotope fractionation (IIF) across a wide mass range, from Li to U. This ongoing investigation, using multiple ICP-MS platforms and key elements, is enhancing the understanding of mass bias effects and improving the reliability of isotope ratio determinations. Collectively, these efforts are establishing high-precision, SI-traceable methodologies for environmental isotope analysis.

3.1 Development of SI traceable methods for determination of isotope ratios of Li, B, Cr, Cd,

Ni, Sb, Pb, U by MC-ICP-MS and single collector ICP-MS

Accurate determination of isotope ratios for elements such as Li, B, Cr, Cd, Ni, Sb, Pb, and U is essential in various scientific disciplines, including environmental monitoring, geochemistry, and nuclear forensics. Central to achieving this accuracy is the availability of well-characterized, SI-traceable certified reference materials (CRMs) for these elements. After an extensive search, the following isotopic CRMs were recorded; Li isotope measurements are commonly referenced against the LSVEC standard (NIST RM 8545), while boron isotope analyses utilize NIST SRM 951a as a primary reference material. Chromium isotope determinations often refer to NIST SRM 979, for Cd BAM-I012, for Pb the NIST SRM 981 and for U IRMM 184 are commonly used. However, the availability of CRMs for elements like B (NIST SRM 951a) and Ni (NIST SRM 3136) are not available anymore, while for Sb is non-existent, posing challenges for precise isotope ratio measurements. In the framework of the WP2 a re-characterisation of the reference material LSVEC for Li isotope ratio is underway by an interlaboratory comparison that aims to determine the absolute Li isotope ratio and to improve the measurement uncertainty of the reference material. A range of instrumental techniques are employed, including multi-collector ICP-MS (MC-ICP-MS), sector field ICP-MS, quadrupole ICP-MS, and ICP-MS/MS. The performance of these techniques was assessed and compared in terms of accuracy and precision.

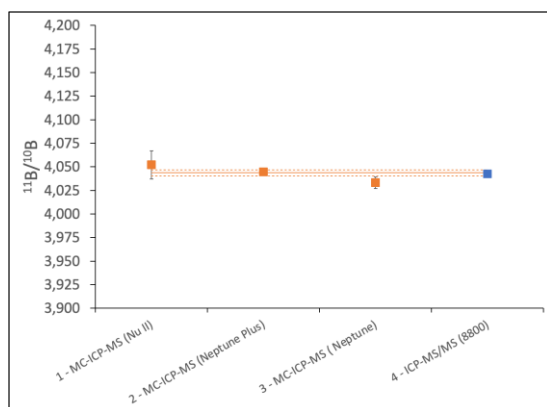
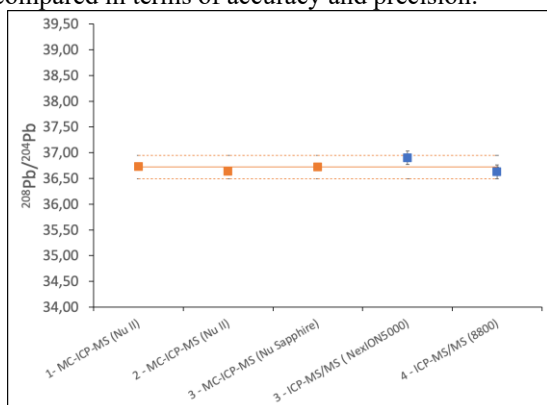


Figure 1: Comparison of isotope ratios for selected elements obtained with different mass spectrometers.

3.2 Development of analyte separation methods for high precision analysis

In order to obtain accurate and precise isotopic ratios in environmental samples, they need to be properly prepared. Several steps are usually applied before isotope ratio measurement. Depending on the type of the sample, there may be pre-treatment step needed. For solid samples, it consists of a digestion or extraction, while for liquids, usually a preconcentration is needed. Next is the separation step to isolate the element of interest from the sample matrix, and finally, the determination of the isotope ratios by measurement of the isotope responses and correction for instrumental isotopic fractionation. For the element isolation from the matrix different resins are being tested, as shown in Table 1.

Isotopic system	Resin
Li	AG 50W-X12
B	sublimation
	AG 50W-X8 and Amberlite IRA 743
	AG 50W-X8 and Microsublimation
Cr	BioRad AG 1-X8
Ni	Ni-Spec and others
	Chelex 100 chelating resin
Cd	BioRad AG 1-X8
	BioRad MP-1M
Pb	Sr spec
	DGA resin
	Pb Resin Triskem
	Anion exchange BioRad AG-1 X-8
U	Anion exchange BioRad AG-1 X-8

Table 1: Resins used for matrix removal.

3.3 Evaluating and modelling instrumental mass fractionation in ICP-based mass spectrometers

Instrumental isotope fractionation is a significant challenge in mass spectrometry, particularly in MC-ICP-MS. This phenomenon can lead to biased isotope ratio measurements, necessitating the development of correction methods. Traditionally, IIF has been corrected using empirical equations such as Power, Exponential and Russel law. However, a few studies show inaccuracy or significant deviations from true values when applying these conventional models. In the frame of WP2, current methods are being improved and new approaches developed based on inter-element normalisation and without a priori assumptions. One method that is being improved in the gravimetric isotope mixture approach, a primary method for the determination of SI-traceable isotope ratios. The latest variation of the approach introduces ion chromatography to determine the elemental mass fractions in the enriched isotope solutions. It significantly simplifies the classical isotope mixture approach. This new approach has been published [1] and it will be applied in the interlaboratory comparison on Li isotope ratios (CCQM-K182/P233) for testing the achievable uncertainty level and the comparability of

laboratory results. Although the primary method is a strong asset, for routine use, the method has, unfortunately, some throwbacks like enriched isotopes are not available for many stable elements, and/or the required uncertainty level does not justify the costs and efforts of applying this method. Therefore, additional methods are required. For the isotopic systems where the gravimetric isotope mixture cannot be applied, and iRM are not available, modelling of the IIF is being tested. Another method that is being optimised is the regression method to correct for instrumental isotope fractionation. The method is based on simultaneous measurement of analyte, for which isotope ratios are to be determined, and internal standard with known isotope ratios. In this case, the IIF correction factor can be accurately determined for the internal standard from its measured and a priori known isotope ratios and then be extrapolated to the analyte. Altogether, the work done in WP2 will establish high-precision, SI-traceable methodologies for environmental isotope ratio analysis.

4 Work Package 3: Development of radioactive reference materials

The aim of WP3 was to produce two radioactive reference materials, a liquid and a solid, to mimic contaminated water and soil. The matrix of the liquid reference material was seawater and was the same as the reference material developed in WP4. Thus, the liquid RM was as close as possible to a real environmental sample, and the measurements included sample preparation steps, such as concentration and removal of interfering ions. Following a different approach, the solid material chosen was synthesised from scratch, in order to control the amount and activity concentration of radionuclides added and improve the homogeneity. A silica-type material was used, as it is readily synthesised via a *sol-gel* process and can be ground to yield a sand-like material. Those two reference materials will be used in an interlaboratory comparison, so that partners of WP3 can test their usual measurement methods.

4.1 Spiking procedure

The procedure used to obtain materials with well-controlled radionuclide levels is similar for both the solid and the liquid. First, starting materials, ie solutions of one radionuclide or several isotopes of the same element, were characterised at two different laboratories, at NPL and at CEA, using radiometric techniques and mass spectrometry. Specific uranium and plutonium isotopic compositions were selected, after discussion within the partners of WP3, shown in Table . Those solutions were first mixed and then used to spike seawater, or with silica liquid precursors.

Reference Material	Uranium	Plutonium
Liquid	Natural	$^{240}\text{Pu};^{239}\text{Pu}$ mass ratio ~ 0.1
Solid	Slightly enriched	$^{240}\text{Pu};^{239}\text{Pu}$ mass ratio < 0.1

Table 2: U and Pu isotopic compositions chosen for both RMs.

All the liquids used were weighed with high precision balances, so that the concentration of each radionuclide could be derived from the masses added. In addition, the characterisation of both final materials was performed by two metrology laboratories (CEA and NPL). These two approaches to characterise the property values of a reference material are described in the ISO 17034 standard [2], and their results can be compared.

The homogeneity and stability of the two reference materials were assessed at NPL and CEA, following the ISO 33405 standard [3] and this work is the subject of an article to be published.

4.1.1 Liquid RM

The seawater used as matrix was sampled from the German Exclusive Economic Zone (EEZ), as described in section 5.1, filtered, acidified and sterilised by γ -ray irradiation. The initial radioactive content in the sterilised and acidified seawater was assessed by several labs, before spiking. Forty litres of seawater were mixed with the radionuclide solutions and homogenised by stirring for two weeks. After homogenisation, the liquid RM was bottled into 80 samples and sent for characterisation, and to participants.

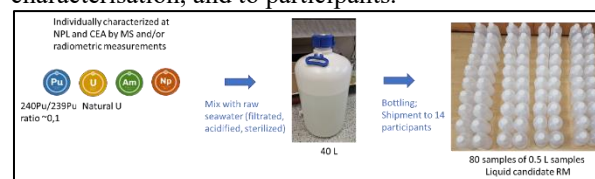


Figure 2: Schematics of the preparation procedure for the liquid RM samples.

4.1.2 Solid RM

The synthesis of the solid RM was adapted from Harms and Gilligan [4]. The radionuclide solutions (in nitric acid) were mixed with two silica precursors (tetraethyl orthosilicate and triethoxyoctylsilane), ethanol and nitric acid. The second silica precursor was used for its hydrophobic properties and generated a less hygroscopic material than pure silica one. After five days of stirring, the liquid reaction medium was transferred to trays, in order to facilitate the evaporation of ethanol. The complete solidification occurred 13 days after mixing, and the solid was dry after 22 days. It was then ground into a fine powder (particles smaller than 250 μm) with a jar miller and bottled into 82 samples.



Figure 3: Schematics of the preparation procedure for the solid RM samples.

A batch of inactive solid was also synthesised using the same procedure, so that participants could test their dissolution procedure beforehand.

4.2 Organisation of an interlaboratory comparison

Both reference materials will be used in two interlaboratory comparisons. Participants will use radiometric and/or mass spectrometry measurements to determine the concentration of U, Pu, Am and Np, as well as the isotopic ratios of U and Pu, especially the $^{235}\text{U}:^{238}\text{U}$ mass ratio and the $^{240}\text{Pu}:^{239}\text{Pu}$ mass ratio. Around fifteen laboratories will take part in each comparison, including partners of WP3, and additional participants. The results are expected by the end of March 2025.

5 Work Package 4: Development of SI traceable certified reference material

The reference materials are crucial for metrological traceability of the measurement results in case of calibration of the measuring instruments as well as for providing objective evidence for the quality of measurement result by ensuring the validity of the methods used for the measurement. This work package of the project is dedicated to preparation and certification of one of the two reference materials in the MetroPOEM project for the isotope ratios of the target elements with stable isotopes. The studies in this WP is divided into tasks which are collection, processing, certification measurements which include stability, homogeneity and characterization measurements, and finally the value assignment. All the preparation steps are carried out following the requirements of ISO 17034 [2].

The target elements within the scope of the project are boron, lithium, chromium, nickel, cadmium, antimony, lead, uranium. The isotope ratio values of these elements are the most widely used ones in different areas for making decisions and scientific works. The method used for the certification measurements are mostly the ones developed in WP2 of this project and requires matrix separation before introduction into the plasma. The parameters aimed to be certified in the project for stable elements and their corresponding concentrations are given in table 3.

Element	Concentration $\mu\text{g kg}^{-1}$	Measurand
B	5000 – 6000	$n(^{11}\text{B})/n(^{10}\text{B})$
Li	140 – 170	$n(^6\text{Li})/n(^7\text{Li})$
Cd	10 – 15	$n(^{114}\text{Cd})/n(^{111}\text{Cd})$ $n(^{113}\text{Cd})/n(^{111}\text{Cd})$
Cr	12 – 18	$n(^{53}\text{Cr})/n(^{52}\text{Cr})$
Ni	10 – 16	$n(^{60}\text{Ni})/n(^{58}\text{Ni})$
Pb	6 – 8	$n(^{204}\text{Pb})/n(^{206}\text{Pb})$ $n(^{207}\text{Pb})/n(^{206}\text{Pb})$ $n(^{208}\text{Pb})/n(^{206}\text{Pb})$
Sb	5 – 10	$n(^{123}\text{Sb})/n(^{121}\text{Sb})$
U	3 – 5	$n(^{234}\text{U})/n(^{238}\text{U})$ $n(^{235}\text{U})/n(^{238}\text{U})$

Table 3. Concentration ranges of elements to be measured in the seawater candidate material and reporting measurands.

5.1 Sampling of the raw material

The sampling was conducted as part of the regular monitoring research cruise AT 020 (Start Bremerhaven, Germany, 2023-05-15, End Bremerhaven, Germany, 2023-05-26) with the RV ATAIR operated by the German BSH covering the entire German EEZ as shown on the map presented in figure 4. The sampling for candidate reference material was conducted at station UE67, which is located at the edge of the German EEZ.

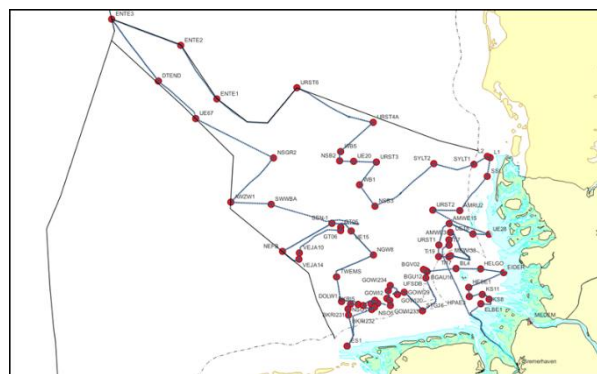


Figure 4: Route of the sampling cruise AT020

A total of 250 L of seawater for the reference material was into brand new 25 L carboys specified for food applications analysis. The carboys were cleaned by using a procedure where subsequent flushing with DI water, 1% acid solutions several times by keeping the inner surfaces of the carboys in contact with 1% HCl for 1 week and then rinsing with ultrapure water.

The water sample was collected by using the trace metal clean PVDF made clean seawater inlet system of the German research vessel ATAIR. The water was pumped into the ship from a depth of 5 m below sea level. The water was directly filtered using precleaned trace metal free filter cartridges (Pall AcroPak 1500 0.8/0.2 μm), into 25 L precleaned carboys. Before collecting the final sample each carboy was rinsed three times with ca. 1 L of seawater filtrate to precondition the surface of the carboy. In total two filter units were necessary to process the total volume ca. 250 L seawater. After filling the carboys they were closed and the outside was rinsed with MilliQ to remove any spilled seawater from the surface. The filtered raw material was acidified using 2 times sub-boiled HNO_3 to stabilize the material. The carboys were sealed and individually packed in clean PE foil and stored at 4°C.

5.2 Processing and bottling of seawater reference material

The collected samples were transferred to Hereon laboratories where 50 mL aliquots from each carboy were taken under cleanroom conditions to allow a preliminary analysis of the trace metal content of individual samples. The purpose of the preliminary analysis conducted by using SeaFAST- ICP-MS/MS (Agilent 8900 QQQ) using a He/H₂ mixed gas mode [5]. The level of the parameters to be certified should be fit for purpose. In most circumstances, it is desired that the levels in the reference materials should be well above

the method limit of detection values for providing results with uncertainties suitable for decision making either during the method development or in the calibration of the instruments. Since the levels for some of the target elements were found to be very low in original raw material, the material was spiked with NIST SRM 3100 series standards for Cd, Cr, Ni, Sb and Pb, where the elements were assumed to be at their natural isotopic composition. Then approximately 120 L of seawater was transferred into a 120 L HDPE tank and the material was homogenised for four hours. After filtration through 0.8/0.2 μm (Pall Corp, Supor® Membrane, AcroPack™ 1000, PN 12992), the material was filled into bottles manually. At the end, a total of 470 bottles each containing 250 mL of candidate reference material were obtained. All the steps in processing of the material, including spiking, homogenization and filling into bottles were carried out in ISO Class 6 Clean Chemistry Laboratory (CCL) at TÜBİTAK ÜME (Figure WP4-2). The whole batch of the reference material units were sent to the γ irradiation facility and irradiated with a total exposure of 25 kGy in order to ensure no biological activity afterwards.



Figure 5: Homogenisation and bottling in ISO Class 6 Clean Chemistry Laboratory at TÜBİTAK ÜME

5.3 Homogeneity and stability tests for seawater reference material

The reference material producer is responsible for the stability and the homogeneity of the material produced in the batch. According to ISO 17034, the producer should ensure the material stability and homogeneity and should provide objective evidence for them. The different approaches for homogeneity and stability tests and the statistical evaluation of the data produced from these test measurements are given in ISO 33405 [3]. In this project, although no instability is expected as the material is natural and stabilized by acidification, the tests were carried out to comply the requirements of standard ISO 17034 and to ensure the stability of spiked elements. Since the measurements require very sophisticated tools, requires large sample amount and specific sample preparation, and finally takes very long time, a combined approach for the assessments of homogeneity, short-term stability and long-term stability is used. The measurements were carried out by the participating partners who can measure the isotopic ratio values for target elements.

In the long-term stability (LTS) test, an isochronous design was applied for testing the stability of the material at 22 °C. The stability of samples was tested at 4 periods of time: 3, 6, 9 and 12 months. The temperature 4 °C served as reference temperature and

taken as the 0th time point. Total number units to be used in long term stability testing were placed at test temperature and at the end of each period, 2 units of material were transferred to and kept at reference temperature. After the period of one year from the start of testing, all units had been transferred to the reference temperature. Since the measurements for each parameter takes long time and requires specific sample preparation steps, and thus to be carried out by different partners, separate sets of samples were reserved for each parameter and sent to the participating laboratories at the end of testing period.

The short-term stability (STS) is done for testing the stability of the material at the transportation conditions that the reference material is potentially subjected to during their transfer to the end users. In this project, a single test temperature, 45 °C with a single test duration, 3 weeks, is tested for short term stability of the material. Two bottles of the material are subjected to test temperature for the test period and then transferred to reference temperature to be measured isochronously with the LTS samples whose reference points would serve as well for STS samples. Since the measurements for each parameter for both long-term and short-term samples were to be carried out by the same project partner, the STS samples were sent to the measuring laboratories together with them. The stability measurements are still in progress at the time of the preparation of this manuscript. The reporting and the evaluation of the results are expected to be complete at the end of March 2025.

5.4 Characterization of seawater reference material

Characterisation is required where the certified value is to be assigned by the reference material producer. The assigned value can be either quantitative or qualitative. There are different approaches for the characterization of the reference materials. One of these approaches is the determination of the value to be assigned by an interlaboratory study between the competent laboratories where the consensus value between the participating laboratories is assigned as the certified value. In MetroPOEM project, this approach is selected for characterization. In addition to the project partners who agreed on getting involved during the preparations of the project, the other experienced laboratories in the field of isotopic measurements were also invited for the characterization measurements. A registration form was sent to the potential participating laboratories. They are asked to fill in the registration form by checking the parameters that they would like to participate in the measurements. The study protocol for the characterisation where the requirements for the measurements were explained was also sent to those laboratories. In total, there are 14 laboratories registered for the characterization study. Each laboratory received 2 units of samples unless they requested more samples for their measurements. The measurements are still in progress and results are expected to be reported by the end of March 2025.

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