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 isotope ratios, where mass spectrometry is a key method. The MetroPOEM project bridges the traceability gap between activity and mass-based measurements.

Low level radioactive standard solutions (^{90}Sr, ^{237}Np, ^{234}U, ^{236}U, natural uranium (U_{nat}), ^{239}Pu, ^{240}Pu, ^{241}Am, ^{239,240}Pu) were distributed to 18 partner laboratories for measurement by mass spectrometric and decay counting techniques. The results and data analysis will be published separately.

SI-traceable high precision methods were developed for isotope ratio determination of Li, B, Cr, Cd, Ni, Sb, Pb and U in seawater. Method development addressed analyte separation from the matrix, evaluation of calibration approaches, isotope fractionation corrections and uncertainty estimation.

Seawater (250 L) was taken from the German North Sea exclusive economic zone (DE-EEZ) to develop two certified reference materials (CRMs). Part of this material was used to generate a CRM with SI traceability for isotope ratios of Li, B, Cr, Cd, Ni, Sb, Pb and U. The second part was used to generate a seawater CRM, spiked with U_{nat}, ^{237}Np, ^{239,240}Pu and ^{241}Am.

A solid silica-based CRM, spiked with U_{nat}, ^{237}Np, ^{239,240}Pu and ^{241}Am, was produced by sol-gel synthesis, with ~10 kg of inactive material for method development.

These materials were characterised in accordance with ISO 17034 by interlaboratory studies between project partners, using techniques developed in the project.

Two Good Practice Guides, on (i) measurement of radioactivity by mass spectrometry, and (ii) sample treatment, uncertainties, and mass bias quantification, are in draft.

Keywords

Environmental pollutants; European Green Deal; mass spectrometry; reference material, traceability; interlaboratory comparison; harmonised methods

Introduction

The MetroPOEM project aims to develop harmonised methods for measurement of priority radioactive and stable pollutants, focusing on the capabilities of mass spectrometry, especially inductively coupled plasma mass spectrometry (ICP-MS) techniques, with the goal of 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 (IRMs) and activity standards. This includes assessing relative instrument performance with respect to current measurement challenges and establishing detection limits in relation to regulatory waste criteria levels and environmental regulations.
- Develop two radioactive reference materials with the sample matrix containing radioactive pollutants for use in an interlaboratory 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.
- Develop measurement methods for isotope ratios that are traceable to the SI by using multicollector ICP-MS (MC-ICP-MS) and apply these methods on more commonly available techniques including inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) and inductively coupled plasma quadrupole mass spectrometry (ICP-QMS) by providing suitable operating procedures focusing on selected stable polluting elements.

This will lead to recommendations for sample processing, treatment, uncertainty budgets and the quantification of the mass bias.

- Implement and validate the methods for isotope ratio measurements established in the previous objective through the development of an aqueous CRM certified for the same stable polluting elements, with the lowest possible uncertainties using MC-ICP-MS instruments, to facilitate the calibration of single collector ICP-MS (SC-ICP-MS), instrument validation and quality control.
- Facilitate the adoption of the technology and measurement infrastructure developed in the project by the measurement supply chain, standards organisations, international organisations, and end users.

These objectives are described in more detail below. Further information about the project can be accessed from the project website: https://www.npl.co.uk/euramet/metropoem

Accurate and high precision isotope ratio analyses play a vital role across a broad spectrum of scientific fields, including environmental science, nuclear forensics, and climate research and has become a cornerstone of environmental analytical chemistry, offering a powerful means to trace pollution sources, understand geochemical processes, and monitor the environmental fate of contaminants.

Rationale

Isotope ratio measurements have been made for over a century, (Aston, 1920). The field advanced significantly in the 1950s with the development of Thermal Ionisation Mass Spectrometry (TIMS), which enabled precise isotopic measurements of many elements. The advent of ICP-MS (Houk *et al.*, 1980) in the 1980s revolutionised the field by allowing for rapid, sensitive, multi-elemental analysis. The subsequent development of MC-ICP-MS in the 1990s marked another major leap, enabling high-precision isotope ratio measurements of elements such as Pb and Sr (Waldner and Furuta, 1993).

Analytical challenges remain for isotope ratio analysis including matrix effects, instrumental mass bias, and sample preparation artifacts, which impact accuracy and precision, requiring robust calibration strategies and correction models. The scarcity of SI-traceable CRMs is one of the critical limitations in the field and hampers method validation, standardisation, and interlaboratory comparisons, limiting the wider adoption of isotope techniques in environmental monitoring and regulation.

Ongoing efforts in metrology aim to address these limitations through the development of high-purity and matrix-matched standards, improved uncertainty quantification, and harmonised protocols that support traceability to the SI, ensuring comparability and reliability across studies and laboratories.

Driven by the need to detect subtle isotopic variations, recent advances have focused on improving analytical precision, traceability to the International System of Units (SI), and minimising measurement uncertainty. Developments in mass spectrometry, such as MC-ICP-MS, sector-field ICP-MS (ICP-SFMS) and ICP-MS/MS, and accelerator mass spectrometry (AMS), have significantly enhanced sensitivity and selectivity. At the same time, improved sample preparation protocols, matrix separation techniques, and calibration strategies have contributed to greater measurement reliability and interlaboratory comparability. These innovations collectively enable the robust quantification of isotopic signatures in increasingly complex environmental matrices.

Underlying studies

Mass spectrometry is increasingly being used in the measurement of radionuclides with half lives of ≥20 years. Until now, approximately 25 radionuclides, including actinides, ^{90}Sr, ^{93}Zr, ^{99}Tc, ^{129}I, and ^{135}Cs, have been measured using mass spectrometry techniques. Mass spectrometry techniques support for activities such as safe and cost-effective decommissioning through accurate waste characterisation, relatively rapid nuclear forensics to determine the source of contamination, improved half-life measurements, and precise environmental radioactivity measurements.

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

Mass spectrometry offers some advantages over α- and β-particle counting techniques including short measurement times (on the order of minutes per sample) and thus the ability 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 contributing to higher sample throughput.

The increasing application of mass spectrometry for radionuclide measurement needs to be supported with underpinning traceable measurement 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 were distributed to participating laboratories for measurement by a range of mass spectrometric techniques and radiometric techniques through an interlaboratory comparison exercise with a final report.

Determination of starting materials

To establish measurement capabilities, radionuclides, and activity levels of interest for participating laboratories, a survey was sent to all laboratories in the consortium to ensure the standards developed would be useful for a comparison exercise. It was decided at the start of the project to focus on ^{90}Sr, ^{234}U, ^{236}U, U_{nat}, ^{237}Np, ^{239}Pu, ^{240}Pu, ^{241}Am, and mixed ^{239}Pu/^{240}Pu. 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.

The survey results produced a range of responses. 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. Thus, standards at environmentally-relevant levels were prepared.

Sample Preparation

All samples were prepared in dilute sub-boiled nitric acid (for example: Bock, 1979), which can be measured directly by some mass spectrometry system designs, the primary aim of the comparison exercise. A series of dilutions were performed from single radionuclide standard solutions prepared at the NPL and diluted in a dedicated source preparation facility containing calibrated five and six figure balances. These same starting standards were used for the preparation of the spiked liquid and solid reference materials, for some radionuclides in WP3. The starting materials had previously been characterised for impurity levels but were remeasured by the NPL with additional measurements being undertaken at the CEA using both decay counting and ICP-MS techniques. The activity concentrations were determined from the mass of material and carrier added, along with the characterisation of the standards by the NPL. Dilution checks were performed using liquid scintillation counting (LSC) for higher activity samples and by 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 at the NPL.

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 all cases, acknowledgement of compliance with national and international regulatory, safety, and security requirements for receipt and handling the samples was required from the laboratories, particularly for fissile materials.

Sample Measurement and next steps

A range of mass spectrometric techniques were used to measure the standards prepared, specifically ICP-QMS, ICP-MS/MS, ICP-SFMS, MC-ICP-MS, TIMS, and AMS. Some laboratories performed additional measurements by decay counting techniques (α-particle spectrometry, LSC and γ-ray spectrometry). A template was prepared for submission of results from each laboratory. This included the activity levels measured, the uncertainty budget, the measurement techniques used, details of any sample preparation and, where relevant, isotopic ratio values. The details submitted through the template forms the basis of data analysis and the production of an interlaboratory comparison report, which is in progress. The report will provide a comprehensive overview of the advantages and limitations of different mass spectrometric techniques for measurement of the same starting materials, as well as a comparison to decay counting techniques. 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 these techniques.

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

In WP2, SI traceable high precision methods were developed for the determination of the isotope ratio across the periodic table, covering the measurement of both radioactive and stable species in environmental matrices, using seawater as the liquid model. The method development process included both manual and automated procedures for isolating analytes from the sample matrix. It also involved assessing various calibration strategies, applying corrections for instrumental isotope fractionation and establishing comprehensive uncertainty budgets. A range of analytical techniques, spanning SC-ICP-MS and MC-ICP-MS, ICP-SFMS, ICP-QMS, and ICP-MS/MS, were employed and systematically compared for performance.

Development of SI traceable methods for determination of isotope ratios of Li, B, Cr, Cd, Ni, Sb, Pb, U by MC-ICP-MS and SC-ICP-MS

Today, many laboratories with limited or no prior experience in mass spectrometry routinely produce isotope ratio data using ICP-MS systems and so the availability and use of well-characterised IRMs are essential. IRMs play a critical role in ensuring the reliability and comparability of results by supporting robust method validation, quality control, and instrument calibration and so the availability of accessible, traceable, and matrix-matched reference materials becomes increasingly important to uphold analytical accuracy and confidence (Vogl and Pritzkov, 2010).

At the start of the project an extensive literature and market research was done on the availability of IRMs and was listed in Table 1. Non-radioactive species are included for completeness.

Table 1: Compilation of IRMs for Li, B, Cr, Cd, Ni, Sb, Pb and U

Element	**Reference material**	**Isotope ratio values with expanded uncertainty, $k = 2$**
Li	LSVEC	$n(^{6}\text{Li})/n(^{7}\text{Li}) = 0.08215(23)$
B	BAM-AE123	$n(^{11}\text{B})/n(^{10}\text{B}) = 4.042(6)$
Cr	NIST SRM 979	$n(^{53}\text{Cr})/n(^{52}\text{Cr}) = 0.11339(15)$
Ni	NIST SRM 3136	$n(^{60}\text{Ni})/n(^{58}\text{Ni}) = 0.3854(30)$
Cd	BAM-I012	$n(^{114}\text{Cd})/n(^{111}\text{Cd}) = 2.2437(7)$
Sb[†]	BAM inhouse standard NRC candidate material	$n(^{123}\text{Sb})/n(^{121}\text{Sb}) = 0.7479(11)$

[†] For Sb, no isotopic CRM is available. Three candidate materials were chosen to be used within MetroPOEM. Currently, IUPAC tabulated values must be used for the isotope ratio (Meija *et al.*, 2016). New absolute isotope ratios can be provided only once suitable calibration strategies have been selected and calibrated measurements have been carried out.

Element	**Reference material**	**Isotope ratio values with expanded uncertainty, $k = 2$**
Pb	NIST SRM 981	$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb}) = 0.059042(37)$ $n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb}) = 0.91464(33)$ $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb}) = 2.1681(8)$
	NIST SRM 983	$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb}) = 0.000371(20)$ $n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb}) = 0.071201(40)$; $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb}) = 0.013619(24)$
U	IRMM 184	$n(^{234}\mathrm{U})/n(^{238}\mathrm{U}) = 0.000053196(16)$ $n(^{235}\mathrm{U})/n(^{238}\mathrm{U}) = 0.0072631(11)$ $n(^{236}\mathrm{U})/n(^{238}\mathrm{U}) = 0.00000012410(96)$
	NBL CRM 145	$n(^{234}\mathrm{U})/n(^{238}\mathrm{U}) = 0.000052841(82)$ $n(^{235}\mathrm{U})/n(^{238}\mathrm{U}) = 0.0072543(40)$

Different calibration approaches for isotope ratio measurements of the elements, such as internal and/or external corrections, the mass bias regression model, and isotope mixtures, using these reference materials are being evaluated and compared for accuracy and precision.

A range of instrumental techniques are employed, including MC-ICP-MS, ICP-SFMS, ICP-QMS, and ICP-MS/MS. The performance of these techniques was assessed and compared in terms of accuracy and precision.

Development of analyte separation methods for high precision analysis

To obtain accurate and precise isotopic ratios across the periodic table (including radioactive species) for environmental samples, proper sample preparation is essential. Depending on the type of the sample, there may be a pretreatment step needed. For solid samples, it consists of a digestion or extraction, while for liquids, a preconcentration step is usually needed. This is followed by a separation step to isolate the element of interest from the sample matrix. Finally, the determination of the isotope ratios by measurement of the isotope responses and correction for instrumental isotopic fractionation. Automated isolation methods are also being developed using seaFAST (Ebeling *et al.*, 2022; Vassileva *et al.*, 2016; Zhu *et al.*, 20124) and prepFAST systems (Retzman *et al.*, 2017; Retzman *et al.*, 2025; Zimmermann *et al.*, 2019).

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

To achieve traceability of measurement data to national and international measurement standards, all published isotope ratio data should be rigorously corrected for all metrologically significant sources of bias to ensure accuracy and comparability. In addition, each dataset should be accompanied by a comprehensive uncertainty budget that transparently accounts for all significant contributions to measurement uncertainty. This supports data traceability, facilitates interlaboratory comparisons, and upholds the integrity of scientific and regulatory applications relying on isotope measurements.

Instrumental isotope fractionation (IIF) is a significant challenge in mass spectrometry and can lead to biased isotope ratio, particularly in MC-ICP-MS, thus necessitating the development of correction methods. The power, exponential, and Russel laws are all empirical equations usually applied for IIF corrections, although these laws may have some shortcomings. In WP2, current methods are being improved and new approaches developed based on inter-element normalisation and without *a priori* assumptions. One of the key methodologies being improved is the gravimetric isotope-mixture approach, a recognised primary method for determining SI-traceable isotope ratios. A recent advance introduces ion chromatography for quantifying the elemental mass fractions in enriched isotope solutions, significantly streamlining the classical procedure (Flierl *et al.*, 2024); it will be implemented in upcoming CCQM interlaboratory comparisons.

While the gravimetric isotope-mixture method offers exceptional accuracy and traceability, it has limitations for routine application. These include the limited availability of enriched isotopes for many stable elements and the high costs and complexity associated with achieving very low uncertainties. Therefore, complementary methods are being explored. Where the gravimetric approach is impractical and no IRMs exist, IIF modelling is being investigated as an alternative. In addition, the regression method for IIF correction is under active development.

Reference materials

A 250 L sea water sample was taken from the DE-EEZ as a basis for the development of two different CRMs. The raw material was subjected to further processing steps, including spiking with additional elements where necessary based on preliminary analysis and homogenisation.

Part of this candidate reference material was characterised for isotope ratios of Li, B, Cr, Cd, Ni, Sb, Pb and U to generate a reference material with SI traceability for isotope ratios (WP 4). Additionally, ČMI generated ~80×0.5 L liquid reference material aliquots of sea water spiked with U_{nat}, ^{237}Np, ^{239,240}Pu and ^{241}Am (WP 3). A synthetic solid silica-based reference material was produced by sol-gel synthesis at CEA spiked with ^{234,235,236,238}U, ^{237}Np, ^{239,240}Pu and ^{241}Am, as well as ~10 kg of an inactive material for testing dissolution procedures (WP 3). The preparation and homogeneity testing of both radioactive reference materials are separately described (Chambon *et al.*, in press).

These materials were characterised by applying the requirements of ISO 17034, either through measurement by a metrological laboratory, by the mass of each starting solution used, or by interlaboratory studies between the project partners, using techniques developed in the project.

Work Package 4: Development of SI traceable certified reference material

This work package is dedicated to preparation and certification of a reference material in MetroPOEM for the isotope ratios of B, Li, Cr, Ni, Cd, Sb, Pb, and U isotope values. The parameters aimed to be certified in the project for stable elements, and their corresponding concentrations are given in Table 2. For B, Li and U no spiking was necessary, but the other elements were spiked to have final concentrations adequate for certification. The production process of the reference material encompasses collection, processing, certification measurements which include stability, homogeneity and characterisation measurements and finally the value assignment. The reference material is produced by applying the requirements of ISO 17034 (ISO, 2016).

Table 2: Parameters have been measured and certified in the seawater candidate reference material for B, Li, Ni, Cd, Pb, and U. For Cr and Sb, the certification will follow later.

Element	**Measurand**
B	$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$
Li	$n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$
Cr	$n(^{53}\mathrm{Cr})/n(^{52}\mathrm{Cr})$
Ni	$n(^{60}\mathrm{Ni})/n(^{58}\mathrm{Ni})$
Cd	$n(^{114}\mathrm{Cd})/n(^{111}\mathrm{Cd})$ $n(^{113}\mathrm{Cd})/n(^{111}\mathrm{Cd})$
Pb	$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$
Sb	$n(^{123}\mathrm{Sb})/n(^{121}\mathrm{Sb})$
U	$n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$

Collecting, processing and bottling of seawater material

The sea water sample was collected from the North Sea 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 shown in Figure 1.

The water sample was collected into precleaned 25 L carboys using the trace-metal free PVDF clean seawater inlet system. The sample was directly filtered into the carboys using precleaned trace-metal free filter cartridges (Pall AcroPak 1500 0.8/0.2 µm). A total of 250 L seawater was collected from at a depth of 5 m below sea level and then acidified using HNO_3 that had been sub-boiled distilled twice to stabilise the material. The carboys were cleaned by flushing with deionised water and 1% acid solutions several times. At the sampling site, before collecting the sample, each carboy was rinsed three times with ~1 L of seawater. After filling the carboys, the caps were closed and sealed individually in clean PE bags after rinsing the outside with MilliQ pure water to prevent contamination and stored at 4°C until preliminary analysis was carried out.

Preliminary analyses were carried out at Hereon laboratories by subsampling 50 mL aliquots from each carboy under cleanroom conditions. The purpose of the preliminary analysis, conducted using SeaFAST-ICP-MS/MS (Agilent 8900 QQQ) in the He/H_2 mixed gas mode, was to determine trace elemental content was fit for purpose (Ebeling *et al.*, 2022). After analyses, half of the total collected material was transferred to TÜBİTAK UME for further processing. Since the levels for some of the target elements were found to be very low in the 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. After spiking with adequate amounts, approximately 120 L of seawater was transferred into a 120 L HDPE tank and the material was mixed for 4 hours. The material was then filtered through 0.8/0.2 µm filters as before and manually dispensed into individual bottles. A total of 470 bottles, each containing 250 mL sea-water material, were prepared for certification. All the steps in processing of the material, including spiking, homogenisation, and filling into bottles, were carried out in an ISO Class 6 Clean Chemistry Laboratory at TÜBİTAK UME (Figure 2).

The entire batch of the reference material units were sent to the γ-ray irradiation facility at TÜBİTAK UME and were sterilised using a total exposure of 25 kGy.

Homogeneity and stability tests for seawater reference material

According to ISO 17034, the reference material producer should ensure material stability and homogeneity, and should provide objective evidence for both. In this project, ISO 33405 (ISO, 2024) was used for the assessment of homogeneity, short-term stability, and long-term stability. In the long-term stability (LTS) test, an isochronous design (for example: Lamberty *et al.*, 1998) was applied for testing the stability of the material at 22 °C. The stability of samples was tested over 4 time periods: 3, 6, 9 and 12 months. The temperature 4 °C served as reference temperature and taken as the 0^{th} time point. Since the measurements for each parameter takes a long time, requires specific sample preparation steps, and is carried out by different partners, separate sets of samples were reserved for each parameter and sent to the participating laboratories at the end of the testing period. The short-term stability (STS) study, to assess the stability of the material during transportation to the end users, was carried out at 45 °C. Two bottles of the material were subjected to the test temperature for 3 weeks and then transferred to the reference temperature to be measured isochronously with the LTS samples. LTS and STS samples, together with the homogeneity samples for each parameter, were measured by the same project partners at the same time as required in an isochronous design. Stability and homogeneity measurements are still in progress.

Characterisation of seawater reference material

The certified values of a reference material can be assigned after carrying out characterisation studies. One of the characterisation approaches is the determination of a certified value by an interlaboratory study among competent laboratories if a consensus value is obtained. In MetroPOEM, this approach was chosen to characterise the seawater reference materials. In addition to the project partners, other laboratories experienced with isotopic measurements were also invited for the characterisation measurements. Partner laboratories were asked to indicate the parameters they would like to measure. A characterisation study protocol was also sent to those laboratories. Together with external participation, there were 14 laboratories who participated in this characterisation study. Two units of samples were shipped to each participating laboratory unless they requested more samples for their measurements.

Work Package 3: Development of radioactive reference materials

To prepare the two radioactive reference materials (liquid and solid), four standard solutions of a mixture of U isotopes, of a mixture of Pu isotopes, of ^{237}Np, and of ^{241}Am were first measured at the NPL and the CEA. These solutions were then mixed to obtain a 4 radionuclide (4RN) mixture, which was also characterised. Eventually, the 4RN mixture was used to spike a matrix, seawater for the liquid candidate reference material and a mixture of silica and liquid precursors for the solid candidate reference material shown in Figure 3 (Chambon *et al.*, in press).

After thoroughly mixing, the liquid candidate reference material was bottled and sent to 15 partners, for an interlaboratory comparison. This reference material is representative of slightly contaminated seawaters. For the solid material, the silica precursors and the radioactive solutions were thoroughly mixed as a liquid and the reaction medium underwent solidification after a few days. This solid was then milled to yield a powder, which models a slightly contaminated sand (Chambon *et al.*, in press). Samples of 100 g of solid reference material were sent to 15 partners of a second interlaboratory comparison.

The assigned values of both reference materials were determined by direct measurement of the two candidate RMs by two metrological laboratories, the CEA and the NPL, at the same time as homogeneity and stability studies. Furthermore, they were also determined by two gravimetric methods by using either the characteristics of the four standard solutions or the characteristics of the 4RN spiking mixture, as well as the corresponding dilution factors.

In the intercomparisons, partners used their own instruments and preparation techniques, to evaluate the content of ^{235}U, ^{236}U, ^{238}U, ^{237}Np, ^{239}Pu, ^{240}Pu, and ^{241}Am as well as the ^{235}U:^{238}U, ^{236}U:^{238}U, ^{239}Pu:^{240}Pu isotopic ratios. Radiometric techniques such as γ-ray or α-particle spectrometry and mass spectrometry were used where appropriate.

Discussion

The work to date on MetroPOEM contributes to bridge the traceability gap between radioactivity and mass-based measurement of priority pollutants, through measurement of stable and radioactive pollutants. These measurements are achieved using a range of mass spectrometric techniques; harmonised methods are being developed that will help end users with current and planned ambitions for measurements using these techniques. For long-lived radiogenic isotopes, analytical procedures, including analyte separation methods and instrumental mass fractionation techniques, have been investigated, which will be taken forward for reference material measurement. Solid and liquid materials containing priority pollutants have been developed and are being measured by participating laboratories, leading to further reports on the performance of different mass spectrometry designs that will be valuable to end users. These will be delivered as:

- Two interlaboratory comparison reports describing and comparing the measurement of:
    (i) traceable low-level radioactive standards (^{90}Sr, ^{237}Np, ^{234}U, ^{236}U, U_{nat}, ^{239}Pu, ^{240}Pu, ^{241}Am, and ^{239,240}Pu) and
    (ii) seawater and silica-based reference materials (^{235}U, ^{236}U, ^{238}U, ^{237}Np, ^{239}Pu, ^{240}Pu, and ^{241}Am)

  by different types of mass spectrometers and methods, including describing detection limits, sample preparation requirements, sample introduction methods, total procedural time, and uncertainty budgets.
- Two Good Practice Guides on the use of mass spectrometry for:

    (i) low-level radioactive pollutants detection and
    (ii) on sample processing, treatment, uncertainty budgets, and the quantification of mass bias.
- Two reports describing the development of:
    (i) one aqueous certified reference material that is certified for the same stable polluting elements with lowest possible uncertainties, and
    (ii) measurement methods for isotope ratios that are traceable to the SI and summarising the advantages/disadvantages of applying them on more commonly available techniques by providing suitable operating procedures focusing on stable polluting elements.

These documents will be freely available by the end of the project (September 2025) from the project website (https://www.npl.co.uk/euramet/metropoem); the website will be maintained by NPL beyond the end of the project.

A report, describing two radioactive reference materials, developed and shipped to partners for their radioactive content characterisation has already been published on the project website.

Conclusion

Mass spectrometry is increasingly being used for the measurement of medium- and long-lived radionuclides as a rapid complement to radiometric techniques. Additionally, mass spectrometric techniques of low-level stable pollutants measurements are continually being tested for their isotope ratio precision. In both cases, as the numbers of end users and publications increase, it is essential that traceability of priority pollutant measurements by mass spectrometry are supported by underpinning traceable standards and reference materials.

The MetroPOEM consortium provides a firm platform to achieve these goals, utilising specialist facilities at NMIs to obtain starting materials, develop, and test standards and reference materials in line with international standards, containing priority pollutants at relevant levels for end users. This provides the starting point for a network of mass spectrometry users for pollutant measurement from which best practices can be continually improved.

Project outcomes also support standards and metrology organisations, including BIPM (particularly the CCRI(II) task group on mass spectrometry (BIPM, 2025)), ISO (including Technical Committee 147/subcommittee 3 on Radioactivity Measurements (ISO, 2025) and the ISO/REMCO Committee on reference materials), and CEN (TC 230 water quality, TC 264 Air quality, TC 444 characterisation of solid matrices).

The outcomes of the project will improve confidence in measurement for areas including nuclear waste characterisation, environmental monitoring, and forensic studies determining the source of contamination, especially critical for decision-making organisations. This will contribute to the continued advance of mass spectrometric techniques, improving measurement capabilities for end users with regards to the number of pollutants measurable, the detection limits achievable, and improved pollutant monitoring.

Disclaimer

Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation by any of the partner laboratories, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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