# Publishable Summary for 21GRD09 MetroPOEM
# Metrology for the harmonisation of measurements of environmental pollutants in Europe

## Overview

European Green Deal's ambition for zero pollution requires the development of highly sensitive techniques to detect ultra-low amounts of pollutants and to determine their isotope ratios. Mass spectrometry is a key method for determination of non-radioactive polluting elements and is of increasing importance for long-lived radionuclides. This project will bridge the gap between both methods and will establish new tools for tracing pollutants. Measurement uncertainties and detection limits will be significantly reduced using newly developed reference materials and SI-traceable measurement procedures with an immediate impact for tracking pollution sources by commonly available mass spectrometers.

## Need

This project supports the strategies described by the upcoming European Metrology Network (EMN) on Pollution Monitoring (POLMO) and the established EMN on Radiation Protection (supporting the Basic Safety Standards directive). According to their strategies, there is a strong need to improve data quality for monitoring and reporting pollution in the air, water, and soil. In addition, the lack of suitable traceability chains and appropriate quality control compromises the comparability and robustness of measurements.

To detect radioactive isotopes and stable polluting elements in the environment, fast, sensitive and inexpensive analytical procedures are needed. Mass spectrometry techniques have a great potential to address this requirement. Despite the increasing application of single collector ICP-MS (Inductively Coupled Plasma Mass Spectrometry), this potential cannot be fully realised unless techniques can be validated with traceable multi-element reference materials. However, multi-element certified reference materials are usually not available and even single-element certified reference materials are limited to very few elements. Nevertheless, these reference materials are urgently needed to calibrate mass spectrometric measurements, due to mass bias effects occurring during the measurements in mass spectrometers.

The orientation document, issued by EURAMET´s Ionising Radiation Technical Committee and the EMN on Radiation Protection, clearly described a metrological need for "*traceability of radionuclide concentration measurements in the environment*". This topic refers to the classification of the Green Deal as "*a zero-pollution ambition for a toxic-free environment'*". There is a need to increase the use of modern mass spectrometric techniques for measurements of both radioactive and non-radioactive pollutants in monitoring labs and beyond. However, this will require increased access to certified reference materials traceable to the SI.

## Objectives

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:

1. To establish and compare the selectivity and detection limits of different types of mass spectrometers (e.g., AMS, HR-ICP-MS, ICP-MS/MS, ICP-QMS, MC-ICP-MS, SIMS, SNMS, TIMS) for selected radioactive pollutants (e.g., U, Np, Pu, Am) using isotope reference materials



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European Partnership Co-funded by the European Union

and/or 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 or environmental regulations.

2. 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 stable polluting elements (e.g., Li, B, Cr, Cd, Ni, Sb, Pb, U). To produce recommendations for sample processing, treatment, uncertainty budgets, and if feasible, the quantification of the so-called mass bias.
3. To develop two radioactive reference materials with the sample matrix containing radioactive pollutants (e.g., U, Np, Pu, Am) for use in an inter-laboratory comparison employing techniques used in objective 1, which will demonstrate the variations in parameters including detection limits, sample preparation requirements, sample introduction methods, total procedural time, and uncertainty budgets.
4. To implement and validate the methods for isotope ratio measurements established in objective 2 by the development of one aqueous certified reference material (CRM) that is 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.
5. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (e.g., accredited laboratories), standards developing organisations and international organisations (JRC, CIPM CCs [CCQM-IRWG, CCQM-IAWG, CCRI], IAEA, ICRM) and end users (e.g., environmental monitoring agencies).

**Progress beyond the state of the art and results**

*Measured selectivity and detection limits of different types of mass spectrometers for selected radioactive pollutants using single and mixed activity standard solutions*

Non-radiometric techniques show great potential for the measurement of radioactive pollutants. However, the traceability and validation of the methods are missing. The project will go beyond the state of the art by establishing the capabilities of different mass spectrometry designs, such as:

- Accelerator Mass Spectrometry/Spectrometer (AMS),
- High Resolution Inductively Coupled Plasma Mass Spectrometry/Spectrometer (HR-ICP-MS),
- Inductively Coupled Plasma Tandem Mass Spectrometry/Spectrometer (ICP-MS/MS),
- Inductively Coupled Plasma Quadrupole Mass Spectrometry/Spectrometer (ICP-QMS),
- Multi-Collector Inductively Coupled Plasma Mass Spectrometry/Spectrometer (MC-ICP--MS),
- Secondary-Ion Mass Spectrometry/Spectrometer (SIMS),
- Secondary Neutral Mass Spectrometry/Spectrometer (SNMS) and
- Thermal Ionisation Mass Spectrometry/Spectrometer (TIMS).

This will be achieved by using single and mixed activity standard solutions of actinides ($^{237}$Np, $^{234,235,236,238}$U, $^{239,240}$Pu, $^{241}$Am), accessible by mass spectrometry, at activities relevant to regulatory limits. The focus will be on relative instrument performance concerning current measurement challenges. It aims to establish detection limits at levels below current environmental regulations, reduce isobaric interferences, and compare decay counting techniques. The range of radionuclides chosen is well suited for comparison. This is based on the half-lives (<500 years to >$4\times10^9$ years), the presence of multiple spectral interferences that must be overcome to ensure accurate measurement, and the precise isotopic ratio measurements ($^{239}$Pu/$^{240}$Pu, $^{236}$U/$^{238}$U) for source identification.

*SI-traceable measurement methods for isotope ratios of stable polluting elements*

SI-traceable isotope ratios for Li, Pb, and U as pilot elements with relative measurement uncertainties ($u_{rel}$, of <0.01 %) will be realised. The process is based on the *ab initio* calibration for SI-traceable isotope ratios without any *a priori* assumptions, introduced for Mg as a three-isotope system in 2016. This approach will be expanded to other multi-isotope systems and will set the basis for the certification of the first iRM (e.g., Li) with SI-traceable isotope ratios and $u_{rel}$ ≤0.01 %. For many stable elements, enriched isotopes are not available, or the required uncertainty level does not justify the costs and efforts of applying a gravimetric isotope mixture approach to obtain SI-traceable isotope ratios. For quantitative elemental analysis, and for general isotope ratio applications, less expensive and laborious approaches based on inter-element normalisation will be developed.

*Inter-laboratory comparison with two new reference materials containing radioactive pollutants*

Existing radioactive Reference Materials (RM) and Certified Reference Materials (CRM) adapted to mass spectrometry measurements on environmental samples are limited and often lack relevant parameters, including isotopic ratios. The project will go beyond the state-of-the-art by developing two RMs – liquid and solid – containing the radioactive pollutants U, Np, Pu, Am for use in an inter-laboratory comparison. The project will employ techniques used for the measurement of the activity standards solutions. This will demonstrate the variations in parameters such as detection limits, sample preparation requirements, sample introduction methods, total procedural time, and uncertainty budgets. Eventually, this approach will help characterise the matrix related mass bias. Reference Materials, produced in this project, will be used in future QC measurements.

*Aqueous certified reference material with stable polluting elements (and traces of radioactive pollutants) for the calibration of single-collector ICP-MS*

One certified seawater reference material with clearly defined concentrations at natural levels will be developed for use in the validation of analytical procedures, supporting proficiency testing and quality control in future monitoring campaigns.

**Outcomes and impact**

*Outcomes for industrial and other user communities*

This project will enable and harmonise measurement methods for the detection and characterisation, of both radioactive isotopes and stable polluting elements, in support of the EU Green Deal's aim toward a zero pollution, toxic-free environment. The measurement of the species in this project (Li, B, Cr, Ni, Cd, Sb, Pb, U, Np, Pu and Am) will benefit the users of such data, such as monitoring organisations and the owners of potentially polluting facilities. This project, by providing information to the ICP-MS (of whatever type) measurement community, will allow them to select the most appropriate technology (from AMS, HR-ICP-MS, ICP-MS/MS, ICP-QMS, MC-ICP-MS to single collector ICP-MS) to meet their needs. As a result, users seeking to invest in one of the available ICP-MS based modalities will be able to make informed decisions. The Europe-wide collaboration developed in the project will provide the foundation for future inter-laboratory comparison exercises for the determination of species of interest in a variety of environmental matrices where ICP-MS based techniques offer significant advantages over decay counting. The new RMs developed in this project will address the ongoing need to produce suitable and relevant (in terms of matrices and analytes) RMs that can validate state-of-the-art measurement capabilities.

*Outcomes for the metrology and scientific communities*

The scientific outcome of the proposed research will deliver validated and traceable analytical approaches for the analysis of the concentration of pollutants, as well as determining the source and monitoring any contamination of pollutants through isotope ratio measurements. This will close existing metrological gaps and will lead to a harmonisation of the different methods currently applied for the analysis of isotope ratios to support the investigation of natural environmental processes and anthropogenic impacts.

Combining the expertise in isotope ratio measurements of the Comité Consultatif pour la Quantité de Matière: métrologie en chimie et biologie (CCQM) and radioactivity measurement by the Comité Consultatif des Rayonnements Ionisants (CCRI) will provide new and innovative tools for advancing the application of mass spectrometry for contributing to improved half-life determinations.

*Outcomes for relevant standards*

This project will deliver an improved system of metrology and will establish an infrastructure that directly supports the application of the following EU regulations or EU directives:

- Council Directive 2013/51/Euratom (22 October 2013): requirements for protecting the health of the general public concerning radioactive substances in water intended for human consumption.
- Council Directive 2013/59/Euratom (5 December 2013): basic safety standards for protection against the dangers arising from exposure to ionising radiation; Chapter VIII – Public Exposures.
- Treaty establishing the European Atomic Energy Community, Chapter III – Health Protection, Article 35: Each Member State shall set up the facilities necessary for the permanent control of the level of radioactivity in the atmosphere, water and soil and for controlling compliance with basic standards. The Commission shall have the right of access to such control facilities; it may examine their operation and efficiency.
- EU Regulation 995/2010: the origin of legal timber by, for example, determining the Sr isotope composition.
- EU Regulation 2729/2000, 2220/2004, 2030/2006, 555/2008 and 1169/2011: the provenance of food.
- Directive 2009/29/EC, decision No 406/2009/EC, directive 2009/31/EC: Climate research ($\delta^{11}B$), greenhouse gases (pathways of $\delta^{13}C$), carbon storage (possibly applicable for the geological assessment of Sr and Nd).

By implementing new traceability chains, different methods will be combined in the field of pollution monitoring, which will then lower the detection limits. This will result in better protection of the environment, provide new tools for complex studies in climate observation, support validated data collection of the European Research Centres and enhance the implementation of the ALARA goal expressed in the radiation protection regulation of the EC.

*Longer-term economic, social and environmental impacts*

The integration of highly specialised MS techniques, such as Accelerator Mass Spectrometry/Spectrometer (AMS) and Secondary-Ion Mass Spectrometry/Spectrometer (SIMS), into the project, considerably widens the horizon for environmental monitoring or forensic studies and harmonises these detection methods with more commonly applied ICP-MS methods. The outcomes of the project will contribute to meeting the challenge of achieving highly sensitive and cost-effective pollution control. Using ICP-MS techniques in routine pollution monitoring allows the rapid determination of multiple elemental pollutants (both radioactive and stable) within a single sample. This ability, linked to the automated high sample throughput of ICP-MS systems, allows the capture of more and better sample information from single measurements. These factors will help to make a rapid and detailed mapping of pollutants, within defined areas, relatively straightforward. As a result, remediation strategies can be closely targeted and operated with good resolution. The cost of these activities will be reduced without losing effectiveness.

The development of validated and traceable methods will improve societal confidence in the measurement and quantification of pollutants across many sectors, such as manufacturing, industrial decommissioning and the long-term decommissioning and remediation of aged and disused nuclear sites. Accurate waste classification engenders public confidence and ensures inventories are correct for future infrastructure planning, such as the scale and design of pollutant remediation programmes.

The outputs from the project may be employed in several diverse fields including routine real-time monitoring, emergency response, geological dating and climate change studies through isotopic ratio measurements, and in other activities, such as nuclear forensics, decommissioning non-nuclear industries (such as the oil industry in the North Sea) and radiopharmaceutical facilities, where use is made of long-lived radioactive precursors. The collaboration between European laboratories established in this project is expected to continue beyond the end of the project.

**List of publications**

n/a

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

| Project start date and duration: | 1 October 2022, 36 months | |
|---|---|---|
| Coordinator: Dirk Arnold, PTB | Tel: +49 531 592 6100 | E-mail: Dirk.Arnold@ptb.de |
| Project website address: https://www.npl.co.uk/euramet/metropoem | | |
| Internal Beneficiaries:<br>1. PTB, Germany<br>2. BAM, Germany<br>3. CEA, France<br>4. CMI, Czechia<br>5. JSI, Slovenia<br>6. LNE, France<br>7. STUK, Finland<br>8. TUBITAK, Türkiye | External Beneficiaries:<br>9. AU, Denmark<br>10. DTU, Denmark<br>11. Hereon, Germany<br>12. HZDR, Germany<br>13. IFE, Norway<br>14. IFIN-HH, Romania<br>15. LUH, Germany<br>16. MUL, Austria<br>17. NMBU, Norway<br>18. UH, Finland<br>19. VINS, Serbia | Unfunded Beneficiaries: |
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