

## **Title: Isotope ratios as a tool for environment metrology**

### **Abstract**

Isotope ratio measurements provide valuable information and are a key parameter in many research fields including meteorology/climatology, geochemistry, oceanography, environmental studies and material provenance determination. The outcomes of isotope ratio measurements are also applied across a wide range of environmental sectors from strategic decision making for climate change policies to the identification of pollutants and raw materials, and can also be used for the attribution of illicit use of nuclear materials and to support food safety and use policies. Due to wide use of isotope ratios and the nature of these environmental applications it is essential that such measurements are traceable and that the uncertainties stated can be justified, therefore new methods and reference materials need to be developed to support this.

### **Keywords**

Isotope ratio measurement, radioactive isotopes, mass-spectrometry, ICP-MS, Lithium, Boron, Strontium, Lead, Uranium.

### **Background to the Metrological Challenges**

At present, no standardised measurement procedures exist for the accurate and comparable measurement of selected isotopes needed to support their widespread application in environmental research and EU environmental Directives such as Water Framework Directive (WFD) 2000/60/EC or Marine Strategy Framework Directive (MSFD) 2008/56/EC. In particular, such measurements are needed for the determination of the provenance of contaminants via their isotopic ratios (e.g. Lithium (Li), Boron (B), Strontium (Sr), Lead (Pb) and Uranium (U)) to trace the sources of such pollutants and support environmental controls.

Isotope ratio measurements are mainly, but not exclusively – made by mass spectrometry techniques. Thermal ionisation mass spectrometry is traceable, extremely effective and accurate for the measurement of isotope ratios, however the technique isn't well suited to high throughput and cannot accomplish the multi-element analysis that inductively coupled plasma mass spectrometry (ICP-MS) excels at. ICP-MS is a widely used measurement technique that is particularly suited to high sample throughput, however instrumental isotopic fractionation (commonly called mass bias) is a key issue for ICP-MS, especially when different sample matrices are considered and therefore new traceability and calibration strategies are required.

Despite the importance of isotope ratios measurements and considerable efforts in the past, SI traceable measurements remain a highly demanding task, especially for ICP-MS. Thus, the International Committee for Weights and Measures (CIPM) Consultative Committee for the Amount of Substance (CCQM) has requested a '...traceability exception related to delta scale isotope ratio measurements...'. Currently, such delta scale measurements are predominantly based on arbitrarily selected materials without SI-traceable isotopic composition. Moreover, currently used certified reference materials (CRMs) are being rapidly depleted and lack data for a number of elements (e.g. Li, and Sr). Therefore, new and replacement CRMs for isotope ratio measurements are urgently needed.

### **Objectives**

Proposers should address the objectives stated below, which are based on the PRT submissions. Proposers may identify amendments to the objectives or choose to address a subset of them in order to maximise the overall impact, or address budgetary or scientific / technical constraints, but the reasons for this should be clearly stated in the protocol.

The JRP shall focus on the traceable measurement and characterisation of isotope ratios as a tool for environment metrology.

The specific objectives are

1. To develop traceable methods and uncertainty budgets for isotope ratios using multi-collector ICP-MS and apply these methods on single collector ICP-MS by developing operating procedures for a range of naturally occurring elements, but concentrating on Li, B, Sr, Pb, and U. This should include recommendations for: sample processing and treatment; quantification of mass bias in measurements for  ${}^7\text{Li}/{}^6\text{Li}$ ,  ${}^{11}\text{B}/{}^{10}\text{B}$ ,  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ,  ${}^{207}\text{Pb}/{}^{204}\text{Pb}$  and  ${}^{238}\text{U}/{}^{235}\text{U}$ .
2. To implement the methods from objective 1 by developing an aqueous CRM for  ${}^7\text{Li}/{}^6\text{Li}$ ,  ${}^{11}\text{B}/{}^{10}\text{B}$ ,  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ,  ${}^{207}\text{Pb}/{}^{204}\text{Pb}$  and  ${}^{238}\text{U}/{}^{235}\text{U}$  with low uncertainty (< 2 ‰ for Li and B and < 0.5 ‰ for Sr, Pb and U) using multi-collector instruments.
3. To improve the accuracy and reliability of heavy element isotope ratio measurements by:
  - a. improving the half-life data of  ${}^{231}\text{Pa}$ ,  ${}^{230}\text{Th}$ ,  ${}^{238}\text{U}$  with absolute activity determinations and mass measurements using ICP-MS
  - b. development of CRMs with traceable  ${}^{231}\text{Pa}/{}^{235}\text{U}$  and  ${}^{230}\text{Th}/{}^{234}\text{U}/{}^{238}\text{U}$  mass ratios
  - c. determining the uncertainty budgets for these measurements.
4. To facilitate the take up of the technology and measurement infrastructure developed in the project (in particular the CRM developed in objective 2) by the measurement supply chain (accredited laboratories, instrument manufacturers), standards developing organisations (such as those linked to the WFD 2000/60/EC, MSFD 2008/56/EC, the Promotion of the use of biofuels and other renewable fuels for transport Directive 2003/30/EC, the renewable energy Directive 2009/28/EC, fuel quality Directive 2009/30/EC, Emissions Trading Directive 2009/29/EC and Geological Storage of Carbon Dioxide Directive 2009/31/EC) and end users (such as environmental monitoring and regulation bodies e.g. International Atomic Energy Agency (IAEA), World Meteorological Organisation (WMO), and International Association of Geoanalysts (IAG)).

These objectives will require large-scale approaches that are beyond the capabilities of single National Metrology Institutes and Designated Institutes. To enhance the impact of the research, the involvement of the appropriate user community such as industry, standardisation and regulatory bodies is strongly recommended, both prior to and during methodology development.

Proposers should establish the current state of the art, and explain how their proposed research goes beyond this.

EURAMET expects the average EU Contribution for the selected JRPs in this TP to be 2.0 M€, and has defined an upper limit of 2.3 M€ for this project.

EURAMET also expects the EU Contribution to the external funded partners to not exceed 35 % of the total EU Contribution to the project.

Any industrial partners that will receive significant benefit from the results of the proposed project are expected to be unfunded partners.

## Potential Impact

Proposals must demonstrate adequate and appropriate participation/links to the “end user” community, describing how the project partners will engage with relevant communities during the project to facilitate knowledge transfer and accelerate the uptake of project outputs. Evidence of support from the “end user” community (e.g. letters of support) is also encouraged.

You should detail how your JRP results are going to:

- Address the SRT objectives and deliver solutions to the documented needs,
- Feed into the development of urgent documentary standards through appropriate standards bodies,
- Transfer knowledge to the meteorology/climatology, geochemistry, oceanography, material sciences and environmental sectors.

You should detail other impacts of your proposed JRP as specified in the document “Guide 4: Writing Joint Research Projects (JRPs)”

You should also detail how your approach to realising the objectives will further the aim of EMPIR to develop a coherent approach at the European level in the field of metrology and include the best available contributions from across the metrology community. Specifically the opportunities for:

- improvement of the efficiency of use of available resources to better meet metrological needs and to assure the traceability of national standards
- the metrology capacity of EURAMET Member States whose metrology programmes are at an early stage of development to be increased
- organisations other than NMIs and DIs to be involved in the work

### **Time-scale**

The project should be of up to 3 years duration.