

## Title: Traceability for mercury measurements

### Abstract

Pollution by mercury is a major global, regional and national challenge as it threatens human health and the environment. The main threat is to pregnant women, babies and marine mammals that eat contaminated fish. In Europe, member states are obliged to terminate existing discharge, emissions and losses of Hg. Mercury is reactive, difficult to store and handle, and extremely difficult to measure as it easily disappears/adsorbs in e.g. sample containers even before the measurement analysis has been carried out. A calibration infrastructure needs to be realised and implemented, a metrological in-line measurement method developed, a speciation analysis performed - including the development and metrological validation of multi-collector ICP-MS methods to determine if isotopic signatures can be assigned to different sources of mercury, an understanding of mercury migration and transformation artefacts (e.g. using historical samples from environmental specimen banks) developed, and traceable measurements for emerging requirements in mercury science provided. This will support the requirements of national and international legislation (e.g. the UNEP Minamata Convention on Mercury), which aims at controlling mercury emissions and releases.

### Conformity with the Work Programme

This Call for JRPs conforms to the EMRP Outline 2008, section on “Grand Challenges” related to Energy and Environment on pages 8, 9 and 24.

### Keywords

Mercury, metals, speciation, emission, fuels, traceability, comparability, isotope ratio measurements, sensors, compact fluorescent lamps (CFLs), mass independent fractionation, mass dependent fractionation, MC ICP-MS, environmental specimen banks

### Background to the Metrological Challenges

Due to its toxicity, the use of mercury is being phased out and/or limited to less than 1000 mg/kg in products. Mercury is a global contaminant that enters the environment from natural sources, historical burden in soil and sediments, and from industry. Today the main source is likely from coal-fired power plants, but a scientifically litigable proof is missing. In the UNEP 2013 document “Global Mercury Assessment” the global emissions to air from anthropogenic sources were estimated at 1960 tonnes (2010) with a large uncertainty of 1010 to 4070 tonnes. Mercury is also entering the environment by other means in unknown amounts.

The Group on Earth Observations (GEO) is aiming to develop a global observation system for mercury in support of the goals of GEOSS etc. While the WMO's Global Atmosphere Watch (GAW) have established data centres and quality control programs to enhance integration of air quality measurements from different national and regional networks. Similarly, the International Global Atmospheric Chemistry project has strongly endorsed the need for international exchange of calibration standards.

Some NMIs have developed capabilities for the measurement of mercury, but this does not extend to environmental measurement. This capability has been limited to providing non-matrix specific mono-elemental mercury reference materials. Consequently, at the moment it is not possible to defensibly assess mercury at relevant concentrations in European directives (Directive 2004/107/EC, Art. 3; Directive 2010/75/EU), because of a lack of underpinning traceability and validated methodologies for low concentrations and for different mercury species. Also the written standards EN-15852 and EN-15853 and the US EPA's methods 30A and 30B need a metrological backbone. The Directive 2008/105/EC requires that all Member States monitor the environmental concentrations of Priority Hazardous Substances (PHS) and report to the EC whether national waters meet Environmental Quality Standards (EQS), or not. The EQS

for mercury will be measured in prey tissue to account for food web magnification. European Member States are legally obliged to progressively reduce discharges, emissions and losses of PHS to zero within 20 years. Mercury levels in water bodies across Europe exceed the EQS and are unlikely to meet targets. A number of mercury-related standardisation mandates have been prepared M/036, M/360 and M/232 [1, 2, 3] to address these issues.

Mercury pollution has traditionally been monitored by measuring the concentrations of Hg species in inorganic and organic matrices. MC-ICPMS now allows small differences in Hg isotope abundances to be measured in environmental abiotic and biotic matrices. Also, the direct identification of different isotopic signatures of different Hg species is now possible within the same sample (these may have a completely different biogeochemistry history). This technique can help to track the transport and fate of mercury in the environment. Various geologic and environmental matrices are being characterised to inventory the isotope signatures of different source materials, and to document the ranges in Hg mass dependent fractionation (MDF) and mass independent fractionation (MIDF) in materials around the globe. Gradients in Hg concentrations and isotope signatures have been shown to be associated with Hg point sources. To improve the utility of isotopic source apportionment the data inventories of Hg MDF and MIDF values need to be expanded and improved for a variety of sample types and locations. Such robust, defensible and traceable measurements of mercury are needed to underpin the global effort to reduce the concentration of mercury in the environment, meet the obligations of legislation and to protect human health.

Highly reliable environmental samples are needed that document different contamination levels and patterns. There are 14 Environmental specimen banks (ESBs) in Europe, which contain cryo-archived samples from marine, limnic and terrestrial environments that provide authentic records of industrial contamination of air, soil and water. The mercury levels recorded in these samples will enable high quality assessment and metrological validation.

## Scientific and Technological 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 JRP-Protocol.

The JRP shall focus on the traceable measurement and characterisation of mercury.

The specific objectives are

1. To realise and implement a calibration infrastructure, built upon traceable primary standards, enabling the defensible and traceable assessment of mercury thresholds specified in European legislation and as part of the global mercury observing system.
2. To develop a metrological in-line measurement method for continuous and semi-continuous Hg<sup>0</sup> and Hg(II) measurement in (harsh) matrices like stationary source emissions or liquid media, including the use of sensor technology.
3. To perform a speciation analysis of mercury across all environmental compartments (e.g. water, soil, flue gases, biogas, biota and solids), aiming at minimising species interconversion post-sampling. This should include the development and metrological validation of multi-collector ICP-MS methods for measuring mass dependent fractionation and mass independent fractionation of mercury isotopes. It should then be determined if isotopic signatures can be assigned to different sources of mercury.
4. To understand mercury migration and transformation artefacts associated with e.g. changing environmental conditions (i.e. historical samples from environmental specimen banks should be used), in order to develop robust methods for (representative) sampling, filtration, preservation and storage.
5. To provide traceable measurements for emerging requirements in mercury science such as the evaluation of mercury concentrations in indoor air from the use of mercury containing compact fluorescent lamps.

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 R&D work, the involvement of the user community such as industry, and standardisation and regulatory bodies, as appropriate, is strongly recommended.

Proposers should establish the current state of the art, and explain how their proposed project goes beyond this and EMRP JRP ENV02 (PartEmission) 'Emerging requirements for measuring pollutants from automotive exhaust emissions' with regards to the measurement of mercury.

EURAMET expects the average size of JRPs in this call to be between 3.0 to 3.5 M€, and has defined an upper limit of 5 M€ for any project. The available budget for integral Research Excellence Grants is 30 months of effort.

## Potential Impact

Proposals must demonstrate adequate and appropriate participation/links to the "end user" community. This may be through the inclusion of unfunded JRP partners or collaborators, or by including links to industrial/policy advisory committees, standards committees or other bodies. Evidence of support from the "end user" community (eg letters of support) is encouraged.

You should detail how your JRP results are going to:

- feed into the development of urgent documentary standards through appropriate standards bodies
- transfer knowledge to enable the traceable measurement and characterisation of mercury

You should detail other impacts of your proposed JRP as detailed in the document "Guide 4: Writing a Joint Research Project"

You should also detail how your approach to realising the objectives will further the aim of the EMRP to develop a coherent approach at the European level in the field of metrology and includes 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 Member States and countries associated with the Seventh Framework Programme whose metrology programmes are at an early stage of development to be increased
- outside researchers & research organisations other than NMIs and DIs to be involved in the work

## Time-scale

The project should be of up to 3 years duration.

## Additional information

The references were provided by PRT submitters; proposers should therefore establish the relevance of any references.

- [1] EC Mandate M/036, Standardisation mandate to CEN for a manual reference method for the calibration of automated measurement systems for total mercury emissions into the air and main performance characteristics of the automated measurement systems.
- [2] EC Mandate M/360, Standardisation mandate to CEN for standard measuring methods for the determination of total gaseous mercury in ambient air and the total deposition of mercury.
- [3] EC Mandate M/232, Standardisation mandate to CEN for the determination of the total emission of some heavy metals and metalloids to the air.