EMPIR Call 2019 – Energy, Environment, Normative and Research Potential

Selected Research Topic number: **SRT-n07**
Version: 1.0

Title: Metrology for traceable protocols for elemental and oxidised mercury concentrations

Abstract

Mercury is one of the top ten chemicals of major public health concern and a substance which disperses into and remains in ecosystems for decades, causing severe illness and intellectual impairment to exposed populations. With the signing of the UNEP Minamata Convention in 2013 and its ratification in 2017, the world's governments are committed to reducing mercury emissions from the energy and other industrial sectors. Research is needed to develop the required metrologically traceable certification protocols for elemental mercury (Hg^0) and oxidised mercury (Hg^{2+}) generators. Such protocols will allow for the generation of stable and comparable data to assess the effectiveness of protective measures undertaken under national and international legislation and standardisation.

Keywords

Elemental mercury, oxidised mercury, traceability, certification protocols, preconcentration, validation, uncertainty evaluation

Background to the Metrological Challenges

Mercury is a trace component in all fossil fuels. Whereas natural sources such as volcanoes are responsible for about half of the atmospheric mercury emissions, of the human generated half, about 65 % is emitted by stationary combustion. Once it is released into the environment, mercury can circulate through air, land, water and animals for thousands of years. The current levels of mercury in the atmosphere are up to 500 % above pre-industrial levels. Mercury poses one of the greatest current direct threats to human, animal and environmental health across the globe. Robust, defensible and traceable measurements of mercury are essential to underpin global efforts to reduce the concentration of mercury in the environment, meet the obligations of legislation and to protect human health. As such mercury emissions are regulated by the Industrial Emissions Directive (IED) 2010/75/EU, the Air Quality Directive 2004/107/EC, the Waste Incineration Directive 2000/76/EC and the Minamata Convention, a global treaty to protect human health and the environment from the adverse effects of mercury, which entered into force in 2017. At the moment it is not possible to defensibly assess mercury at relevant concentration levels in European directives, because of a lack of underpinning traceability and validated methodologies for low concentrations and for different mercury species. Nevertheless, requirements for traceability of mercury measurements from stationary sources do exist in the IED.

In Europe, traceable methods and calibration standards for Hg^0 are based upon mercury vapour pressure equations that currently differ from each other. This discrepancy is of great concern. Valuable steps to develop measurement methods and primary standards for mercury in the gas phase have been made within the EMRP JRPs ENV02 PartEmission (Emerging requirements for measuring pollutants from automotive exhaust emissions) and ENV51 MeTra (Traceability for mercury measurements). Such primary standards can be used for the direct calibration of Hg^0 analysers and certification of Hg^0 generators used in the field and the indirect calibration or certification via transfer standards. The methods developed considerably strengthen the Hg^0 traceability chain at emission and ambient levels, which is essential to control and assess mercury concentrations in the environment.

Mercury also occurs in oxidised forms in the environment. These forms are reactive and can be transformed into species such as methylmercury, the most toxic mercury species because of its bioaccumulation in aquatic systems. Methylmercury in these systems can accumulate in fish and marine mammals consumed by humans. Within the current EMPIR project 16ENV01 MercOx (Metrology for oxidised mercury), a primary mercury standard is being used to establish a traceable calibration methodology for the most important oxidised mercury-containing species, especially $HgCl_2$. Hg^0 is much easier to generate and more reliable than Hg^{2+} for

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the field calibration of mercury analysers. In Europe, the current quality control regulation only accepts Hg^{2+} generators for the calibration of analysers in the field. A certification protocol for liquid evaporative Hg^{2+} generators is under development within 16ENV01 MercOx to cover higher mercury concentrations present in emission sources, and a feasibility study of the protocol is being carried out. To proceed with the development of a documentary standard, full validation of the protocol must be achieved. Moreover, concentrations of mercury an order of magnitude lower, present in the atmosphere, require different approaches for the preparation of Hg^{2+} sources for calibration purpose. A novel experimental design based on quantitative transformation of Hg^{2+} from a traceable Hg^0 source by a portable cold plasma source seems to be the most promising solution.

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 metrology research necessary to support standardisation in the measurement of elemental and oxidised mercury emissions.

The specific objectives are

1. To develop and validate a traceable certification protocol for elemental mercury (Hg^0) generators used in the field based on (1) direct comparison and (2) indirect comparison with primary standard Hg^0 generators. The validation should include repeatability, reproducibility and uncertainty evaluation of the certification procedures at emission and ambient levels extended to the sub ng/m^3 level.
2. To validate a certification protocol for the certification of oxidised mercury (Hg^{2+}) generators used in the field for low mercury concentrations present in the atmosphere and higher concentrations from emission sources. The validation should include (1) metrological evolution of state-of-the-art dual Hg^0 and Hg^{2+} analytical systems, (2) repeatability, reproducibility and uncertainty evaluation of the certification procedures at representative concentration levels extended to the low ppb level.
3. To organise a performance evaluation to gather data on the characteristics of at least three Hg^0 and Hg^{2+} generators on the market.
4. To support the development of a suitable calibration system for mercury measurements in the atmosphere, as part of the global mercury observing system used to measure the effectiveness of the implementation of the Minamata Convention, by the dissemination of scientific outcomes through guidance documents for accurate field measurement and uncertainty assessment.
5. To facilitate the take up of methods, technology and measurement infrastructure developed in the project by the standards developing organisations (e.g. CEN/TC 264/WG 8 “Mercury Emissions”) and end-users (energy sector, heavy industry).

The proposed research shall be justified by clear reference to the measurement needs within strategic documents published by the relevant Regulatory body or Standards Developing Organisation or by a letter signed by the convenor of the respective TC/WG. EURAMET encourages proposals that include representatives from industry, regulators and standardisation bodies actively participating in the projects. The proposal must name a “Chief Stakeholder”, not a member of the consortium, but a representative of the user community that will benefit from the proposed work. The “Chief Stakeholder” should write a letter of support explaining how their organisation will make use of the outcomes from the research, be consulted regularly by the consortium during the project to ensure that the planned outcomes are still relevant, and be prepared to report to EURAMET on the benefits they have gained from the project.

Proposers should establish the current state of the art, and explain how their proposed research goes beyond this. In particular, proposers should outline the achievements of the EMRP and EMPIR projects ENV02 PartEmission, ENV51 MeTra and 16ENV01 MercOx and how their proposal will build on those.

EURAMET expects the average EU Contribution for the selected JRPs in this TP to be 0.8 M€, and has defined an upper limit of 1.0 M€ for this project.

EURAMET also expects the EU Contribution to the external funded partners to not exceed 30 % of the total EU Contribution across all selected projects in this TP.

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 energy and heavy industrial sector.

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.