Title: Metrology for oxidised mercury

Abstract

Mercury is one of the most toxic metals, and as such it is 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). In addition to its elemental form mercury exists in oxidised forms (Hg (II)), that are reactive and can be transformed into organic mercury species, such as methylmercury, the most toxic organic species and the most prone to bioaccumulation in aquatic systems. Currently, traceable calibration methods only exist for elemental mercury, but are also needed for oxidised mercury species in order to meet the requirements of EU regulation. Methods for measuring oxidised mercury and to accurately compare the total mercury concentration in generated standard elemental and oxidised mercury gases are also needed, as well as, sample transportation methods, traceable reference standards, validated methods for the on-line measurement of mercury in field conditions and a comparison of mercury species inter-conversion.

Keywords

Mercury, oxidised mercury, mercury chloride, speciation, conversion, reference standard, traceability, emission, on-line measurement

Background to the Metrological Challenges

Mercury and its various compounds cause a range of serious health impacts including brain and neurological damage, in particular, compounds containing mercury are more toxic to humans and the environment than elemental mercury. Of these compounds containing mercury, gaseous mercury (II) chloride $HgCl_2$, the primary oxidised form of mercury, which is generated by coal-fired power plants and waste incineration processes, represents a serious environmental concern primarily due to its reactivity and high water solubility. Therefore, it is important to be able to identify and quantify the presence of different forms of oxidised mercury (Hg (II)). It is also important, as these different forms of Hg (II) act as intermediates between elemental and organic compounds of mercury in the environment and can produce the most toxic organic form of mercury, methylmercury.

Gaseous Hg (II) can be formed in the atmosphere through the oxidation of gaseous elemental mercury ((Hg^0)). Gaseous Hg^0 comes from natural sources (~50 %) such as volcanoes and anthropogenic sources such as coal-fired power plants, cement works, steel and gold producing factories and waste incinerators. The atmosphere also contains particulate bound mercury, however, so far, there is only one commercially available instrument that claims to be able to measure all three forms of atmospheric mercury, although the instrument has been shown to underestimate gaseous Hg (II) concentrations by as much as a factor of 2 - 13. Further to this, both bulk and species-specific mercury isotope ratio measurements for airborne samples are still in their infancy, and lack robust sampling and measurement methods, proper estimation of measurement uncertainty and metrological traceability.

Currently, CEN TC264 WG8 on Mercury are developing standard methods for the measurement of mercury in emissions but want to expand this to cover Hg (II) emissions. In order to support this, reliable reference gases need to be developed for Hg (II) with known uncertainties. This is particularly needed for the direct measurement of gaseous $HgCl_2$. At the moment, such Hg (II) species have to be reduced to Hg^0, often using a thermal catalytic process to be quantified. Reference gases, are needed to quantify this conversion as well as to assess the ability to quantitatively transfer $HgCl_2$ through the measurement system. Major challenges also exist during sample transportation as Hg^0 and several Hg (II) species are easily adsorbed on to surfaces.

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 oxidised mercury (Hg (II)).

The specific objectives are

1. To develop traceable calibration methods, based on evaporation, sublimation or oxidation, for the most important Hg (II) species including $HgCl_2$. This should include the measurement of the output of liquid evaporative generators, the development of real-time on-site measurement techniques and transfer standards, or the development of reliable portable reference gas materials and sources.
2. To develop and compare different methods for measuring Hg (II) and to accurately compare the total mercury concentration in standard gas for elemental mercury (Hg^0) and Hg (II)). The methods should include the conversion of mercury species to elemental mercury and/or direct measurement. High accuracy bulk and species-specific (e.g. Hg^0 and Hg (II)) isotope ratio measurements should also be performed to determine mercury migration pathways, its origin and species inter-conversions.
3. To develop sample and conversion transportation methods that use traceable reference standards for elemental and Hg (II). In addition, to compare measurement methods for species inter-conversion including the long term efficiency of the methods and their reliability in different matrices. This should include the validation of conversion methods with new calibration standards meeting the uncertainty requirements of the industrial emissions directive, theoretical approaches for predicting mercury chemistry, and/or compound specific mass spectrometric measurements.
4. To test and validate new and existing methods, using gas standards or generators, for the on-line measurement of mercury in field conditions. This should include the direct measurement of mercury via different conversion and optical detection methods, and/or sorbent traps. Reliable sample conditioning and transportation, and matrix gas effects on different parts of the measurement system should also be investigated.
5. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (accredited laboratories), standards developing organisations (such as CEN/TC264/WG8 and those linked to the IED Directive 2010/75/EU, the Air Quality Directive 2004/107/EC and the Waste Incineration Directive 2000/76/EC) and end users (environmental monitoring and regulation bodies).

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. In particular, proposers should outline the achievements of the EMRP projects ENV02 PartEmission and ENV51 MeTra and how their proposal will build on those.

EURAMET has defined an upper limit of 1.8 M€ for the EU Contribution to 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 environmental 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.