



## Publishable Summary for 19NRM03 SI-Hg Metrology for traceable protocols for elemental and oxidised mercury concentrations

### Overview

Currently, mercury gas generators used in the field are not certified against primary standards and therefore lack traceability. The aim of this project is to develop metrological traceable protocols for the certification of mercury gas generators used in the field. In this way, the project will achieve significant improvements in the comparability and uncertainty of mercury measurement results. The project will develop and validate certification protocols, traceable to SI-units, for the most important mercury species in gas emission sources and in the atmosphere, thereby supporting the standardisation activities of the European Committee for Standardization (CEN).

### Need

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 concentrations are essential to a) underpin global efforts to control and reduce the concentration of mercury in the environment, b) meet the obligations of legislation and c) protect human health. As such, mercury emissions are regulated by the Industrial Emissions Directive (IED) 2010/75/EU, the Air Quality Directive (AQD) 2004/107/EC, the Waste Incineration Directive (WID) 2000/76/EC and the Minamata Convention. Currently, it is not possible to defensibly establish regulatory specifications for mercury concentration levels in European directives, because of a lack of traceable measurement data obtained with validated methodologies for the different mercury species.

Although great efforts have been made in developing primary mercury standards and SI-traceable calibration methods for different mercury species, there are no standardised procedures that ensures the dissemination and uptake of the developed metrological traceability by calibration and testing laboratories and in the field. Scientifically sound certification protocols, to determine the output of elemental mercury ( $Hg^0$ ) and oxidised mercury ( $Hg^{II}$ ) gas generators in the form of formally accepted documentary standards, are of fundamental importance to guarantee the accuracy and comparability of the mercury measurement data in Europe and globally. Furthermore, mercury gas generators certified using SI-traceable standards will provide the traceability and uncertainty needed by calibration and testing laboratories under ISO/IEC 17025:2017 accreditation to demonstrate their conformity in assessments.

European and international standardisation bodies have recognised the importance of standardising methods for measuring mercury in air. This project will meet this need by feeding the output of this research into existing and new documentary standards under development by standards development organisation technical committee CEN/TC264 "Air Quality" WG8 "Mercury Emissions".

### Objectives

The overall goal of this project is to develop protocols for SI-traceable calibration, evaluation and certification of elemental mercury ( $Hg^0$ ) and oxidised mercury ( $Hg^{II}$ ) gas generators used in the field. This research will feed into the standardisation technical committee CEN/TC264/WG8.

The specific objectives of the project are:

1. To develop and validate a protocol for the SI-traceable certification of elemental mercury ( $Hg^0$ ) gas generators used in the field based on (1) direct comparison and (2) indirect comparison with the primary mercury gas standard. The validation will 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 ( $Hg^{II}$ ) gas generators used in the field for low mercury concentrations present in the atmosphere and higher concentrations from

emission sources. The validation will include (1) metrological evaluation of state-of-the-art dual Hg<sup>0</sup> and Hg<sup>II</sup> analytical systems, (2) repeatability, reproducibility and uncertainty evaluation of the certification procedures at representative concentration levels extended to the low ng/m<sup>3</sup> level.

3. To organise a performance evaluation to gather data on the characteristics of at least three Hg<sup>0</sup> and three Hg<sup>II</sup> gas 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 observation 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 protocols, methods, technology and measurement infrastructure developed in the project by the standards developing organisations (e.g. CEN/TC264/WG8 "Mercury Emissions") and end-users (energy sector, instrument manufacturers, atmospheric air monitoring networks and heavy industry).

### **Progress beyond the state of the art**

Within the projects EMRP ENV02 PartEmission and EMRP ENV51 MeTra a primary mercury gas standard, which is traceable to SI-units, has been developed. With this development, the first steps were taken to establish the traceability chain for mercury measurements in air which is essential to control and assess mercury concentrations in the environment. This project will go beyond the state of the art by developing and validating metrologically sound protocols for the certification of mercury gas generators, ensuring a traceability chain from the primary mercury gas standard to measurement data in the field.

In previous project EMPIR 16ENV01 MercOx, the primary mercury gas standard was used to establish a traceable calibration methodology for the most important Hg<sup>II</sup> species. However, essential performance characteristics of Hg<sup>II</sup> gas generators and state-of-the-art dual analysers, preventing SI-traceable measurement results, have not been addressed yet. In this project, the converter efficiency of the analyser used, gas generator selectivity, transportation efficiency of the Hg<sup>II</sup> calibration gas to the analyser and storage and stability of the Hg<sup>II</sup> solution used, will be investigated in depth. Furthermore, the methodology for the certification of liquid evaporative HgCl<sub>2</sub> generators, is described in a protocol in EMPIR 16ENV01 MercOx. To ensure the protocol is applicable for this wider range of Hg<sup>II</sup> gas generators, this project will adjust the EMPIR 16ENV01 MercOx protocol by testing different types of gas generators.

Performance evaluation data, including uncertainties, of mercury gas generators on the market will be obtained. This data is essential for a) establishing a benchmark for equipment, b) understanding performance requirements for the protocols under development, c) encouraging the use of the best available methods for generating Hg<sup>0</sup> and Hg<sup>II</sup> gas mixtures and d) making sure the developed protocols are fit for purpose for equipment routinely used in the field.

### **Results**

*Development and validation of a SI-traceable certification protocol for elemental mercury gas generators used in the field (objective 1)*

Work has been carried out compiling data of the performance characteristics and uncertainty sources of commercially available elemental mercury gas generators used in the field. Little information is available on the performance characteristics of the generators. All the more reason to perform the validation activities described throughout this project. Furthermore, uncertainty calculations have been set up for different types of elemental mercury gas generators.

Experimental approaches have been developed for the certification protocol and to assess the performance characteristics during the validation of the certification protocol. During the validation, the multipoint, bracketing and single point calibration methods will be tested to determine the most suitable approach for the certification of elemental mercury gas generators. Meanwhile the project is developing the first draft of the protocol for the SI-traceable certification of elemental mercury gas generators used in the field.

*Validation of certification protocols for oxidised mercury gas generators used in the field (objective 2)*

In order to fulfil objective 2, the first step done by the project was to compile data about the performance characteristics and uncertainty sources of state-of-the-art dual analytical systems and commercially available oxidised mercury gas generators. Based on the findings a review was written by Lumex about state-of-the-art dual analytical systems, the review is published on the project website ([www.si-hg.eu](http://www.si-hg.eu)). Several systems have been developed able to determine oxidized and elemental mercury in parallel. In the course of these developments, major obstacles in trace analysis of highly reactive chemical compounds have been overcome.

Yet, several problems remain i.e., the tendency of interconversion between mercury species during sampling and analysis, and the evaluation of the efficiency of the converter under different conditions. Another challenge is the qualification of a suitable SI-traceable calibration device for the instruments. Such a device would allow a more comprehensive metrological characterization of the systems, and hence the critical assessment and validation of analytical results produced by these instruments, and finally the comparison with data generated by other research groups with different equipment.

Furthermore, uncertainty calculations have been set up for different types of oxidised mercury gas generators. Tests are planned to evaluate the thermal converter efficiency and undesirable species interconversion of state-of-the-art dual analytical systems and gas transfer efficiency of the gas generators, including the effect of oxidised mercury reversible adsorption, irreversible (or very slow reversible) adsorption and chemisorption/reduction of gas generators.

#### *Performance evaluation of elemental and oxidised mercury generators on the market (objective 3)*

In collaboration with the stakeholder committee possible collaborators will be contacted to participate in the performance evaluation of elemental and oxidised mercury gas generators later on in the project.

#### **Impact**

During the first months of the project, to maximise the impact of the project and ensure a wide dissemination of the knowledge generated, the consortium gave four presentations to different groups, as described below. A website was created ([www.si-hg.eu](http://www.si-hg.eu)) and a thirty-member stakeholder committee was set up containing members from industry end users, regulation policy, standardisation bodies, instrument manufactures, NMI's and academic institutes.

#### *Impact on industrial and other user communities*

Once developed and validated by the project, the SI-traceable protocols for the certification of  $\text{Hg}^0$  and  $\text{Hg}^{\text{II}}$  gas generators used in the field, and the traceability chain for mercury measurement results will be disseminated to end users dealing with mercury emissions. Comparable and reliable results are critical for industry to improve their corporate social responsibility and enhance decision making by helping to assess which sectors are most problematic for mercury emissions, to meet required regulatory limits and to optimise mercury controls in order to reduce mercury emissions for society and improve environmental health.

Once the updated protocols are correctly implemented by calibration and testing laboratories, they will improve their mercury measurement results, reducing the uncertainty during calibration and certification of equipment and demonstrating their capabilities, which are fundamental to comply with the accreditation requirements (e.g. ISO/IEC 17025:2017).

Finally, using results from the project manufacturers of mercury gas generators and analysers will be able to demonstrate the accuracy of their instruments and, where possible, improve them in terms of better calibration and measurement performance and lower detection limits.

#### *Impact on the metrology and scientific communities*

Comparable atmospheric mercury measurements are of fundamental importance for the European regional programmes such as the Arctic Monitoring and Assessment Programme (AMAP), European Monitoring and Evaluation programme (EMEP) as part of the Convention of Long-range Transboundary Air Pollution, the Mediterranean Action Plan (MAP) and the Global Mercury Observation System (GMOS), which will be supported in their tasks within the framework of the Minamata Convention. Global Environmental Observation (GEO) greatly needs improved methodologies, tools, and comparable data for sound metrological implementation of their mercury related programmes. The developed certification protocols will be disseminated to these programmes as well as the validation reports, which will also include the usage of the protocols in practice.

- New CMCs for mercury in air ( $5 \mu\text{g m}^{-3}$  –  $100 \mu\text{g m}^{-3}$ , U, 4 % ( $k = 2$ )) and mercury in sorption tubes ( $2 \text{ ng}$  –  $100 \text{ ng}$ , U = 10 % ( $k = 2$ )) have been submitted to the KCDB.

#### *Impact on relevant standards*

The output of this project will provide CEN/TC264 "Air Quality" WG8 "Mercury Emissions" with the underpinning research and development required to produce standard methods to determine the concentration of mercury in gaseous emissions. CEN/TC264/WG8 strongly advocates the need to support the metrological validation to

determine the output in concentration of Hg<sup>0</sup> and Hg<sup>II</sup> gas generators. To address this need, CEN/TC264/WG8 started a new working item proposal (NWIP) “Calibration of elemental and oxidised mercury gas generators for SI-traceable mercury concentration measurements in air”.

- Presentation “Introduction of the 19NRM03 SI-Hg project” given at WG8 meeting on 02-06-2020, online.
- Presentation “Update of the 19NMR03 SI-Hg project” given at WG8 meeting on 14-04-2021, online.

This work will also improve current analytical methods for elemental and oxidised mercury concentration analysis in a number of standards committees including CEN/TC264/WG8; 390030 – Emissiemetingen en Algemene Aspecten (Emission Measurements and General Aspects); UK BSI committee EH/2/1 on stationary source emissions; ISO TC146 SC1 (Stationary Source Emissions); VDI/DIN Kommission Reinhaltung der Luft, Fachbereich IV (Clean Air commission, Department IV); International Monitoring Programs (i.e., Global Monitoring Plan of the Minamata Convention GMP-MC, EMEP, 4<sup>o</sup>Air Quality Directive); Parties of the Minamata Convention (COP); EURAMET TC-MC; CCQM GAWG; CCQM IAWG; ISO/REMCO.

- Presentation “Introduction of the 19NRM03 SI-Hg project” given at EURAMET TC-MC meeting on 05-02-2020, Bern, Switzerland.
- Presentation “Introduction of the 19NRM03 SI-Hg project” given at NEN 310193 Aardgas meeting on 18-05-2021, online.

*Longer-term economic, social and environmental impacts*

A solid metrological infrastructure will improve the quality, comparability and uncertainty of mercury measurement results in the field at emission and atmospheric monitoring stations. These results will have a longer-term impact on:

- The quantification of anthropogenic sources of mercury pollution and the evaluation of the fate and transport of mercury through the environment.
- Industries which emit mercury and help them to meet the requirements of mercury abatement and emissions legislation with greater confidence and at lower cost.
- Enforcement of directives which regulate mercury emission and help policies to set up methods for reducing mercury emissions to be based on credible and defensible data.

Furthermore, it will help to better understand human exposure to mercury, how this can be limited and avoided, thereby working towards improving human health in Europe and globally, especially those more susceptible to the effect of mercury, such as pregnant women.

**List of publications**

- I. de Krom, W. Bavius, R. Ziel, E.A. McGhee, R.J.C. Brown, I. Zivkovic, J. Gacnik, V. Fajon, J. Kotnik, M. Horvat, H. Ent, Comparability of calibration strategies for measuring mercury concentrations in gas emission sources and the atmosphere, Atmospheric Measurement Techniques, 14 (2021), 2317, <https://amt.copernicus.org/articles/14/2317/2021/>

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

Project start date and duration:		1 October 2020, 3 years	
Coordinator: Iris de Krom, VSL		Tel: +31 (0)15 269 1500	
Project website address: <a href="http://www.si-hg.eu">www.si-hg.eu</a>		E-mail: idekrom@vsl.nl	
Chief Stakeholder Organisation: Uniper Technologies Ltd.		Chief Stakeholder Contact: David Graham	
Internal Funded Partners:	External Funded Partners:	Unfunded Partners:	
1. VSL, Netherlands	5. CNR, Italy		
2. JSI, Slovenia	6. Lumex, Germany		
3. LGC, UK	7. PSA, UK		
4. VTT, Finland	8. TÜV Rheinland, Germany		
RMG: -			