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 metrological 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 ensure the dissemination 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 Hg0 and Hg^{II} analytical systems, (2) repeatability, reproducibility and uncertainty evaluation of the certification procedures at representative concentration levels extended to the low ng/m^3 level.
3. To organise a performance evaluation to gather data on the characteristics of at least three Hg^0 and three Hg^{II} 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. During the project the first calibration and measurement capabilities (CMCs) for mercury in air have been accepted to the KCDB. 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^{II} species. However, essential performance characteristics of Hg^{II} 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^{II} calibration gas to the analyser and storage and stability of the Hg^{II} solution used, will be investigated in depth. Furthermore, the methodology for the certification of liquid evaporative $HgCl_2$ generators, is described in a protocol in EMPIR 16ENV01 MercOx. To ensure the protocol is applicable for this wider range of Hg^{II} gas generators, this project will adjust the EMPIR 16ENV01 MercOx protocol by testing different types of gas generators. Last, a good practise guide will be provided by the project regarding storage and stability of Hg^{II} solutions.

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^0 and Hg^{II} 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)

Data and information have been compiled about the performance characteristics and uncertainty sources of commercially available elemental mercury gas generators used in the field. Based on these findings, a review was written, which was published on the project website. Little information is available on the performance characteristics of the generators. All the more reason to perform the validation activities described in the project plan. 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. Based on these approaches, a first draft of the protocol has been set up. The protocol specifies the procedures for establishing traceability to the SI units for the quantitative output of Hg^0 gas generators that are employed in regulatory applications for mercury monitoring or testing. It includes methods to determine the output of a mercury gas generator by comparison

with a reference standard and to calculate the uncertainty of the mercury concentration generated by the gas generator in relation to the known uncertainty of the reference standard. The mercury concentration in a gas mixture prepared with a mercury gas generator is compared with a metrologically traceable reference standard to calibrate the output of a candidate gas generator. The validation protocol covers comparisons at one concentration level (single-point calibration) and at several concentration levels (multipoint calibration), depending on the requirements of the user of the gas generator. The measurement data will be obtained using a measurement sequence that allows for drift compensation and zero correction. The single and multipoint approaches have been set up for the data processing 1) without zero correction and 2) with zero correction. A presentation with an overview of the draft protocol has been shared with CEN/TC264/WG8 to solicit further input and published on the project website. Currently measurements are ongoing to validate the principle of the drafted certification protocol by performing measurements with mercury concentrations relevant for emission measurements. Last, software for data processing is under development.

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

In order to meet objective 2, the first step done by the project consortium was to compile data about the performance characteristics and uncertainty sources of state-of-the-art dual analytical systems and commercially available Hg^{II} gas generators. Based on these findings, a review was written about the state-of-the-art dual analytical systems. The review was published on the project website. Furthermore, uncertainty calculations have been set up for different types of Hg^{II} gas generators. Several systems have been developed capable of determining the concentrations of Hg^0 and Hg^{II} in parallel. In the course of these developments, major obstacles in trace analysis of highly reactive chemical compounds have been overcome, e.g., real-time measurement for both Hg^{tot} and Hg^0. Yet, several problems remain e.g., 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 enable 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. A new calibration strategy has been developed for Hg^0 and Hg^{II} gas generators, suitable for ng m^{-3} mercury levels, providing traceability to SI units. On the other hand, radioactive ^{197}Hg isotopes are used and a cold plasma gas generator based on the conversion of Hg^0 into Hg^{II} in combination with temperature programmed desorption quadrupole mass spectrometry (TPD-QMS) to develop and validate existing metrological infrastructure for Hg^{II}.

Initial experiments aiming to estimate the sorption effects have been conducted. A method to determine the HgII-Hg0 converter efficiencies has been developed and is currently applied to dual analytical systems and Hg^{II} gas generators. A new method for the accurate quantification of Hg fraction in span gas from Hg^0 and Hg^{II} gas generators, which can provide traceability to directly to SI units (kg) was developed and applied for the characterisation of two generators (Hg^0 and $HgCl_2$). Currently, there is an ongoing effort to decrease the total relative measurement uncertainty of the method to below 5%.

Finally, experimental procedures have been developed for 1) the chromatographic purity determination of Hg^{II} solutions and salts and 2) the storage and stability study of Hg^{II} solutions used in liquid evaporative gas generators. Furthermore, the certification protocol for Hg^{II} gas generators is under development.

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

In collaboration with the stakeholder committee potential collaborators are identified for participation in the performance evaluation of Hg^0 and Hg^{II} gas generators later in the project. Signing of Letter of Agreement is in progress with the potential collaborators. Finally, the protocols for the performance evaluation campaign are currently under development.

Impact

During the first half of the project, to maximise the impact of the project and ensure a wide dissemination of the knowledge generated, the consortium gave six presentations for standardisation groups and metrology committees. A website was created (www.si-hg.eu) and a stakeholder committee with 33 members was set up containing members from industry end users, regulation policy, standardisation bodies, instrument manufactures, NMIs and academia. Two news letters were distributed to the stakeholder committee in month

3 and month 12. Furthermore, the first SI-Hg webinar took place in which the first results of the project were presented.

Impact on industrial and other user communities

Once developed and validated by the project, the SI-traceable protocols for the certification of Hg^0 and Hg^{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 certification 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 partners who are manufacturers of mercury gas generators and analysers will be able to demonstrate the accuracy of these instruments and, where possible, improve them in terms of better calibration and measurement performance and lower detection limits.

Project partners gave presentations during the CEM 2022 (2-3-2022 online).

- New calibration and measurement capabilities (CMCs) for mercury in air (5 µg m^{-3} – 100 µg m^{-3}, U = 4 % (k = 2)) and mercury in sorption tubes (2 ng – 100 ng, U = 10 % (k = 2)) have been accepted to the KCDB.
- New CMCs for mercury in air (0.1 µg m^{-3} – 2.1µg m^{-3}, U = 5 % (k = 2)) have been submitted to the KCDB.
- New CMCs for mercury in calibration gas (30 ng m^{-3} – 300 ng m^{-3}, U < 10 % (k = 2)) is intended to be submitted to the KCDB before the end of the project.

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.

Project partners were invited to give a presentation during the Minamata online session about reactive mercury in air (1-3-2022, online).

Project partners gave presentations at the CEM 2022 virtual conference (2-3-2022, online)

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^0 and Hg^{II} 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”.

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°Air Quality Directive); Parties of the Minamata Convention (COP); EURAMET TC-MC; CCQM GAWG; CCQM IAWG; ISO/REMCO.

Project updates are given during CEN/TC264 WG8 meetings (2-6-2020, 14-4-2021, 26-10-2021 and 31-3-2022, online). Presentations for CEN/TC264 WG9 and NEN 310 193 natural gas have been given about metrology for mercury measurements results in air (18-5-2021 and 28-1-2022).

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/amt-14-2317-2021.html
- D. Amico, A. Tassone, N. Pirrone, F. Sprovieri, A. Naccarato, Recent applications and novel strategies for mercury determination in environmental samples using microextraction-based approaches: A review, Journal of Hazardous Materials, 433 (2022), 128823, https://doi.org/10.1016/j.jhazmat.2022.128823

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

Project start date and duration:	1 October 2020, 36 months	
Coordinator: Iris de Krom, VSL Tel: +31 (0)15 269 1500 E-mail: idekrom@vsl.nl Project website address: www.si-hg.eu		
Chief Stakeholder Organisation: Uniper Technologies Ltd.	Chief Stakeholder Contact: David Graham	
Internal Funded Partners: 1. VSL, Netherlands 2. JSI, Slovenia 3. LGC, UK 4. VTT, Finland	External Funded Partners: 5. CNR, Italy 6. Lumex, Germany 7. PSA, UK 8. TÜV Rheinland, Germany	Unfunded Partners:
RMG: -		