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

Overview

Mercury gas generators used in the field are not calibrated against primary standards and therefore lack metrological traceability. The project developed and validated two protocols for the SI-traceable calibration of 1) elemental mercury (Hg^0) and 2) oxidised mercury gas generators used in the field. In this way, the project achieved significant improvements in the comparability and uncertainty of mercury measurement results. End users dealing with mercury emissions can implement the protocols to obtain comparable and reliable results which 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. Calibration and testing laboratories, can improve their mercury measurement results, reduce the uncertainty during calibration and certification of equipment and demonstrate their capabilities, which are fundamental to comply with the accreditation requirements (e.g. ISO/IEC 17025:2017). 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. Finally, the protocols and validation reports will be transferred to the European Committee for Standardization (CEN) which can convert the protocols into a written documentary standards.

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. Before the start of the project, it was 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, previous to the project start, there were no standardised procedures that ensure the dissemination of the developed metrological traceability by calibration and testing laboratories and in the field. Scientifically sound calibration 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 calibrated 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 met 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 was 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 were:

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 present project the first calibration and measurement capabilities (CMCs) for mercury in air were accepted to the Key Comparison Database (KCDB). In this project metrologically sound protocols for the calibration of mercury gas generators were developed and validated, 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. In this project, the converter efficiency of the analyser used and storage and stability of the Hg^{II} solution used, were investigated in depth. Furthermore, the methodology for the calibration 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 adjusted the EMPIR 16ENV01 MercOx protocol by testing different types of gas generators. Last, a good practise guide was produced by the project regarding storage and stability of Hg^{II} solutions and salts (https://zenodo.org/records/10039501). Such solutions and salts are used to operate liquid evaporative Hg^{II} gas generators used for field measurements in emission sources.

Performance evaluation data, including uncertainties of mercury gas generators on the market, were 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 was 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 was available on the performance characteristics of the generators. So, the project performed the necessary validation activities. Furthermore, uncertainty calculations have been set up for different types of elemental mercury gas generators.

Experimental approaches have been developed for the calibration protocol and to assess the performance characteristics during the validation of the calibration protocol. Based on these approaches, a first draft of the protocol has been set up. The protocol is the first in Europe to specify 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 calibration 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 was obtained using a measurement sequence that allows for drift compensation by 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 script was developed to process the data and 1) calculate the output mercury concentration of the candidate generator, 2) determine the interpolation function for the output mercury concentration in case of a multipoint calibration, 3) calculate the deviation between the candidate generator setpoint and the calculated output mercury concentration and 4) calculate the uncertainty of the calculated candidate generator output mercury concentration.

Validation measurements were performed over a large range of mercury concentrations. Based on the first validation measurements the protocol was improved and the protocol was further validated during the performance evaluation of elemental mercury gas generators on the market (objective 3). Furthermore, the performance of serval analytical methods for mercury in atmospheric samples was tested and compared. The first part of the work was the direct comparison of the bell-jar saturated air mercury calibrator (based on Dumarey equation) with the reduced NIST SRM 3133 at various temperature ranges. The robustness of the calibration approaches was tested by the determination of mercury in atmospheric samples. To assess the internal calibration system of a direct mercury analyser, it was compared with the external calibration based on reduction of NIST SRM 3133 for low ambient concentrations (<15 ng m^{-3}).

With the completion of the developed and validated calibration protocol for Hg^0 gas generators the objective was achieved.

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 (www.si-hg.eu). Furthermore, uncertainty calculations have been set up for different types of Hg^{II} gas generators.

To ensure SI traceability for Hg^{II} measurement results a method was developed to determine the Hg^{II}-Hg^0 converter efficiencies of mercury analysers and the stability and storage of $HgCl_2$ solutions and salts was determined for the first time.

A method to determine the Hg^{II}-Hg^0 converter efficiencies was developed for the first time and was applied to characterise a dual analyser system using Hg^{II} and Hg^0 gas generators. The uncertainty associated with this method was estimated to be 4 % (k = 2).

Furthermore, 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 gas generators (Hg^0 and $HgCl_2$). The measurement uncertainty (expanded with k = 2) is 9 %. As this method uses continuous cold vapour (CV) generation of an isotopically labelled Hg^{II} gas from solution, determination of the conversion efficiency of this CV was necessary. This was performed by using a ^{197}Hg radiotracer and measuring activity in the CV waste, CV efficiency at the flow rates used was determined to be 99.7 %.

Finally, based on a storage and stability study of $HgCl_2$ solutions and salts a good practice guide was written. Using the method developed to determine the converter efficiency of mercury analysers and the results from the storage and stability study the first European calibration protocol for Hg^{II} gas generator was developed. The calibration protocol describes step by step the calibration process needed to confirm the output of different

types of dynamic Hg^{II} gas generators, e.g., liquid evaporative gas generators, dry based gas generators and Hg^0 to Hg^{II} converter systems. Furthermore, the expanded uncertainty of the mercury concentration can be determined. The process consists of two main parts. Firstly, calibration of an analyser using a traceable mercury Hg^0 gas standard and secondly, measurement of the output from the dynamic Hg^{II} gas generator using the calibrated analyser.

Determination of the converter efficiency of an analyser was performed for the first time. This is a significant step forward. However, it is not credible to apply a correction of 86 % without further alternative confirmation tests. During the project there was no time left to verify the results obtained for the converter efficiency. For future research the results could be verified using alternative methods, for example methods based on wet chemistry to determine the output of an oxidised mercury gas generator. With the completion of the developed and validated calibration protocol for Hg^{II} gas generators the objective was achieved.

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

The performance evaluation organised during the project, for the first time, gathered data on the characteristics of three Hg^0 and three Hg^{II} gas generators available on the market. All generators could be tested according to the calibration protocols developed within the project. Based on the validation measurements performed at the beginning of the project the protocols were already improved. Based on the results of this performance evaluation no new improvements were done. The results obtained with the different gas generator clearly shows the importance of a metrological calibration. All candidate generators tested show a different bias. Through calibration according to the SI-Hg calibration protocols for Hg^0 and Hg^{II} gas generators all measurement results become traceable to the SI units and comparable. This is essential to underpin global efforts to control and reduce the concentration of mercury in the environment, comply with legislation and protect human health.

With the completion of the performance evaluation of three Hg^0 and three Hg^{II} gas generators the objective was achieved.

Dissemination of scientific outcomes through guidance documents for accurate field measurement and uncertainty assessment as part of the global mercury observation system used to measure the effectiveness of the implementation of the Minamata Convention (objective 4).

The project was able to promote the need of proper instrumental calibration to obtain reliable measurement result of Hg^0 and Hg^{II} in the atmosphere and emission sources. This was achieved during the project via presentations given during a stakeholder webinar, conferences (e.g., ICMGP, Gas Analysis and CEM), the Minamata online recordings and a stakeholder seminar. Four open access peer-reviewed paper were published and a comparison at a climatic-environmental observatory was organised and reported. The project successfully achieved the objective.

Impact

During the course of the project, to maximise the impact of the project and ensure a wide dissemination of the knowledge generated, the consortium gave 17 presentations during conferences and 18 presentations for standardisation groups and metrology committees. A website was created (www.si-hg.eu) and a stakeholder committee with 41 members was set up containing members from industry end users, regulation policy, standardisation bodies, instrument manufactures, NMIs and academia. Two newsletters were distributed to the stakeholder committee in month 3 and month 12. Furthermore, the first SI-Hg webinar took place and the project organised a session during the ICMGP 2022 conference in collaboration with the GMOS-trains programme “Metrological traceability for mercury analysis and speciation”, during which the first results of the project were presented. Finally, during the Conference on Emission Monitoring in Barcelona, Spain the final SI-Hg workshop was organised on 19 September 2023. During the final meeting the project results were presented to 20 stakeholders from all over the world.

Impact on industrial and other user communities

Once developed and validated by the project, the SI-traceable protocols for the calibration 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 calibration protocols are correctly implemented by calibration and testing laboratories, they will improve their mercury measurement results, reducing the uncertainty during calibration and calibration 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.

– New calibration and measurement capabilities (CMCs) for mercury in air (5 µg m^{-3} – 100 µg m^{-3}, U = 4 % (k = 2) and 0.1 µg m^{-3} – 2.1µg m^{-3}, U = 5 % (k = 2)) and mercury in sorption tubes (2 ng – 100 ng, U = 10 % (k = 2)) have been accepted to the KCDB.

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 calibration 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).
- The SI-Hg project organised a special session at the ICMGP 2022 conference in collaboration with the GMOS-train programme “Metrological traceability for mercury analysis and speciation” (7-2022, online).
- Project partners gave presentations at the CEM 2022 virtual conference (2-3-2022, online), gas analysis conference (19-5-2022, France), ICMGP 2022 conference (7-2022), RAP 2023 conference (5-2023) and CEM 2023 conference (9-2023).

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, 31-3-2022 and 26-4-2023 online and 18-11-2022 in The Netherlands).
- 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://doi.org/10.5194/amt-14-2317-2021
- 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
- M. Martino, A. Tassone, L. Angiuli, A. Naccarato, P. R. Dambruoso, F. Mazzone, L. Trizio, C. Leonardi, F. Petracchini, F. Sprovieri, N. Pirrone, F. D'Amore, M. Bencardino, First atmospheric mercury measurements at a coastal site in the Apulia region: seasonal variability and source analysis, Environmental Science and Pollution Research, 29 (2022), 68460 – 68475, https://doi.org/10.1007/s11356-022-20505-6
- A. Tassone, O. Magand, A. Naccarato, M. Martino, D. Amico, F. Sprovieri, H. Leuridan, Y. Bertrand, M. Ramonet, N. Pirrone, and A. Dommergue, Seven-year monitoring of mercury in wet precipitation and atmosphere at the Amsterdam Island GMOS station, Heliyon, 9 (2023), E14608, https://doi.org/10.1016/j.heliyon.2023.e14608

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
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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: -		