METROLOGICAL CALIBRATION OF MERCURY GAS GENERATORS

Mercury (Hg) is ubiquitously present in the atmosphere, thus monitoring of the Hg concentrations in emission sources and the atmosphere has become a global requirement in recent years. Industrial sites are required to implement adequate monitoring equipment (e.g., analysers and gas generators) and report their emissions to relevant authorities. To obtain accurate and reliable measurement results the appropriate calibration of monitoring equipment is required. Furthermore, documentary standards set requirements for the calibration and also validation and quality control of CEMs.

EN 14181:2014 sets requirements for the quality assurance of automated measuring systems. There are requirements for the calibration and validation and for quality control. Specific guidance for Hg measurement is given in EN 14884:2022 where different test require the use of Hg gas generators, such as the zero and span checks, linearity test, response time and converter efficiency. For the first 3 experiments both elemental mercury (Hg^0) and oxidised mercury (Hg^{II}) gas generators can be used for the last one only Hg^{II} gas generators. According to these documentary standards Hg CEMs are calibrated using Hg gas generators. But how are Hg gas generator calibrated?

For decades gaseous Hg concentration measurements have been calibrated based on Hg vapour pressure equations (e.g., the Dumarey or the Huber equation). Currently these equations differ from each other by more than 7 % at 20 °C and this discrepancy is of great concern as it hampers comparable and reliable measurement results for Hg concentrations in the atmosphere and emissions sources. In the past decade considerable effort has been put into the development of certified reference standards and calibration methods for Hg concentrations traceable to the International System of Units (SI) to ensure comparable and reliable Hg measurement results.

Notwithstanding these efforts, there are no standardised procedures that ensure the dissemination of the SI traceable calibration methods from certified reference standards via Hg gas generators to monitoring equipment used for emission and atmospheric monitoring. Scientifically and metrologically sound calibration protocols, used to assess the performance of Hg gas generators in the form of formally accepted documentary standards, are of fundamental importance to guarantee the accuracy and comparability of the Hg measurement results in gas emission sources and in the atmosphere in Europe and globally.

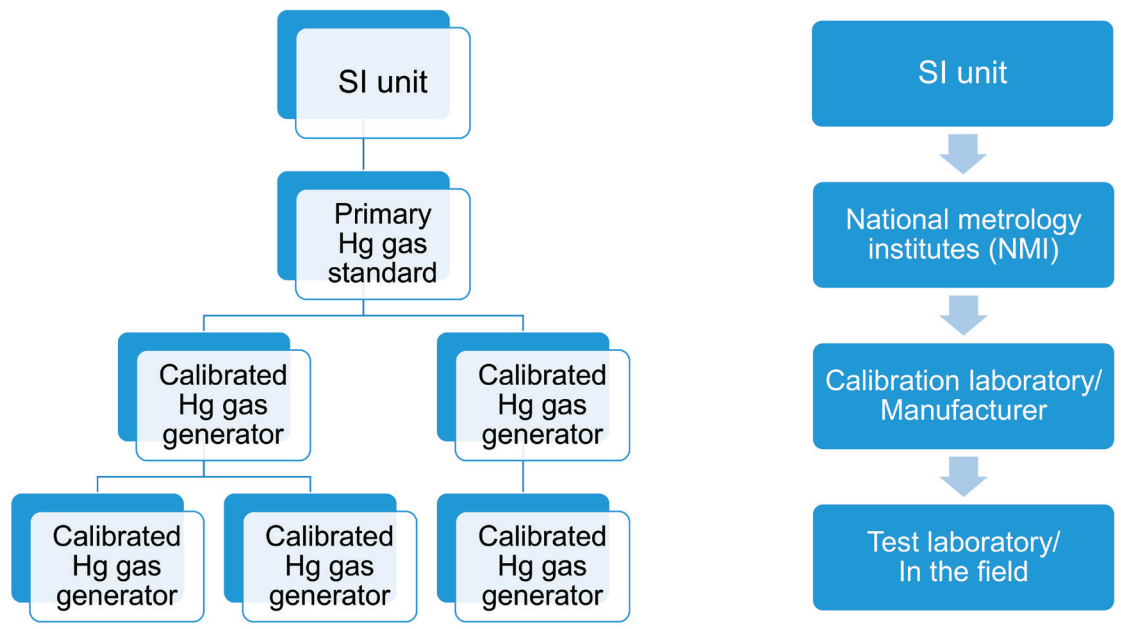

Figure 1: SI traceable calibration chain for Hg gas generators.

Within the EMPIR (European Metrology Programme for Innovation and Research) SI-Hg project (Metrology for traceable protocols for elemental and oxidised mercury concentrations - 19NRM03 www.SI-Hg.eu) such metrologically sound calibration protocols were developed and validated.

The protocols specify procedures for establishing traceability to the SI for the quantitative output of Hg gas generators that are employed in regulatory applications for Hg monitoring or testing. It includes methods to determine the output of a Hg gas generator by comparison with a reference standard and to calculate the Hg concentration and the corresponding uncertainty generated by a candidate generator in relation to the known uncertainty of the reference standard. The Hg concentration in a gas mixture prepared with a candidate generator is compared with a Hg concentration prepared with a metrologically traceable reference standard to calibrate the output of a candidate generator. For the comparison both gas mixtures, from the candidate generator and reference standards are directed to a Hg analyser.

By performing calibrations according to the protocol a traceability chain starting from a metrologically certified reference standards can be established by comparison of a candidate generator to the primary standard or reference standard according to the measurement procedure described in the protocol. After calibration the candidate generator receives an SI traceable certificate and can be used as a reference generator for calibration of other candidate generators, and so forth (Figure 1). This way a chain of calibrations is obtained from the primary standard to gas generators used every day for monitoring of Hg concentrations in emission sources and in the atmosphere.

The traceability chain for Hg^0 concentrations is straightforward as there are primary gas standards available at National Metrology Institutes. However, such gas standards do not exist for Hg^{II} and traceability to the SI is established using the Hg^0 standards. Furthermore, in online monitoring, Hg^{II} needs to be converted to Hg^0, since online analysers are only capable of measuring total Hg. To ensure SI traceable measurement results for Hg^{II} concentrations can be obtained a method was developed to determine the converter efficiency of Hg analysers. Furthermore, the best storage conditions and the stability for $HgCl_2$ solutions and $HgCl_2$ salts were determined. For the generation of Hg^{II}

gas mixtures $HgCl_2$ solutions are used in liquid evaporative Hg gas generators. The results obtained were incorporated in the calibration protocol developed for Hg^{II} gas generators.

To determine if the developed calibration protocols are fit for purpose validation measurements were performed by evaluating Hg gas generators available on the market. During the performance evaluation candidate generators were calibrated according to the protocols and based on the measurement data characteristics were determined, e.g., the stabilisation period, short-term drift, precision, i.e., reproducibility and repeatability of the concentration generated, linearity, bias, sensitivity to sample gas pressure, sensitivity to surrounding temperature and sensitivity to electrical voltage. All Hg gas generators could be tested according to the calibration protocols developed within the project. The results obtained with the different Hg gas generators clearly show the importance of a metrological calibration (Figure 2).

The SI-Hg project successfully developed calibration protocols for Hg^0 and Hg^{II} gas generators. Validation of the protocols was obtained through the performance evaluation of Hg gas generators available on the market. Based on the results calibration protocols, validation reports and good practice guides were written. These documents are available online (www.SI-Hg.eu and/or Search Metrology for traceable protocols for elemental and oxidised mercury concentrations (zenodo.org)). The documents have been handed over to CEN/TC 264 "Air Quality" WG8 "Measurement of Total Mercury Emissions". This standardisation committee will work on the conversion of the protocols into written documentary standards. Once, the documentary standards are in place they will replace other non-comparable references used in industry to calibrate Hg gas generators and ensure SI traceable measurement results for Hg concentrations in emission sources and the atmosphere. This is essential to underpin global efforts to control and reduce the concentration of Hg in the environment, comply with legislation and protect human health.

This project (19NRM03 SI-Hg) has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

Acknowledgments go to the SI-Hg project consortium, VSL, JSI, LGC Limited, VTT, CNR, Lumex Analytical GmbH, P. S. Analytical Limited and TÜV Rheinland Energy GmbH.

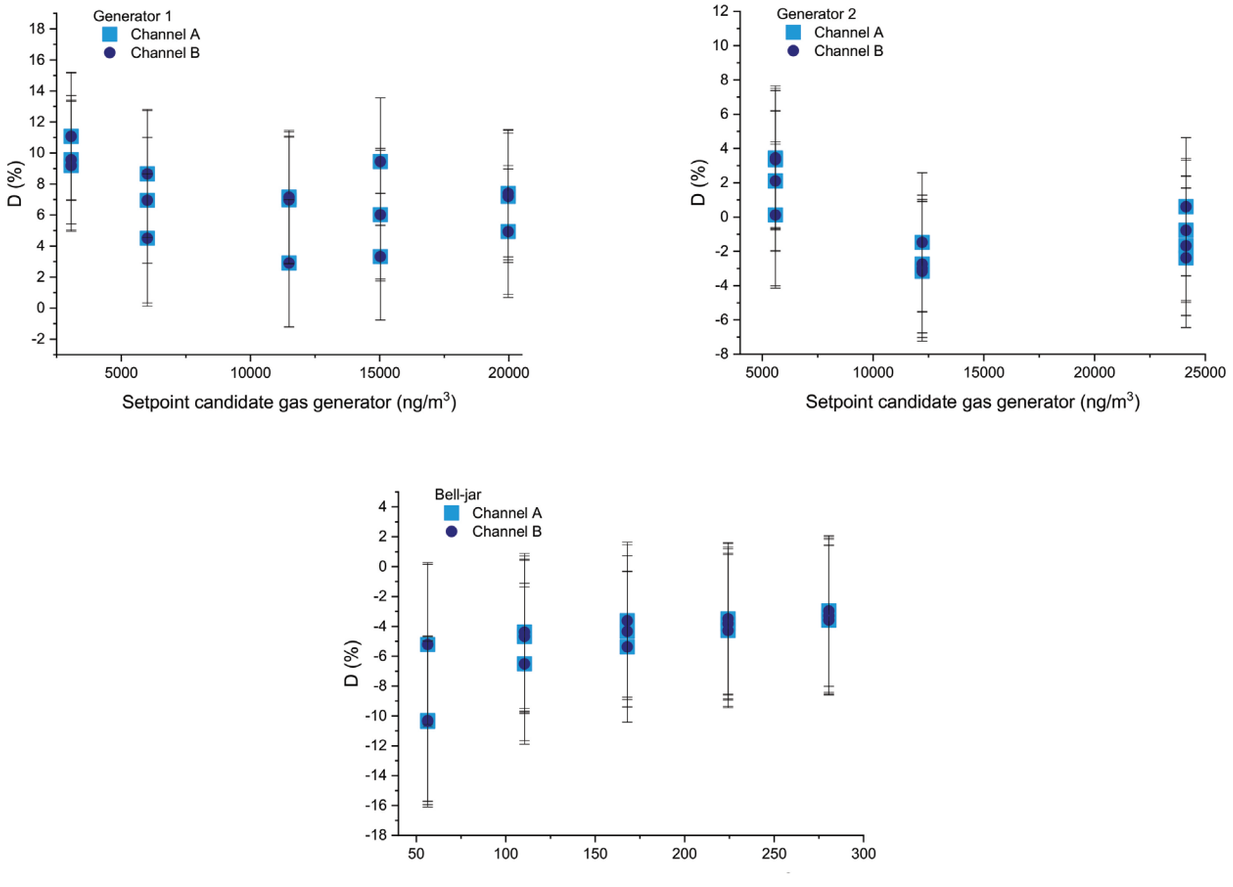

Figure 2: Results for the relative deviation (D %) of the Hg^0 concentration from the candidate generator setpoint against the calibrated output of the candidate generator traceable to the VSL primary standard. Generator 1 and Generator 2 are automatic saturation gas generators from different suppliers. The bell-jar was tested in the range from 50 ng m^{-3} to 300 ng m^{-3} with a deviation of +7%. Generator 1 was tested in the range from 3000 ng m^{-3} till 20000 ng m^{-3} with a deviation of -5% and Generator 2 was tested in the range from 5000 ng m^{-3} till 25000 ng m^{-3} with a deviation of -0.5%. Furthermore, the setpoints of Generator 2 are traceable to NIST. These results show comparability between the VSL primary Hg gas standard and a NIST calibrated gas generator.

Author Contact Details

: Iris de Krom – Scientist • VSL

• Address: Thijsseweg 11 Delft, The Netherlands • Tel: 0031 (0)15 269 1500

• Email: idekrom@vsl.nl • **Web: www.vsl.nl/en**