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1 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.

2 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".

3 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 Hg^0

- and Hg^{II} analytical systems, (2) repeatability, reproducibility and uncertainty evaluation of the certification procedures at representative concentration levels extended to the low ng/m³ level.
3. To organise a performance evaluation to gather data on the characteristics of at least three Hg⁰ 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).

4 Results

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

Metrological sound calibration protocol to determine the output of Hg⁰ gas generators

Mercury (Hg) is ubiquitously present in the atmosphere, thus monitoring of the Hg concentrations in the atmosphere and emission sources 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.

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. Using one or the other will create a bias in the results obtained. The use of SI-traceable calibration methods will replace the use of these non-comparable methods. Therefore, in this project VSL developed the metrological sound calibration protocol to determine the output of Hg⁰ gas generators, which is available online (<https://zenodo.org/records/10124313>). The other partners, PSA, Lumex, TÜV Rheinland, JSI, VTT, CNR, LGC, provided input for the protocol, as the partners have different backgrounds as NMIs, instrument manufactures and test laboratories they provide different points of view to ensure the protocol is applicable through the whole traceability chain from calibrations at NMI to calibrations in the field.

The calibration protocol specifies the procedures for establishing traceability to the SI units for the quantitative output of Hg⁰ 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 mercury concentration and the corresponding uncertainty of the mercury concentration generated by the candidate 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. For the multipoint calibration data a method was developed to determine the interpolation function. This will allow to use the generator at any set point in within the calibration range. For the process of the data VSL developed a script using Python 3.8.8 ([vanswindenlaboratory/SI-Hg: v1.0 release \(zenodo.org\)](https://vanswindenlaboratory.github.io/SI-Hg-v1.0-release/)).

By performing calibrations according to the protocol a traceability chain starting from primary standards can be established by comparison of a candidate generator to the primary standard or reference standard according to the measurement procedure described in this calibration 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 mercury concentrations in emission sources and in the atmosphere.

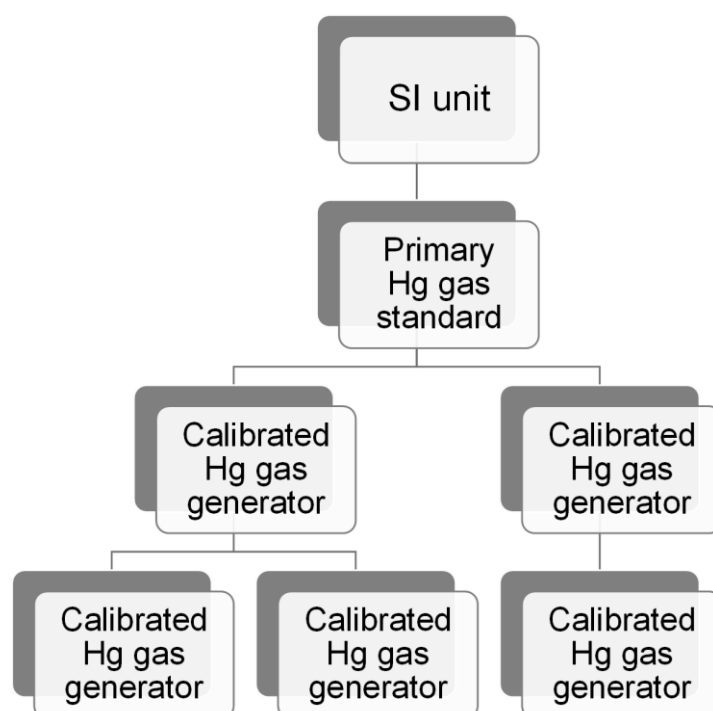


Figure 1 – SI traceable calibration chain for mercury gas generators.

Validation

The reason of the validation is to determine if the procedures in the protocol can be carried out in the laboratory using gas generators and if the data processing methods described give reliable results. The protocol was subjected to a validation for higher Hg concentrations, in the $\mu\text{g m}^{-3}$ range, by project partners VSL, PSA and TÜV Rheinland, these concentrations are relevant for emission monitoring. The results are reported in “Validation report for the calibration of elemental mercury gas generators including information on repeatability, reproducibility and uncertainty evaluation at emission and ambient levels extended to the sub ng m^{-3} level” (<https://zenodo.org/records/10217266>). JSI performed measurements with Hg concentrations in the ng m^{-3} range relevant for air monitoring. During the validation precision (repeatability and reproducibility), deviation and uncertainty evaluation of the calibration procedure were investigated.

The validation measurements in the $\mu\text{g m}^{-3}$ range started at VSL which used the primary mercury standard to perform SI traceable calibrations of in house generators and a gas generator provided by PSA. After the measurements at VSL the PSA generator received SI traceable calibration values and was used as a reference generator for calibration of other candidate generators by TÜV Rheinland. Finally, the PSA generator was returned to VSL for recalibration to determine the stability of the generator over time.

The calibration could be performed according to the protocol, nevertheless, several improvements were implemented based on the validation measurements regarding:

1. Statement of the complementary gas used, during the validation it was shown to influence the results
2. The setpoints of the reference standard and candidate generator, select Hg concentrations such that the measuring system produces responses which are within $\pm 50 \%$
3. The relative standard deviation (RSD) of the responses obtained must be $\leq 2\%$, to ensure the output of the reference standard and candidate generator are stable.
4. Use of the reproducibility uncertainty source for the calculation of the uncertainty, when the measurements, especially those obtained on different days, are not comparable within the uncertainty it is advised to add uncertainty for the reproducibility to the uncertainty calculation.

The calibration of two candidate generators was repeated on several days to determine the precision (Figure 2).

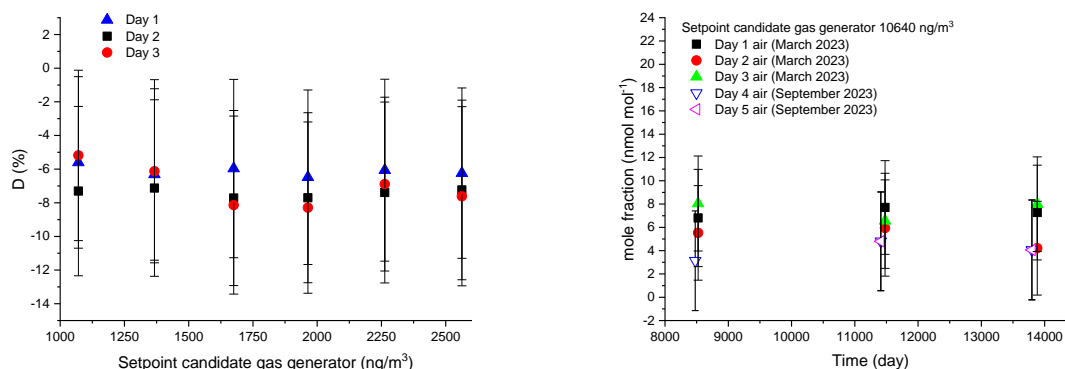


Figure 2 – Precision and deviation of the multipoint (left) and single point (right) calibration of Hg^0 gas generators according to the protocol.

It is possible to repeat the measurements on different days and obtain precise results, the repeatability and reproducibility of the results obtained are within the expanded uncertainty of the results. The most important uncertainty source for the Hg concentration is the uncertainty of the reference standard. The uncertainty increased with a maximum of 16 % due to the stability and repeatability of the measurements or the comparison uncertainty. The primary reference standard has an uncertainty of 4 % for $\mu\text{g m}^{-3}$ Hg concentrations or 5 % for ng m^{-3} Hg concentrations ($k = 2$). After the calibration the calibrated mercury concentrations have expanded uncertainties which increased up to a maximum of 4.6 % and 5.8 %.

The PSA generator was used at several stages of the traceability chain. At VSL it was possible to calibrate the gas generator. Next, the generator was sent to TÜV Rheinland where the gas generator was used as the reference standard to calibrate another candidate generator. Then, to check the stability of the calibration the gas generator was returned to VSL after 6 months for recalibration. The results of the recalibration are comparable within the expanded uncertainty of the results obtained six months earlier (Figure 2).

Based on the results obtained during the validation the protocol was ready for further validation during the performance evaluation (see section 4.3).

JSI used the NIST 3133 standard reference materials to calibrate the internal calibration of a direct mercury analyser based on atomic absorption spectrometry with Zeeman background correction (Zeeman AAS). Measurements of atmospheric Hg using the calibrated Zeeman AAS were compared with two methods: manual gold amalgamation atomic fluorescence spectrometry (AFS) calibrated with the chemical reduction of NIST 3133 and automated gold amalgamation AFS calibrated using the mercury bell-jar syringe technique. The comparisons showed that factory-calibrated Zeeman AAS underestimates concentrations under 10 ng m^{-3} by up to 35 % relative to the two other methods of determination. However, when a calibration based on SRM NIST 3133 was used to perform a traceable calibration of Zeeman AAS, the results were more comparable with other methods. The expanded relative combined uncertainty for Zeeman AAS ranged from 8 % for measurements at the 40 ng m^{-3} level to 91.6 % for concentrations under 5 ng m^{-3} using the newly developed calibration system. High uncertainty for measurements performed under 5 ng m^{-3} was due mainly to instrument noise and concentration variation in the samples.

CRN organised a field campaign with the aim to determine the consistent quality of mercury measurements at the monitoring station located in Rende, Italy. This campaign consisted in the comparison of the performances of multiple Hg analysers produced by different producers, operating in parallel under the same experimental conditions, each calibrated with SI-traceable calibrated gas generators. Participants JSI and VTT were invited to perform field measurements using elemental gas generators and oxidised mercury generators for the determination of the mercury concentration at the monitoring station in Rende. Measurements were carried out using instrumentation from different companies, namely Hg analysers from Tekran, P S ANALYTICAL, Lumex, and Mercury Instruments, and gas generators from Tekran, P S ANALYTICAL, IAS GMBH, and JSI. Also remote tubes from P S ANALYTICAL and MerPASs from Tekran were included in the intercomparison campaign. All calibration curves obtained in the intercalibration campaign showed good linearity, including those performed through the whole sampling system. However, the observed differences in the calibration slopes were not successfully explained; therefore, further tests are required to address these issues and to

explain the observations. The best alignment of calibration slopes is obtained using bell-jar and NIST SRM 3133 calibration under same experimental conditions (through the Tekran speciation unit's sampling inlet).

A report regarding the quality of mercury measurements during the comparison was written by CNR (<https://zenodo.org/records/10209928>).

Conclusion

During the project a calibration protocol was developed to determine the output of elemental mercury gas generators by comparison with a reference standard and to calculate the mercury concentration and the corresponding uncertainty of the mercury concentration generated by the candidate gas generator in relation to the known uncertainty of the reference standard. The first validation measurements showed the protocol was ready for further validation during a performance evaluation (see section 4.3).

The final protocol and validation reports will be transferred to CEN/TC 264 "Air Quality" WG8 "Measurement of total Hg emissions". The standardisation committee has a new working item proposal to work on the conversion of the protocol into a written documentary standard. This will replace other reference used in industry to calibrate mercury gas generators and ensure SI traceable measurement results for mercury concentrations in emission sources.

With the completion of the developed and validated calibration protocol for Hg⁰ gas generators the objective was achieved.

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

Evaluation of thermal converter efficiency from state-of-the-art dual analytical systems

Apart from its elemental form (Hg⁰), mercury also occurs in oxidised forms (Hg^{II}) in the environment. For the control and assessment of mercury concentrations in the environment it is essential to be able to monitor all mercury species. In the previous EMPIR 16ENV01 MercOx project SI traceable calibration methods were developed for the most important oxidised mercury-containing species, especially for HgCl₂. SI traceability for the developed methods is obtained via the primary elemental mercury standard. To accomplish the traceability chain, a Lumex state-of-the-art two-channel analytical system was developed for the simultaneous real-time analysis of Hg⁰ and total mercury (Hg^{tot}), which is Hg⁰ + Hg^{II}. In online monitoring, Hg^{II} needs to be converted to Hg⁰, since online monitors are only capable of measuring Hg⁰. With the development of the two-channel analytical system it is possible to determine the Hg⁰ and Hg^{II} concentration in air instead of only the Hg^{tot} concentration. However, essential performance characteristics need to be determined of the state-of-the-art dual analyser, to obtain SI-traceable measurement results. In this project, LGC, in collaboration with PSA and Lumex developed a method to determine the converter efficiency of the analyser, from Hg^{II} to Hg⁰.

Therefore, the converter efficiency of the Lumex two-channel analytical system was determined. To determine the efficiency of a thermal converter that transforms oxidised mercury compounds to elemental, Hg⁰ and Hg^{II} concentrations needed to be measured. To obtain these concentrations PSA mercury gas generators 10.534 (Hg⁰) and 10.536 (HgCl₂) were used, respectively. Both species needed to be monitored either selectively or by independent detectors, preferably online, either continuously, or intermittently with a short sampling frequency. Since a traceable online speciation detector, capable of measuring both Hg^{II} and Hg⁰ species was not available, independent but parallel AAS and ICP-MS/MS detectors were used. The RA-915F AAS detector could measure only Hg⁰ or Hg^{II} transformed to Hg⁰ by a converter, and the ICP-MS/MS species independent, Hg^{tot}. The underlying principle of the method is that when Hg⁰ is introduced into the Hg⁰ and Hg^{tot} detectors, both detectors should provide a signal for the Hg^{tot} in that gas mixture. If a Hg^{II} concentration (e.g., HgCl₂) is introduced to the similar parallel detectors without passing through a converter, the elemental detector should not display signal above the detector background, while the Hg^{tot} detector should display a Hg signal proportional to the Hg^{II} fraction and the instrument sensitivity. A schematic diagram of the setup along with the nominal flows and Hg concentrations is presented in Figure 3. The Hg⁰ and HgCl₂ generators were connected to the set-up in turn to measure their outputs independently. In this set-up the thermal converter was integrated with the Lumex analyser. However, the set-up can be easily modified to accommodate separate converters and detectors by linking them with a short piece of PFA tubing.

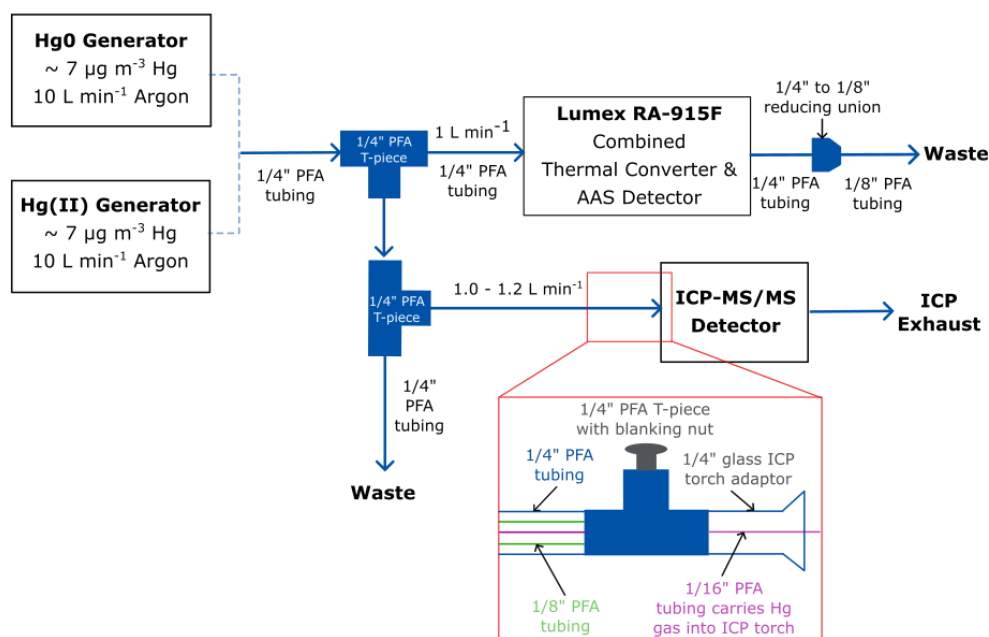


Figure 3 – Schematic diagram of instrumental setup for the determination of thermal converter efficiency. The Hg^0 generator (PSA 10.534) and Hg^{II} generator (PSA 10.536) were connected to the setup independently.

Before measurements were obtained, both generators operated N_2 as complementary gas for at least 72 hours. On the morning of the first day of measurement, the complementary gas was changed to argon for both generators, and they were purged for approximately 3 hours before measurement started. During this time the Lumex converter was heated up. After purging, the Hg sorption effect from the HgCl_2 generator was tested. To determine the converter efficiency, the ICP-MS/MS ^{202}Hg and AAS signals were ratioed for both the Hg^0 and HgCl_2 generators.

The efficiency of the Lumex RA-915F thermal converter was determined on three different days using the same set-up, generator settings, and tubing to ensure consistent conditions (Table 1)

Table 1 – Results from the converter efficiency experiments conducted for the two-channel analytical Lumex converter using the PSA 10.534 and 10.536 Hg^0 and HgCl_2 gas generators. The Lumex/ICP ratio is the ratio of averaged ^{202}Hg ICP-MS/MS signal and the AAS signal over 10 minutes. The standard uncertainty ($k = 1$) of each ratio is in brackets. The converter efficiency uncertainty ($k = 2$) for each day is the combined Hg^0 and HgCl_2 generator signal ratio uncertainties. The overall converter efficiency expanded uncertainty combines the standard deviation of the converter efficiency results over the three measurement days (0.02) and the maximum individual converter efficiency standard uncertainty.

Date	Generator	Lumex/ICP Ratio (R_{Ref} & R_{C})	Converter Efficiency	U_{C} ($k = 2$)
27/10/2022	PSA 10.534 Hg^0	0.000392 (3)	0.88	0.02
	PSA 10.536 HgCl_2	0.000343 (2)		
28/10/2022	PSA 10.534 Hg^0	0.000435 (4)	0.84	0.02
	PSA 10.536 HgCl_2	0.000365 (2)		
01/11/2022	PSA 10.534 Hg^0	0.000724 (12)	0.85	0.03
	PSA 10.536 HgCl_2	0.000617 (4)		
Average Converter Efficiency			0.86	
Standard Deviation			0.02	
Overall Expanded Uncertainty ($k = 2$)			0.04	

The converter efficiency tests indicate a mean efficiency of 86 %. This has implications for the calibrated output of Hg^{II} generators and highlights the importance of testing converter efficiency for all analysers used. In the

future, converter efficiency determinations may benefit from further verification using multiple different techniques.

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 directly to SI (kg) was developed by LGC and applied for the characterisation of two PSA generators (Hg^0 and HgCl_2). The measurement uncertainty (expanded with $k = 2$) is 9%. A paper with these results is in draft. 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 JSI by using a ^{197}Hg radiotracer and measuring activity in the CV waste. CV efficiency at the flow rates used at LGC was determined to be 99.7%.

Storage and stability HgCl_2 solutions and HgCl_2 salt

HgCl_2 solutions are used in liquid evaporative Hg gas generators to calibrate Hg measurement systems and detectors for Hg^{II} and Hg^{tot} . The generators vaporise a HgCl_2 solution of known concentration and mix the vapour with a complementary gas to produce a known Hg^{II} concentration that can be varied to create a multi-point calibration curve. The HgCl_2 solutions are typically diluted from pure salts to create stock solutions that are stored long-term and diluted to create working solutions for the generators.

However, some essential performance characteristics such as the storage and stability of the stock HgCl_2 solutions and salts used in the generators were not assessed. Feedback from industry and research partners such as VDZ (Verein Deutscher Zementwerke e.V.), VTT (Technical Research Centre of Finland), CNR (National Research Council, Italy), and TÜV Rheinland revealed that a wide variety of storage conditions and protocols are used throughout industry including different storage temperatures, bottle types, matrices, and concentrations. Solution stability under these different storage conditions is important to constrain because it is a major control on the Hg^{II} concentration by liquid evaporative generators. If the HgCl_2 solution stability changes over time, uncertainty is introduced to the output of liquid evaporative generators, and therefore the calibration of Hg detectors used in the field. LGC and TÜV Rheinland therefore determined the best storage and stability conditions for HgCl_2 solutions and LGC determined the best storage and stability conditions for HgCl_2 salts. The results were reported in a good practice guide (<https://zenodo.org/records/10039501>).

HgCl_2 solutions

The storage conditions for HgCl_2 solutions tested in this study were chosen to closely reflect the range of conditions used in the field by facilities that use Hg^{II} liquid evaporative generators for Hg detector calibration. The finalised storage conditions tested were storage temperature, bottle material, Hg concentration, solution matrix, and storage duration. Three different storage temperatures were tested, 1) ambient temperatures (stored on open shelving, exposed to indirect sunlight), 2) fridge temperatures, and 3) heating to 60 °C for 24 hours in an oven to simulate transport to hot climates in a “shock heat” experiment. For each temperature a different set of individual HgCl_2 solutions of 50, 200, and 1000 $\mu\text{g kg}^{-1}$ of Hg plus blanks were prepared from HgCl_2 salt in each of the three matrices 1) 0.1 % (v/v) HCl, 2) 0.024 % (v/v) HNO_3 + 0.0144 % (v/v) HCl, and 3) 0.125 $\mu\text{g g}^{-1}$ HNO_3 + 0.125 $\mu\text{g g}^{-1}$ HCl and were stored in each of the three bottle types 1) FEP (fluorinated ethylene propylene), 2) FLPE (fluorinated high density polyethylene), and 3) borosilicate, resulting in 36 different solutions per storage temperature. Over 6 months, the Hg concentration of each solution, except for the shock heat solutions, was measured monthly to monitor long-term stability.

The ambient temperature stability experiments show that all solutions except for those stored in FLPE bottles in 0.125 $\mu\text{g g}^{-1}$ HNO_3 + 0.125 $\mu\text{g g}^{-1}$ HCl experienced no significant change in Hg concentration considering the associated expanded measurement uncertainty ($k = 2$) over the six month study. Of the three solutions in which the Hg concentration decreased, the 50 ng g^{-1} solution experienced an 89 % decrease over the six months, the 200 ng g^{-1} solution a 74 % decrease, and the 1000 ng g^{-1} solution a 30 % decrease (Figure 4). The percentage change over the six month study for all other solutions varied between -3 % and 5 %.

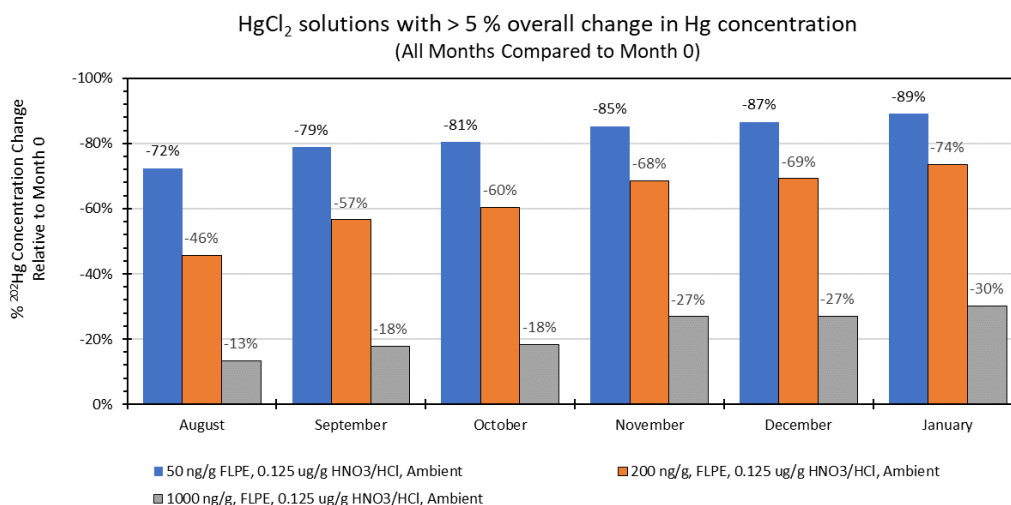


Figure 4 – The percentage change in Hg concentration compared to month 0 for each month over a period of 6 months for the three samples with greater than a 5% reduction in concentration.

In the shock heat experiment, the same three solutions stored in FLPE bottles with 0.125 $\mu\text{g g}^{-1}$ HNO₃ + 0.125 $\mu\text{g g}^{-1}$ HCl showed a significant decrease in Hg concentration after heating at 60 °C for 24 hours. The percentage change in Hg concentration for the 50 ng g⁻¹ solution was -85 %, -61 % for the 200 ng g⁻¹ solution, and -34 % for the 1000 ng g⁻¹ solution (Figure 5). All percentage change in Hg concentration for all other solutions did not exceed 4%.

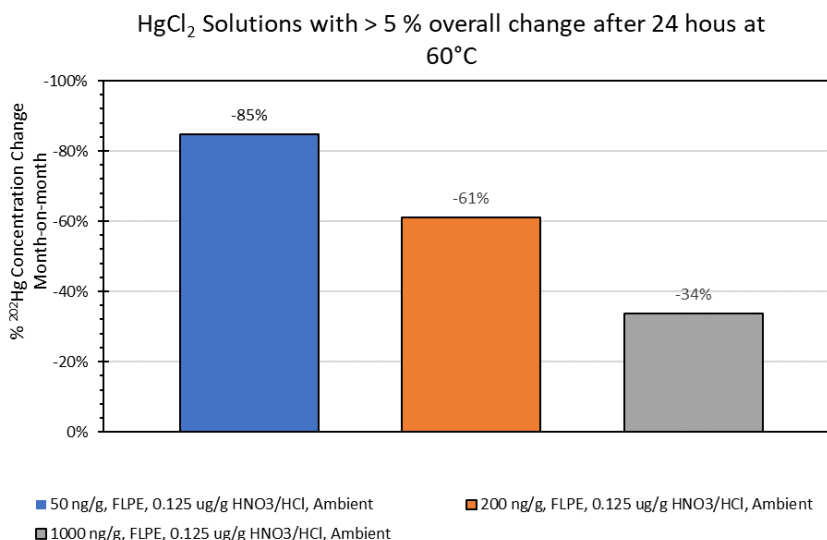


Figure 5 – The percentage change in Hg concentration after heating the HgCl₂ solutions to 60 °C for 24 hours for the three samples with greater than a 5% reduction in concentration.

The results of the fridge temperature experiments show that all solutions stored in 0.125 $\mu\text{g g}^{-1}$ HNO₃ + 0.125 $\mu\text{g g}^{-1}$ HCl irrespective of bottle type experienced a significant reduction in Hg concentration over the six month study period (Figure 6). The only HgCl₂ solution stored in 0.125 $\mu\text{g g}^{-1}$ HNO₃ + 0.125 $\mu\text{g g}^{-1}$ HCl that did not experience significant Hg loss was the 1000 ng g⁻¹ borosilicate solution, which experienced a 6 % loss over the six months. The borosilicate bottles experienced the least Hg loss of the 0.125 $\mu\text{g g}^{-1}$ HNO₃ + 0.125 $\mu\text{g g}^{-1}$ HCl solutions, and again higher Hg storage concentrations also experienced less Hg loss. The FLPE bottles containing 0.125 $\mu\text{g g}^{-1}$ HNO₃ + 0.125 $\mu\text{g g}^{-1}$ HCl experienced the most Hg loss. A 75 % reduction in Hg concentration was observed in the 50 ng g⁻¹ HgCl₂ solution, an 89 % reduction in the 200 ng g⁻¹ solution, and an 88 % reduction in the 1000 ng g⁻¹ solution. A less than 10 % reduction in Hg concentration was observed in the other solutions over the six month study period.

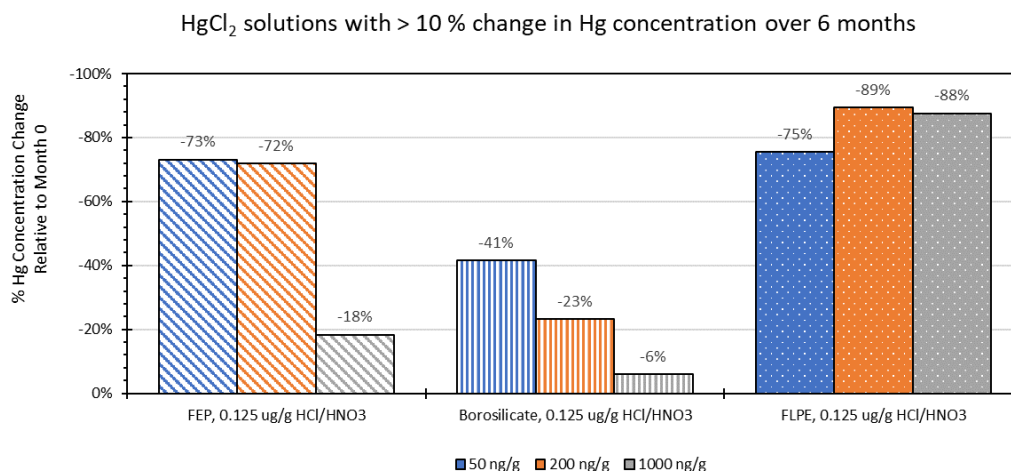


Figure 6 – The percentage change in Hg concentration after storage of HgCl₂ solutions at fridge temperatures for six months. The solutions included are all of those that experienced more than a 10% change in Hg concentration, except for the 1000 ng g⁻¹ borosilicate solution which was included for context.

HgCl₂ salt

The best practice for storing pure HgCl₂ salts that are diluted to prepare working and storage HgCl₂ solution was also investigated. HgCl₂ salt is hygroscopic and therefore repeated exposure to atmosphere and improper storage may affect the moisture content and ultimately the purity and Hg concentration of the salt. Traditionally the best practice for storage of hygroscopic solids is in a desiccator. However, the effects of repeated exposure of the salt to atmosphere during repeated opening to produce stock and working solutions should be assessed. Therefore, two new batches HgCl₂ salt were tested. Both were stored in the same desiccator. Over three months one bottle was opened weekly for two minutes, and the salt stirred with a spatula, the other was left sealed. The total Hg concentration of both salts was determined by isotope dilution mass spectrometry (IDMS). IDMS is a high precision, low uncertainty quantification technique and therefore gave the best resolution to detect any differences in Hg mass fraction between the bottles.

The sealed HgCl₂ salt had an expected Hg mass fraction of 1299 µg kg⁻¹ (Uc = 8.9 µg kg⁻¹; *k* = 2) and an IDMS result of 1300 µg kg⁻¹ (Uc = 28 µg kg⁻¹; *k* = 2) (Table 2). The opened bottle, similarly, had an expected Hg mass fraction of 1298 µg kg⁻¹ (Uc = 9.0 µg kg⁻¹; *k* = 2) and an IDMS result of 1313 µg kg⁻¹ (Uc = 27 µg kg⁻¹; *k* = 2) (Table 2). Therefore, both bottles had expected Hg mass fractions that were within the expanded measurement uncertainty of their associated IDMS result, and when measurement uncertainty was account for, there was no observable difference in Hg mass fraction between HgCl₂ salts stored in a sealed bottle and a bottle that's been opened for two minutes once a week for three months.

Table 2 – Mass fraction and expanded uncertainty (*k* = 2) for the expected and experimental mass fractions of Hg in the sealed and opened HgCl₂ salts stored in a desiccator for three months. The expected mass fraction was calculate using gravimetric data from the preparation of the sample blends for IDMS analysis. The experimental results are the measured Hg mass fractions from the IDMS analysis of the salts.

HgCl ₂ Bottle Status	Expected (Gravimetric)		Experimental Results		
	Hg Mass Fraction	Expanded Uncertainty (<i>k</i> = 2)	Hg Mass Fraction	Expanded Uncertainty (<i>k</i> = 2)	Relative Expanded Uncertainty
	(µg kg ⁻¹)	(µg kg ⁻¹)	(µg kg ⁻¹)	(µg kg ⁻¹)	(µg kg ⁻¹)
Sealed	1299	8.9	1300	28	2.10%
Opened	1298	9.0	1313	27	2.10%

Recommendations

Recommendations for the Storage of HgCl_2 Solutions:

- Solutions prepared from HgCl_2 salts for use with Hg gas generators should only be stored in 0.1 % (v/v) HCl or 0.024 % (v/v) HNO_3 + 0.0144 % (v/v) HCl.
- Solutions prepared from HgCl_2 salts should only be stored in FEP or borosilicate bottles.
- Solutions can be stored at either fridge or ambient temperatures using the bottle types and matrices described in recommendations a and b.
- Temporary heating for up to 24 hours (e.g. during transport) does not affect the Hg mass fraction of the solutions.
- FLPE bottles are not suitable storage containers for HgCl_2 salts in solution with low concentration HCl/ HNO_3 since considerable Hg loss has been observed when stored at both ambient and fridge temperatures.
- HgCl_2 solution matrix decisions should always consider the measurement technique, since for example HNO_3 /HCl mixes may degrade gold traps due to the production of NOCl.

Recommendations for the Storage of HgCl_2 Salts:

- HgCl_2 salts are hygroscopic and should always be stored in a desiccator.
- Stored HgCl_2 salts bottles can be safely opened for up to two minutes at a time for solution preparation for three months without observable effects on the mass fraction of Hg.
- No recommendations can be given for practices after three months from opening since it is out of scope.

Metrological sound calibration protocol to determine the output of Hg^{II} gas generators

Project partner VTT developed the calibration protocol to determine the output of Hg^{II} gas generators, which is available online (<https://zenodo.org/records/10204408>). The other partners, PSA, TÜV Rheinland, JSI, and VSL provided input for the protocol, as the partners have different backgrounds as NMIs, instrument manufactures and test laboratories they provide different points of view to ensure the protocol is applicable through the whole traceability chain from calibrations at NMI to calibrations in the field.

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 elemental mercury (Hg^0) to Hg^{II} converter systems. Using the method developed to determine the converter efficiency of mercury analysers and the results from the storage and stability study metrological traceability to the SI can be obtained. 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 (Figure 7).

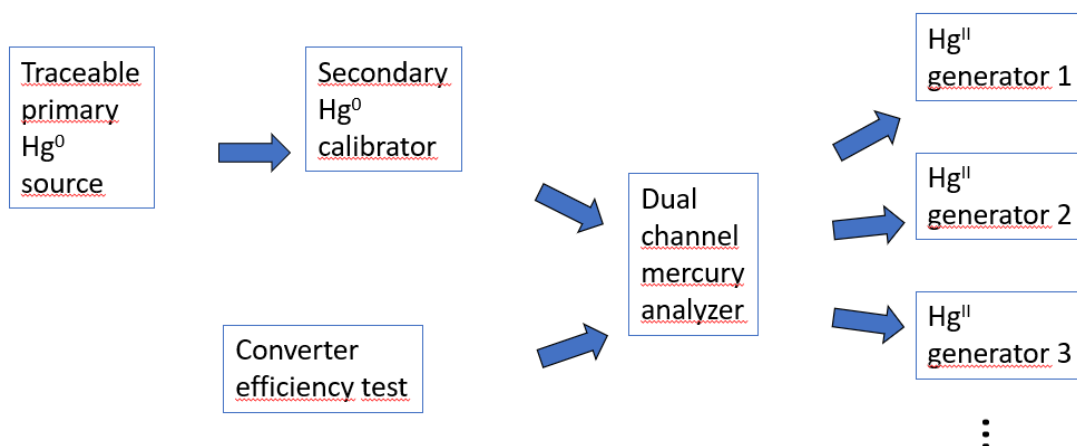


Figure 7 – SI traceability chain of the calibration process for Hg^{II} gas generators.

By performing calibrations according to the protocol a traceability chain starting from primary Hg^0 standards to Hg^{II} concentration measurement results can be established. After calibration the candidate generator receives an SI traceable certificate. This way a chain of calibrations is obtained from the primary standard to gas

generators used every day for monitoring of mercury concentrations in emission sources and in the atmosphere. Validation of the calibration protocol was performed during the performance evaluation (see section 4.3) and reported in “Validation report for the calibration of oxidised mercury gas generators including (1) metrological evaluation of state-of-the-art dual Hg⁰ and Hg^{II} analytical systems, (2) repeatability, reproducibility, and uncertainty evaluation of the calibration procedures at representative concentration levels extended to the low ng/m³” (<https://zenodo.org/records/10204446>).

Conclusion

During the project a method was developed to determine the converter efficiency of mercury analysers and the storage and stability was determined of HgCl₂ solutions and salts, used when operating liquid evaporative Hg^{II} gas generators. These characteristics and the corresponding uncertainties have been determined for the first time and are very important contributions to obtain SI traceability for Hg^{II} concentration measurement results. To ensure the SI traceability from a primary Hg⁰ gas standards is transferred to Hg^{II} gas generators a calibration protocol for the gas generators was developed and validated (see section 4.3) within the project.

The final protocol, good practice guide and validation reports will be transferred to CEN/TC 264 “Air Quality” WG8 “Measurement of total Hg emissions”. The standardisation committee has a new working item proposal to work on the conversion of the protocol into a written documentary standard. This will replace other reference used in industry to calibrate mercury gas generators and ensure SI traceable measurement results for mercury concentrations in emission sources.

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.

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

Characteristics

Hg⁰ and/or Hg^{II} mercury generators are used for the calibration of Hg^{tot} analysis in the field. The performance evaluation organised during the project, for the first time, gathered data on the characteristics of three Hg⁰ and three Hg^{II} gas generators available on the market. During the performance evaluation the following characteristics of the generators were accessed, 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. The performance evaluation is based on the calibration protocols developed for these gas generators that enables them to provide calibration gas mixtures for Hg⁰ and/or Hg^{II} concentrations with traceability to the SI and with a defined uncertainty. Thereby, these off-the-shelf gas generators can fulfil requirements with respect to metrological traceability and measurement uncertainty, as required by, e.g., ISO/IEC 17025.

Hg⁰ gas generators

During the evaluation three Hg⁰ gas generators were tested 1) PSA 10.536 elemental Hg generator, 2) bell-jar and 3) Tekran Model 3425. All generators are saturation gas generators working according to ISO 6145-9 (Gas analysis – Preparation of calibration gas mixtures using dynamic volumetric methods – Part 9: Saturation method). Generator 1 and 3 are continuously generating mercury concentrations, generator 2 requires manual injection of the mercury gas mixtures into an analyser. The measurements for the performance evaluation were performed at VSL (stabilisation period, short-term drift, precision, linearity and bias) and at TÜV Rheinland (sensitivity coefficient to sample gas pressure, surrounding temperature and electrical voltage). VSL performed at least 3 calibrations of the gas generators according to the calibration protocol for Hg⁰ gas generators for multiple Hg⁰ concentrations. Based on the results the characteristics were determined. The stabilisation period varied between 10 minutes and 30 minutes. The short-term drift and precision for all generators was <2%. The interpolation function could be determined for all three generators using the script

developed by VSL to process the data, the best fit for the data of all three generators was a linear function, $c = b_0 + b_1 c_{cand}$ (Figure 8).

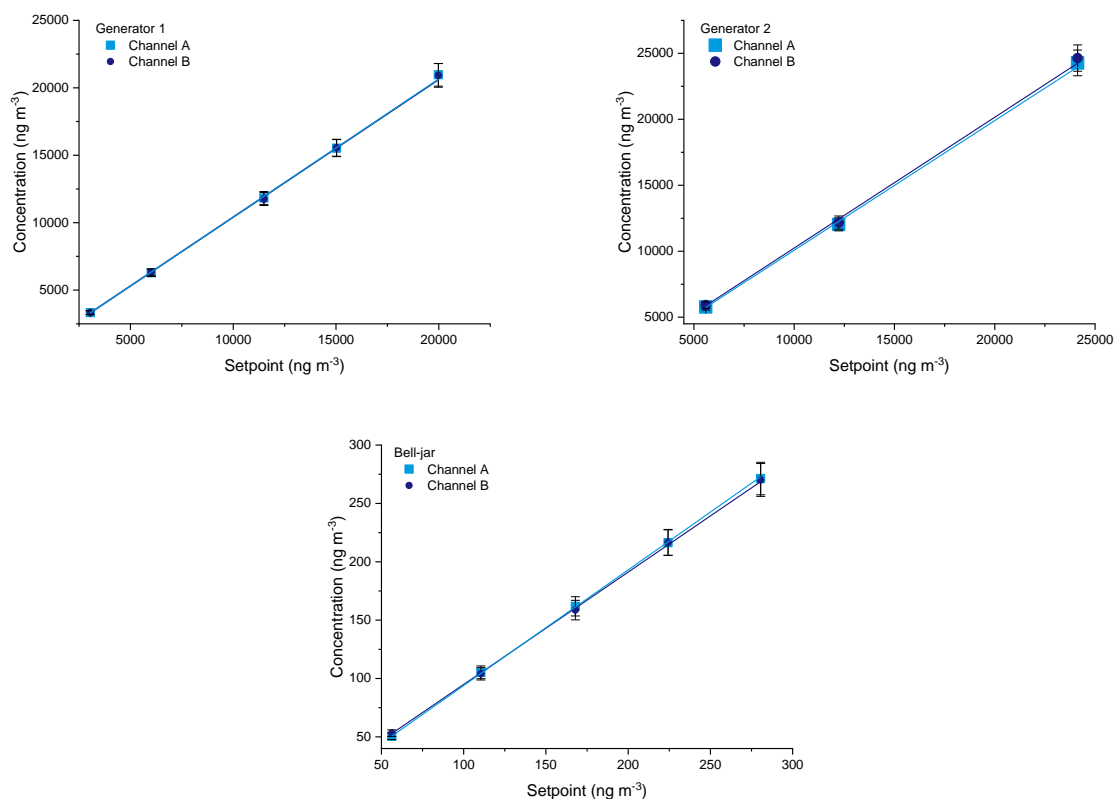


Figure 8 – Calibration results obtained during the performance evaluation. The setpoint of the candidate generator plotted against the calibrated mercury concentration for the three generators. The PSA 10.536 elemental Hg generator is generator 1 and Tekran Model 3425 is generator 2.

Based on the calculated output of the candidate generator the relative deviation (D_{rel}) compared to the setpoint was determined for all three candidate generators (Figure 9). For each generator the data obtained with channel A and channel B of the analyser were comparable within the uncertainty and the data obtained in the different measurement series was also comparable.

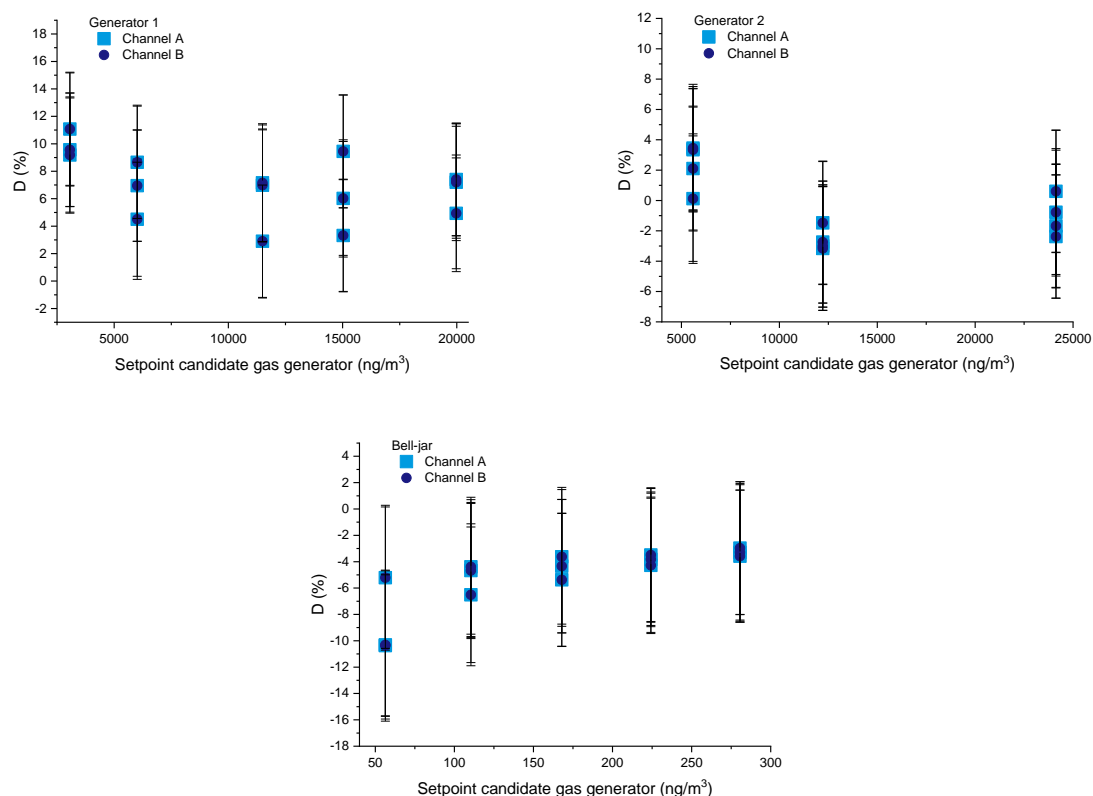


Figure 9 – Results for the relative deviation of the candidate generator setpoint against the calculated output of the candidate generator. The PSA 10.536 elemental Hg generator is generator 1 and Tekran Model 3425 is generator 2.

All three generators could be tested according to the calibration protocol for Hg⁰ gas generators developed within the project. Based on the validation measurements performed at the beginning of the project the protocol was already improved. Based on the results of this performance evaluation no new improvements were done. The results of the performance evaluation with the Hg⁰ gas generators is reported in “Report on the performance evaluation of at least three elemental mercury gas generators on the market” (<https://zenodo.org/records/10219872>).

Hg^{II} gas generators

During the evaluation three Hg^{II} gas generators were provided by IAS GmbH (HovaCAL and HovaCAL SP) and the model developed during the EMPIR 16ENV01 MercOx. The measurements for the performance evaluation were performed at VTT (stabilisation period, short-term drift, precision, linearity and bias) and at TÜV Rheinland (sensitivity coefficient to sample gas pressure, surrounding temperature and electrical voltage). Based on the results the characteristics were determined. The HovaCAL, HovaCAL SP and MercOx generators all have a relatively short stabilisation period of couple of minutes. Baseline drift of the analyser system applied in this study partially prevents more accurate estimation of short-term drift of the generators but both short term drift within hours or longer-term drift within days is relatively small according to corresponding results for repeatability and reproducibility. Output of the generators is linear with correlation coefficient of the linear fit being better 0.99 in all cases at higher concentration range (10 µg m⁻³) studied. At lower concentration range (1 µg m⁻³) detection limit of the analyser system has an effect to that (Figure 10). Measured Hg^{II} concentrations are mostly below the calculated values, typically -4% for the HovaCAL calibrators and -7% for the MercOx calibrator.

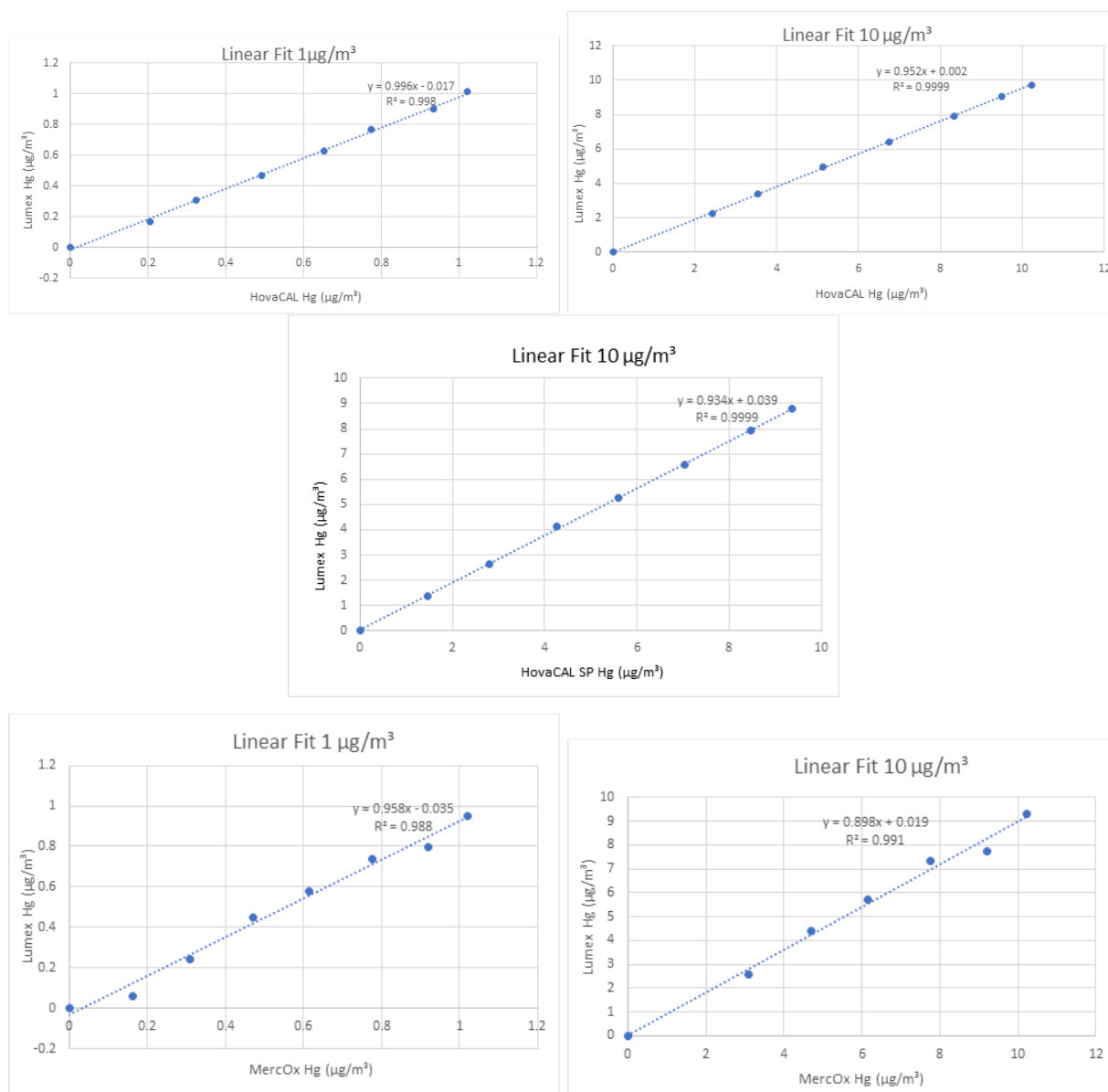


Figure 10 – Calibration results obtained during the performance evaluation. The setpoint of the candidate generator plotted against the analyser response for the three generators.

The results of the performance evaluation showed that the two-step calibration protocol for the selected analyser and Hg^{II} candidate generator is fit for purpose.

The results of the performance evaluation with the Hg^{II} gas generators is reported in “Report on the performance evaluation of at least three oxidised mercury gas generators on the market” (<https://zenodo.org/records/10204452>).

Conclusion

Through the performance evaluation essential data about the characteristics of Hg^0 and Hg^{II} gas generators was obtained. For instrument manufactures 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 gas mixtures and d) making sure the developed calibration protocol is fit for purpose for equipment routinely used in the field. These data are of fundamental importance for standardisation activities of CEN in this field. Therefore, the reports will be disseminated to relevant standardisation committees (e.g. CEN/TC264/WG8).

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.

5 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 ($5 \mu\text{g m}^{-3}$ – $100 \mu\text{g m}^{-3}$, $U = 4 \%$ ($k = 2$) and $0.1 \mu\text{g m}^{-3}$ – $2.1 \mu\text{g m}^{-3}$, $U = 5 \%$ ($k = 2$)) 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 Hg⁰ 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, 4th 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.

6 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/>