D4: Validation report for the calibration of oxidised mercury gas generators including (1) metrological evaluation of state-of-the-art dual Hg^0 and Hg^{II} analytical systems, (2) repeatability, reproducibility, and uncertainty evaluation of the calibration procedures at representative concentration levels extended to the low ng/m^3

19NRM03 SI-Hg D4

Timo Rajamäki[1], Henrik Söderblom[1], Igor Živković[2], Sophie Page[3], Warren Corns[4], Matthew Dexter[4], Iris de Krom[5]

[1] National Metrology Institute VTT MIKES, Tekniikantie 1, 02150 Espoo, Finland

[2] JSI Jozef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

[3] LGC Ltd, National Measurement Laboratory, Queens Road, Teddington, Middlesex, TW11 0LY, UK

[4] P S Analytical, Arthur House, Crayfields Industrial Estate, main Road, Orpington, Kent, BR5 3HP, UK

[5] VSL, Department of Chemistry, Mass, Pressure and Viscosity, Thijsseweg 11, 2629 JA Delft, the Netherlands

Lead partner:	VTT
Project number:	19NRM03
Version No.:	1.4
Due date deliverable:	31-12-2022
Actual submission date:	29-11-2023

VTT

Jožef Stefan Institute

LGC

LUMEX

PSA

TÜVRheinland®
Precisely Right.

VSL
National
Metrology
Institute

Activity number	Activity description	Partners (Lead in bold)
A2.4.1 M22	Based on the outputs from A2.3.1 VTT, in collaboration with LGC, VSL, Lumex, JSI and PSA will provide experimental approaches to validate at least three different types of Hg^{II} gas generators e.g. liquid based and dry based gas generators and Hg^0 to Hg^{II} converter systems. Thereby taking into consideration existing standards such as ISO 10723, EN 14211, ISO 12963, ISO 6143 and ISO 15796 and the US EPA and NIST interim protocols for establishing traceability of Hg^0 evaporative gas generators and Hg^{II} evaporative gas generators. The metrological requirements (e.g. SI-traceability and uncertainty) will also be defined by VTT and VSL and in consultation with the project SC (A4.1.1).	**VTT**, LGC, VSL, Lumex, JSI, PSA
A2.4.2 M24	VTT, PSA and JSI, with support from VSL, Lumex and TÜV Rheinland, will certify at least three different Hg^{II} gas generators (Hg^{II} gas generator, dry based Hg^{II} gas generator and Hg^0 converter Hg^{II} gas generator) according to the protocol developed in A2.3.1. The protocol will be validated for the full range for mercury emissions and low concentrations in the atmosphere in the low ng/m^3 range.	**VTT**, VSL, Lumex, JSI, PSA, TÜV Rheinland
A2.4.3 M25	From the data obtained in A2.4.2, VTT and JSI with support from PSA, Lumex, VSL and TÜV Rheinland will perform a repeatability, reproducibility, bias and uncertainty evaluation for the gas generators, which include Hg^{II} gas generator, dry based Hg^{II} gas generator and Hg^0 converter Hg^{II} gas generator.	**VTT**, JSI, PSA, Lumex, VSL, TÜV Rheinland
A2.4.4 M27	Using the results from A2.4.1 – A2.4.3, a report will be compiled by VTT and JSI, in collaboration with LGC, Lumex, PSA, TÜV Rheinland and VSL, describing the validation of the protocol and how it is to be used in practice as a validation report and guidance document. VTT will send the final protocol to the coordinator. The coordinator will submit it to EURAMET as **D4** "*Validation report for the certification of oxidised mercury gas generators including (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/m^3 level..*	**VTT**, JSI, LGC, Lumex, PSA, TÜV Rheinland, VSL

This project 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.

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Summary

The aim of this task is to validate the traceable calibration protocol for oxidised mercury gas generators used in the field and developed in the 19NRM03 SI-Hg WP2 for mercury concentrations present in the atmosphere at low ng/m^3 levels and higher concentrations from emission sources. Validation of the protocol will be achieved using different types of gas generators, as part of the validation, the repeatability, reproducibility, bias, and uncertainty of the gas generators will be evaluated.

Table of Contents

Introduction

A traceable calibration protocol for calibration of oxidised mercury gas generators was developed that is applicable to different types of dynamic oxidised mercury (Hg^{II}) gas generators commonly used in the field, e.g., liquid-based gas generators (working according to ISO 6145-4), saturated dry based gas generators (working according to ISO 6145-9) and elemental mercury (Hg^0) to Hg^{II} converter systems [1]. The calibration protocol describes the step-by-step process needed to confirm the quantitative output of different types of dynamic Hg^{II} gas generators, to achieve a metrological traceability to the International System of Units (SI) and to determine the expanded uncertainty of the mercury concentration for the output. 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.

In this work the concentrations are expressed in ng/m^3 or µg/m^3 at standard conditions of temperature (293.15 K) and pressure (101.325 kPa).

1. Calibration of the analyser

First, calibration of the selected analyser with an established converter efficiency is performed using a traceable elemental mercury gas standard and second, measurement of the output from the dynamic Hg^{II} gas generator using the calibrated analyser, i.e., calibration of a generator.

1.1 Analyser selection

An analyser is used as a Hg measuring instrument. The specific analyser used, which is suitable for the intended purpose, is chosen using a selection process. In the selection process, at a minimum the operational principle and measurement range needs to be considered: these must cover the range, which is going to be calibrated, and the analyser must be able to measure total mercury concentration (Hg^{tot}) and, preferably, elemental mercury concentration (Hg^{0}) as well. Sensitivity, response function in the used range, detection limit, precision and drift of the analyser must be known.

When studying analytical parameters of oxidised mercury generators, the concentrations of elemental mercury and total mercury are measured. In the ideal case of a Hg^{II} generator the Hg^{0} concentration is absent and the Hg^{tot} concentration corresponds the Hg^{II} concentration. Output gas of a liquid evaporative generator is always humid to some extent, i.e., it contains water in vapour phase.

In this work, a two-channel dual analytical system by Lumex Analytics GmbH was selected. The two-channel dual analytical system consisted of an input unit and two gas channels, for determination of Hg^{0} and Hg^{tot} concentration. To avoid water vapour condensation in the entrance the input unit was heated to 130 °C. The Hg^{0} channel consisted of a heated cell, an atomic absorption spectrometer utilizing the Zeeman background correction (Lumex RA-915F) and a pump. To avoid catalytic reduction of Hg^{II} in the Hg^{0} channel all wetted parts were made of quartz, PTFE, PFA or similar plastic. In the Hg^{tot} channel, Hg^{II} was thermally converted to Hg^{0} and accordingly both Hg^{0} and Hg^{II} were detected to give a response for Hg^{tot}. The Hg^{tot} channel consisted of an atomizer, a heated cell, a similar spectrometer of the same type (Lumex RA-915F) and a pump. The temperature of the atomizer was 700 °C. Two manually operated valves on the input unit could direct ambient air in the channel via an Hg scrubber before entering the measurement cell for zeroing the equipment or analyte gas into the measurement cells for analysis.

1.2 Traceability

The analyser needs to be calibrated to ensure the traceability of Hg^{II} measurements. A traceable primary or secondary Hg^{0} or Hg^{II} gas standard should be used to perform the calibration.

In this work, a secondary elemental mercury generator was used for Hg^{0} calibration of the analyser. This generator was a transportable device that was shipped to other laboratories that do performance evaluation of oxidised mercury gas generators. It has been used on actual test sites to calibrate the dual analytical system used for performance evaluation to ensure the measurement results are traceable to the SI-units. The P S Analytical (PSA) 10.536 elemental mercury generator based on saturation principle was calibrated at VSL using the primary reference standard according to a calibration proposal developed in SI-Hg WP1. The operation of the secondary mercury generator was further established by recalibrating it after returning it to VSL after the performance evaluation campaign.

The primary Hg^{0} gas standard developed at the Van Swinden Laboratory (VSL) was used to calibrate the secondary elemental mercury generator before it was shipped to the actual measurement

laboratories. This primary Hg^0 gas standard was developed to establish metrological traceability of Hg^0 concentration measurement results, based upon a gravimetric approach, for both ambient air levels and higher concentrations [2]. Using specially designed diffusion cells, Hg^0 was vaporized under well-controlled conditions (temperature, flow, and pressure) according to ISO 6145-2. By weighing the diffusion cells at regular time intervals with a high-resolution balance, an accurate mass flow rate, traceable to the SI, was obtained. After mixing the mass flow of Hg^0 with an accurately measured mass flow rate of air, the primary Hg^0 gas standard was obtained in the range between 0.1 µg/m^3 and 100 µg/m^3.
By using the primary Hg^0 gas standard to calibrate the two-channel analytical system, the traceability of Hg^{II} measurements has been established as follows:

- Hg^0 → $HgCl_2$ → Hg^0 (measurement) ↔ Hg^0
- Hg^0 → ($HgCl_2$ + Hg^0) → Hg^{tot} (measurement) ↔ Hg^0

Results of the calibration of the PSA gas generator output for elemental mercury were determined in two ranges due to limitations of the VSL primary gas generator. The first range (Range 1) was valid for the measurements performed in study. c_{cand} is the setpoint and c_i is the calculated output in ng/m^3 including uncertainty *U*.

Range	**Setpoint nr.**	$c_{cand(i)}$ **(ng m^{-3})**	c_i **(ng m^{-3})**	$U(c_i)$ **(ng m^{-3}) (*k* = 2)**	$U(c_i)$ **(%) (*k* = 2)**
1	1	3 046	3 350	137	4.1
	2	6 012	6 415	262	4.1
	3	11 493	12 112	496	4.1
	4	15 027	15 971	652	4.1
	5	19 977	21 198	864	4.1
2	1	19 977	21 198	864	4.1
	2	40 137	42 820	1 738	4.1
	3	60 049	63 182	2 624	4.2
	4	80 016	83 282	3 386	4.1
	5	99 868	104 885	4 258	4.1

The following regression coefficients were determined for a linear function

$$c = b_0 + b_1 c_{cand}$$

	Range 1		**Range 2**	
	Parameters	**Standard error**	**Parameters**	**Standard error**
b_0	142	34	303	160
b_1	1.0493	0.0058	1.0463	0.0043

1.2.1 Establishing Converter Efficiency

To ensure traceability to all mercury species the converter efficiency of the analyser needs to be established. The efficiency of the Lumex RA-915F converter was determined by LGC as part of SI-Hg WP2 task 2.1.

To determine the efficiency of a thermal converter that transforms oxidised mercury compounds to elemental, pure Hg^0 and Hg^{II} gases needed to be measured. In task 2.1, the PSA mercury gas generators 10.534 (Hg^0) and 10.536 ($HgCl_2$) were used. 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 Hg^0 species was not available, independent but parallel AAS and ICP-MS/MS detectors were used. The RA-915F AAS detector could measure only Hg^0 or Hg^{II} transformed to Hg^0 by a converter, and the ICP-MS/MS is species independent, and therefore reports total Hg. The underlying principle of the method is that when Hg^0 gas is introduced into the elemental and total Hg detectors, both detectors should provide signal for the total Hg in that gas. If a pure Hg^{II} gas (e.g., $HgCl_2$) 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 total Hg detector should display Hg signal proportional to the Hg^{II} fraction and the instrument sensitivity. Based on these considerations, two ratios can be calculated **(equations (**1)**(2)**. If the Hg^{II} gas passes through a thermal converter before it reaches the AAS detector, the AAS signal should be related to the converter efficiency. Therefore, **(1(2** can be used to estimate the converter efficiency **(equation (**3)**)**.

(1)
$$R_{Ref} = \frac{C_{AAS}^{Hg^0}}{{}^{i}Hg_{ICPMS}}$$

(2)
$$R_C = \frac{C_{AAS}^{Hg(II)}}{{}^{i}Hg_{ICPMS}}$$

(3)
$$E_C = \frac{R_C}{R_{Ref}}$$

where:

- $\mathbf{R_{Ref}}$ is the reference signal ratio produced by introducing only Hg^0 gas to the detectors
- $\boldsymbol{R_c}$ is the apparent Hg ratio produced by introducing gas from a Hg^{II} generator to the detectors via a thermal converter
- $\mathbf{C_{AAS}^{Hg^0}}$ is the Hg concentration determined by the AAS detector (calibration accuracy is irrelevant), using Hg^0 gas generator source
- $\mathbf{C_{AAS}^{Hg(II)}}$ is the Hg concentration determined by the AAS detector (calibration accuracy is irrelevant), after passing Hg^{II} gas through a thermal converter.
- $\mathbf{{}^{i}Hg_{ICPMS}}$ is the Hg signal from the ICP-MS, monitoring the i-th Hg isotope

Instrument parameters such as flow rates, temperature, and Hg mass flow were selected to fall within prescribed PSA generator manufacturer ranges, and to ensure there were observable differences between gas mixture Hg signals and the background signal. The total output flow rate of the generators was set to 10 L min^{-1} of Ar and the Hg concentration was around 7 µg m^{-3}. A background equivalent concentration (BEC) was obtained at the start of the measurement sequence and between the measurement of each generator output. The AAS BEC for the Hg^0 and $HgCl_2$ generators was 0.3 and 0.4 µg m^{-3} respectively. The ICP-MS background for the Hg^0 and $HgCl_2$ generators were approximately 800 and 1000 cps respectively. These backgrounds were 4 % to 6 % of the generator AAS and ICP-MS signals. No blank correction was performed since the blank source and its conversion efficiency is difficult to estimate for each species. The Lumex through flow rate was 1 L min^{-1} and the flow to the ICP-MS/MS was about 1.2 L min^{-1}. The desired flow rates through different components of the set-up were achieved using PFA tubing of different lengths and diameters to divert and limit flows. The PFA tubing was kept at room temperature, but the lengths were kept as short as possible and the tubing diameters small to minimise any Hg loss during transport. Flex-Cal H (500 mL min^{-1} to 50 L min^{-1}, Messa Lab, S/N 175689) was used to determine the generators' total flow, the waste flow, flow through the Lumex analyser. However, the split flow to the ICP-MS/MS could not practically be measured directly so was calculated as total-waste-Lumex flows. It should be acknowledged that the measurement of one component's flow rate introduced a change of all flows, because of the Flex-Cal H backpressure. Therefore, the flow measurement procedure is iterative, proportionally accounting for the backpressure effect. Since the set-up relies on critical orifice flow control, the exact flows rates were not needed if the total flow from the two generators were the same. Therefore, it was of paramount importance to ensure the total gas flow from the Hg^0 and $HgCl_2$ generators was the same. The mass-flow calibrator, used in this study, provides accurate flow measurements with relative uncertainty of only 0.18 %. The relative standard deviation of all flow measurements was on average 0.09 % of the measured flow rate for both the Hg^0 and $HgCl_2$ generators. A schematic diagram of the setup along with the nominal flows and Hg concentrations is presented in **Figure 1**. The Hg^0 and $HgCl_2$ 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 AAS detector. However, the set-up can be easily modified to accommodate separate converters and detectors by linking them with a short piece of PFA tubing. The coupling of the generators to the ICP-MS was achieved in the same way as described in Petrov *et al.* (2020) [3].

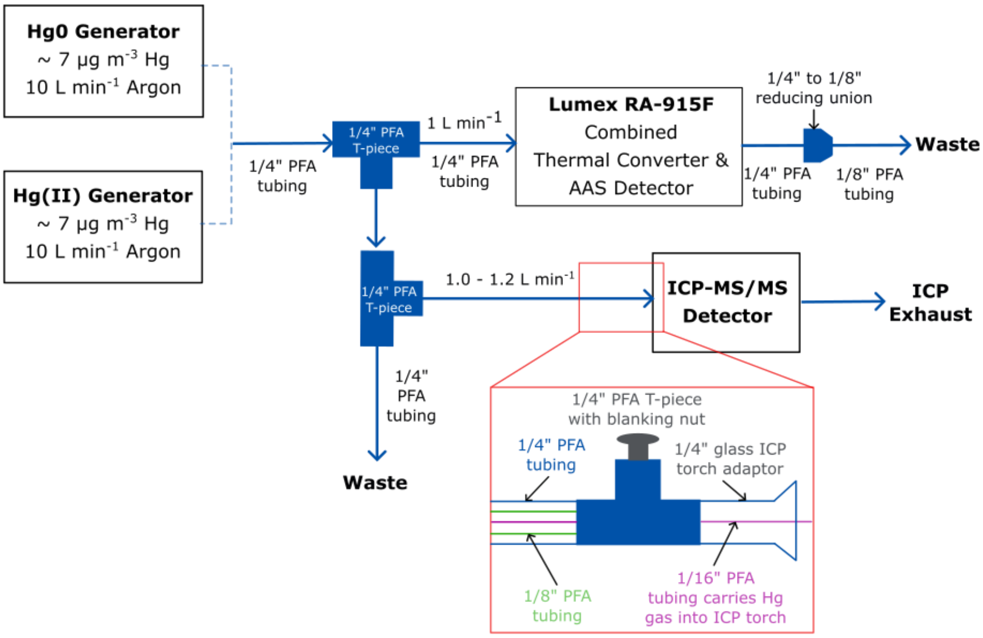


Figure 1: *Schematic diagram of instrumental setup for the determination of thermal converter efficiency. The* Hg^0 *generator (PSA 10.534) and* Hg^{II} *generator (PSA 10.536) were connected to the setup independently. The torch adaptor is based on the set-up from Petrov et al. (2020) [3]. All tubing was kept at room temperature since we did not have facilities to heat the tubing.*

Before measurements were obtained, both generators were purged with N_2 for at least 72 hours. On the morning of the first day of measurement, the purge gas was changed to Ar 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. An increase in Hg signal on both the AAS and ICP-MS/MS detectors was evident within a couple of minutes, signal stabilisation was achieved within 15 minutes, and rinsing to blank levels using only the diluent gas was achieved in less than 30 minutes. Signal stabilisation and rinsing to blank levels were shorter than 10 minutes for the Hg^0 generator.

To determine the converter efficiency, the following sequence was analysed: Blank, $HgCl_2$, Blank, Hg^0, Blank, simultaneously on the ICP-MS/MS and AAS detectors. The Lumex AAS detector measured in continuous mode with a sampling frequency of 1 point per second (1 Hz). A baseline correction was performed at the start of the day using the background Hg signal from the PSA 10.534 generator with 10 L min^{-1} diluent flow, and no reservoir flow. The ICP-MS/MS was operated in time resolved analysis mode, monitoring mercury mass-to-charge ratios 199, 201, and 202, with a 0.1 s sampling time, and 10 minutes of acquisition per sample.

To determine converter efficiency, the ICP-MS/MS ^{202}Hg and AAS signals were ratioed for both the Hg^0 and $HgCl_2$ generators using **(1(2**. The difference in sampling frequency between the detectors meant that point-to-point ratios could not be calculated. Instead, the AAS and ICP-MS/MS signals were averaged over the 10-minute acquisition time, and the averaged signals were ratioed. Converter efficiency was then calculated using **(3**. Uncertainty was calculated using the standard deviation of the ICP-MS/MS and AAS signals. The standard deviations were combined to calculate the standard uncertainty of each ratio, and the ratio standard uncertainties combined to calculate the converter efficiency uncertainty for each measurement day.

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. The total generator flows, flow through the Lumex system, and waste split flow were measured on the morning of each measurement day to ensure flow consistency. However, since the flow conditions were the same for both generators and flow rates were similar across all measurement days, the absolute flow rates are not critical.

The following result for converter efficiency was determined by LGC at SI-Hg WP2 Task 2.1 (**Table 1**):

Table 1: *Results from the converter efficiency experiments conducted between the 27th October and 1st November 2022 for the RA-915F Lumex converter using the PSA 10.534 and 10.536 Hg^0 and $HgCl_2$ generators. The Lumex/ICP ratio is the ratio of averaged ^{202}Hg ICP-MS/MS signal and the AAS signal over 10 minutes* ***(1(2)****. 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 oxidised Hg gas 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.

1.3 Measurement plan

A measurement plan for calibration was made. In the plan, the calibration range and the calibration points within the range were determined, and the measurement sequences needed to investigate the generators repeatability and reproducibility, linearity, and hysteresis, were planned.

The selected calibration points should include at least points close to both minimum and maximum values of the analyser's measurement range, and at least one point between those. In case the analyser output was not linear, at least five test points were needed. It is recommended to distribute the selected points equally over the operational range. Additionally, it is recommended to include typical measurement points used during actual measurements. This ensures enough information for linearity analysis is obtained and optimises the corrections and fitting curves used for the analyser by avoiding large interpolations based on calibration data.

To observe the possible hysteresis from the calibrations results, the selected calibration points were generated in order, from minimum towards maximum value, and same in the opposite direction.

In this work, six different Hg^0 concentrations were selected as calibration points. The specific values of concentration are listed with other results. During the calibration each measurement point was measured more than once, and the average of the recorded readings was used as a measured result for that point. Short term repeatability was calculated as a standard deviation from these.

The calibration was repeated several times during the test work to determine the reproducibility of the analyser. The linearity of the instrument was analysed from the results.

1.4 Analyser preparation

Before starting the actual calibration measurements, the analyser was allowed to warm-up according to the manufacturer’s recommendation. The instrument zero level (baseline) of the analyser was checked after the warm-up time was completed. As recommended, the zero level was checked after every measurement and adjusted if necessary.

In this work, typically a warm-up time of minimum of two hours was needed. The warm-up time may change according to the set-up and/or the equipment, e.g., the manufacturer of the two-channel analyser recommends five hours warm-up time, or even longer.

Zero level for the analyser was checked after the warm-up time. Especially during the first few hours of measurements a drift of the analyser zero level was still observed. Due to this, the analyser zero level was checked frequently until specified stability was observed and the analyser results were corrected taking the analyser zero drift into account.

1.5 Calibration gas mixtures

Calibration gas mixtures were generated using the primary Hg^0 gas standard. The uncertainty of generated gas mixtures needed to be evaluated and documented.

In this work, the reference gas mixtures generated by the secondary Hg^0 gas standard was used to directly calibrate the analyser. Six different Hg^0 concentrations (see 1.3 Measurement plan) are generated.

The calibration is performed at laboratory conditions at ambient pressure and in room temperature (20 °C). Calibration medium (instrument air) is the same as during usage. The calibration points include both minimum and maximum flow control set points, and the actual flow set points during usage.

1.6 Measurements

The generated gas mixture was supplied from the secondary Hg^0 gas standard to the analyser through the inert tubing and fittings made only from PTFE or PFA. The analyser reading was observed and until the signal had stabilized. After the stabilization period the analyser reading was recorded a sufficient period to collect enough data for the result analysis to be achieved considering the setup response time and measurement time, e.g., five minutes.

In this work, after two to five minutes typical stabilisation time, the average response displayed by the two-channel analyser was recorded for both channels (Hg^0 and Hg^{tot}) over a period of approximately one to two minutes (more than 50 points with 1 s intervals). Recorded measurement data included the supplied concentration from the gas standard and the outputs from the analyser.

The calibration is repeated three times on different days to get data for the reproducibility analysis. Accordingly, there was a proper data for the hysteresis and the linearity analyses, too (see 1.3 Measurement plan).

1.7 Data analysis

The recorded measurement data was analysed for hysteresis, linearity, standard deviation, repeatability, and reproducibility.

The hysteresis of the analyser was determined from measurements of the Hg concentrations by going through the measurement points from the lowest Hg concentration to the highest Hg concentration and back to the lowest Hg concentration.

The average and the standard deviation for the recorded analyser readings were calculated.

The calibration data was analysed according to EN ISO 6143:2006 [4]. The obtained regression coefficients could then be used to calculate the mercury concentrations in the real on-site measurements, or from an Hg^0 or Hg^{II} generator.

The analyser software settings and coefficients saved to the device memory needed to be checked and documented and the settings kept constant during the actual use after calibration measurements.

In this work, the measurement points were selected in such an order that concentration levels in upper and lower part of the measurement range alternate. Some measurement points were repeated from the lowest Hg concentration to the highest Hg concentration and back to the lowest Hg concentration and the hysteresis was calculated from the difference of the ascending and descending responses.

The calibration data was analysed according to EN ISO 6143:2006 [4], which is an international standard providing methods to determine the analysis function and to calculate the concentration and corresponding uncertainty of calibration gas mixtures.

A linear fit was used to plot the data obtained with primary Hg^0 gas standard and the two-channel analyser. The regression coefficients and full covariance matrices were obtained for each measurement.

The repeatability was determined by interpolating the calibration data obtained on two latter measurement points as unknown in the calibration on the first measurement whereas the reproducibility was determined by interpolating the calibration data obtained on two latter measurement days as unknown in the calibration on the first measurement day. The repeatability and reproducibility were calculated as the standard deviation of the measurements.

1.8 Results from characterization of Lumex dual channel mercury analyser

To be able to characterize the uncertainty of the generators, the uncertainty of the Lumex dual channel mercury analyser needed to first be determined. The following parameters were included in the model equation of the Lumex dual channel mercury analyser: standard deviation, linearity, repeatability, and reproducibility.

The concentration for $\mathrm{Hg^{II}}$ was obtained with $\mathrm{Hg^{II}} = \mathrm{Hg^{tot}} - \mathrm{Hg^{0}}$. The concentrations were obtained with the following formulas:

$$Hg_{Lumex}^{tot} = P_{reaction} * Hg^{tot}$$

$$Hg^{TOT} = \frac{Hg_{Lumex}^{TOT}}{P_{reaction}}$$

$$Hg_{cal}^{tot} = a_{Hg^{TOT}} Hg^{tot} + b_{Hg^{TOT}} - y_{drift}^{tot} + \delta_{ref.\ gas}^{tot} + \delta_{repeat.}^{tot} + \ \delta_{repro.}^{tot} \ (1)$$

$$Hg_{cal}^{0} = a_{Hg^{0}} Hg^{0} + b_{Hg^{0}} \ - y_{drift}^{0} + \delta_{ref.\ gas}^{0} + \delta_{repeat.}^{0} + \ \delta_{repro.}^{0} \ (3)$$

$$Hg^{2+} = Hg_{cal}^{tot} - Hg_{cal}^{0}$$

$$\begin{aligned} Hg^{II} = {} & \frac{a_{Hg^{tot}}}{P_{react}} Hg^{tot} + b_{Hg^{tot}} - y_{drift}^{tot} + \delta_{ref.\ gas}^{tot} + \ \delta_{repeat.}^{tot} + \ \delta_{repro.}^{tot} \\ & - \left(a_{Hg^{0}} Hg^{0} + a_{Hg^{0}} - y_{drift}^{0} + \delta_{ref.\ gas}^{0} + \ \delta_{repeat.}^{0} + \ \delta_{repro.}^{0} \right) (3) \end{aligned}$$

The drift of analyser baseline was considered as generator specific. Which means that for every characterized generator, the corresponding drift of analyser baseline for that measurement was added to the value of the analyser. This means there was no general drift uncertainty term added to the analyser.

The next sections explain the process of obtaining the different uncertainty terms.

1.8.1 Linearity

The Lumex dual channel mercury analyser had two channels. One channel, $\mathrm{Hg^{tot}}$, gives the total Hg concentration in the studied gas. The other channel, $\mathrm{Hg^{0}}$, gives the $\mathrm{Hg^{0}}$ concentration.

The $\mathrm{Hg^{tot}}$ channel applied a thermic reaction to convert the gas into solely $\mathrm{Hg^{0}}$. This reaction has an efficiency of 86%, which is taken into consideration by using $\mathrm{Hg^{tot}} = \frac{\mathrm{Hg_{Lumex}^{tot}}}{\mathrm{P_{reaction}}}$.

Both channels were calibrated using the PSA 10.536 $\mathrm{Hg^{0}}$ reference gas generator by creating a linear regression model by using the formula:

$$Hg_{PSA} = aHg^{X} + b \ (4)$$

All values were used simultaneously in the model without any weights. The values were collected on four different days: 8.2, 10.2, 13.2 and 14.2. VSL provided the corrections terms for the reference gas concentration, which was applied when calculating the linear regression model:

$$a_{ref.gas} Hg^{ref} + b_{ref.gas} = Hg_{PSA}, \qquad a = 1.0493, \;\; b = 0.142$$

The values Hg^{x} in the eq. 4 were calculated using a moving average to reduce the standard deviation and noise of the obtained values. Lumex dual channel mercury analyser measures datapoints every second. A moving average for a specific datapoint i, was calculated using a sidestep (ss) with the formula:

$$\mu_{MA_i} = \frac{1}{2ss+1} \sum_{j=i-ss}^{i+ss} x_j$$

The mean of the moving averages of the whole dataset is then calculated with:

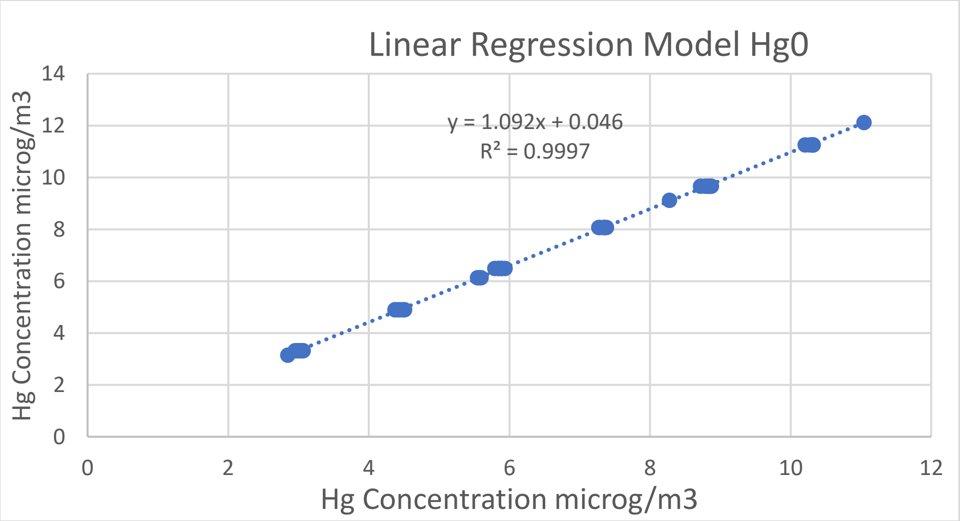
$$\mu_{MA} = \frac{1}{n-2ss} \sum_{i=ss+1}^{n-ss} \mu_{MA_i} \;(5)$$

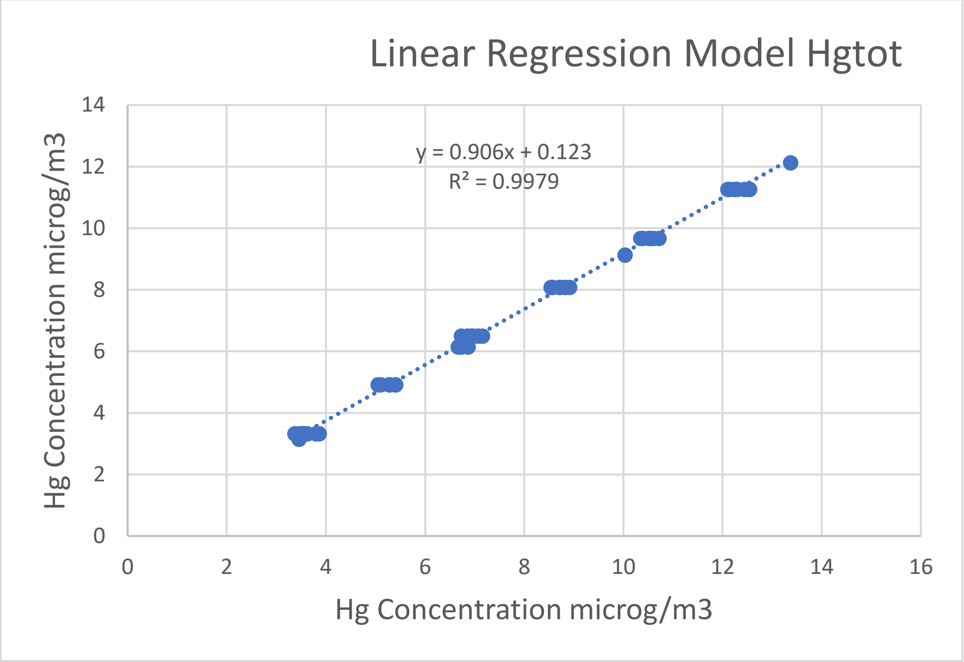
The regression models and the corresponding values were generated by Excel. The formula

$$Hg^{TOT} = \frac{Hg^{TOT}_{Lumex}}{0.86}$$

has been used before calculating the regression model.

The following plots and values were obtained:





The following values for the linear regression model were obtained:

	Value	*Standard Error*
b_{Hg^0}	0.046	0.019
a_{Hg^0}	1.092	0.003

	Value	*Standard Error*
$b_{Hg^{TOT}}$	0.123	0.048
$a_{Hg^{TOT}}$	0.906	0.006

1.8.2 Mean and Standard Deviation

The parameters $\mathrm{Hg}_{\mathrm{Lumex}}^{\mathrm{tot}}$ and Hg^0 were assumed to have a normal distribution, and therefore, their means were calculated using the formula:

$$\mu_{Hg^X} = \frac{1}{n}\sum_{i=1}^{n} x_i$$

where n is the number of datapoints and x_i is the value of a single data point.

The standard deviation of the same parameters was calculated using the formula:

$$\sigma_{Hg^X} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i - \mu)^2} \quad (6)$$

In principle, the values inside the interval of interest are always first transformed by taking the moving-average according to eq. (5). In other words, the mean is the mean of the moving average.

1.8.3 Repeatability and reproducibility

The repeatability was calculated by taking the standard deviation of different measurements on the same day. The day chosen was 31.3.2023, and the analyser had been reset before the start of the measurements.

During these measurement, clean air flows through the analyser between measurement points, which has been assumed to correspond to making separate measurements independent of each other. However, due to the nature of the gas under study, a drift in the zero level can be seen at this measurement as well as drift of analyser zero reading. Therefore, the value given by the analyser at a clean air measurement point, was subtracted from the following Hg^x measurement value.

Both terms were calculated with the linear regressions applied.

The repeatability was calculated by using 5 measurement points. The values were calculated to be:

$$\delta^0_{repeat.} = 0.045$$

$$\delta^{tot}_{repeat.} = 0.042$$

The reproducibility of the analyser was done in the same manner as with the repeatability, but instead the measurement values were taken from three different days: 30.3, 31.3, 4.4. By using only one measurement value per day, the reproducibility value corresponded well with the repeatability. If an average of several measurement points per day were used (ca. 5 points), the reproducibility decreased significantly and may not correspond to the system accurately.

To minimize the time the drift effect on the measurements, the points were chosen as in the beginning of the measurement as possible. The obtained values were:

$$\delta^0_{repro.} = 0.045$$

$$\delta^{tot}_{repro.} = 0.038$$

These uncertainties were calculated assuming they would have a normal distribution. This is incorrect considering the small number of points (reproducibility have as low as 3). Therefore, their uncertainties should have been higher considering a rectangular distribution should have been applied.

1.8.4 Combined standard uncertainty

The parameters presented in the previous sections, can now be used to calculate the combined standard uncertainty. The following tables show the uncertainty budgets for $\mathrm{Hg}^{\mathrm{tot}}_{\mathrm{Cal}}$ and $\mathrm{Hg}^{0}_{\mathrm{Cal}}$, with explanations of the values following:

$$Hg^0_{cal} = a_{Hg^0}Hg^0 + b_{Hg^0} + y^0_{drift} + \delta^0_{repeat.} + \delta^0_{repro.}$$

	Mean	err	Sensitivity	Contribution

Hg^0[1]	μ_{Hg^0}	σ_{Hg^0}	a_{Hg^0}	$1.092\sigma_{Hg^0}$
a_{Hg^0}	1.092	0.003	μ_{Hg^0}	$0.003\mu_{Hg^0}$
b_{Hg^0}	0.046	0.019	1	0.019
y^0_{drift}		S_{res}	1	S_{res}
$\delta^0_{ref.\ gas}$		$0.0205\mu_{ref.gas^0}$	1	$0.0205\mu_{ref.gas^0}$
$\delta^0_{repeat.}$		0.045	1	0.045
$\delta^0_{repro.}$		0.045	1	0.045

$$Hg^{tot}_{cal} = a_{Hg^{TOT}} \frac{Hg^{tot}_{Lumex}}{P_{reaction}} + b_{Hg^{TOT}} + y^{tot}_{drift} + \ \delta^{tot}_{repeat.} + \ \delta^{tot}_{repro.}$$

	Mean	err	Sensitivity	Contribution
Hg^{tot}_{Lumex}[1]	$\mu_{Hg^{tot}_{Lumex}}$	$\sigma_{Hg^{tot}_{Lumex}}$	$\frac{a_{Hg^{tot}}}{P_{reaction}}$	$\frac{0.906}{0.86}\sigma_{Hg^{tot}_{Lumex}}$
$P_{reaction}$	0.86	$\frac{0.01}{\sqrt{3}}$	$\frac{a_{Hg^{tot}}\mu_{Hg^{tot}_{Lumex}}}{P^2_{reaction}}$	$\frac{0.906\mu_{Hg^{tot}_{Lumex}}}{0.7396}\frac{0.01}{\sqrt{3}}$
$a_{Hg^{tot}}$	0.906	0.006	$\frac{\mu_{Hg^{tot}_{Lumex}}}{P_{reaction}}$	$\frac{\mu_{Hg^{tot}_{Lumex}}}{0.86}0.006$
$b_{Hg^{tot}}$	0.123	0.048	1	0.048
y^0_{drift}		S_{res}	1	S_{res}
$\delta^{tot}_{ref.\ gas}$		$0.0205\mu_{ref.gas^{tot}}$	1	$0.0205\mu_{ref.gas^{tot}}$
$\delta^{tot}_{repeat.}$		0.042	1	0.042
$\delta^{tot}_{repro.}$		0.038	1	0.038

The mean values of the linear regression model parameters are the parameter values themselves. The error of the regression slope, a, has been calculated according to

$$S_a = \sqrt{\frac{1}{n-2} * \frac{\sum_{i=1}^{n}(y_i - \hat{y_i})^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}} \ (7)$$

where y_i is the value of the reference gas, $\hat{y_i}$ is the predicted value by the linear regression model, x_i is the value of $\mathrm{Hg^X}$ and, $\bar{x}_i$ is the mean value of $\mathrm{Hg^X}$.

The error of the intercept, b, is calculated by:

$$S_b = S_a * \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x}_i)^2}{n} * \bar{x}^2} \ (8)$$

---

[1] Values may differ since they are taken per measurement.

The mean of the reaction efficiency, $P_{reaction}$, was determined to be $86\% = 0.86$, with an uncertainty, $u_{P_{reaction}}(k = 2) = 4\% = 0.04$. In the calculations the reported $u_{P_{reaction}}(k = 1)\ 2\% = 0.02$ was used. It has been assumed that the parameter has a rectangular distribution, and therefore, the standard deviation was calculated using the formula:

$$\sigma_{P_{reaction}} = \frac{u_{P_{reaction}}}{\sqrt{3}}$$

The values of the mean of the reference gas, $\mu_{ref.gas^{tot}}$ and $\mu_{ref.gas^{tot}}$, were calculated according to:

$$\mu_{ref.gas^X} = \frac{b_{Hg^X} + a_{Hg^X}\mu_{Hg^X} - b_{ref.gas}}{a_{ref.gas}} \quad (9)$$

with the parameter X either being tot or 0. VSL obtained an uncertainty for their regression model to be 4.1% $(k = 2)$ of the reference gas value, and 0.0205 $(k = 1)$ was used in the calculations. The error, $\delta^X_{ref.gas}$, can then be calculated with $\mu_{ref.gas^X}$.

NOTE: The mean value $\mu_{ref.gas^X}$ is not exact. In eq. 9, parameters from two linear regression models are used to determine $\mu_{ref.gas^X}$, which obviously does not result in an exact result. This was one way to integrate the reference gas uncertainty to the uncertainty budget.

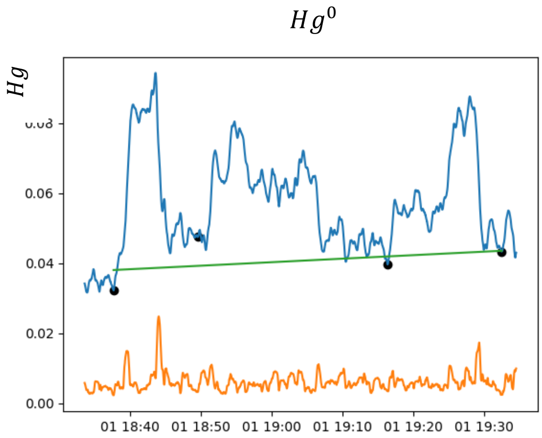
The measurement period specific drift of analyser baseline occurring during a measurement was added as a correction. In this case the error was added to the uncertainty budget as the standard deviation of residuals:

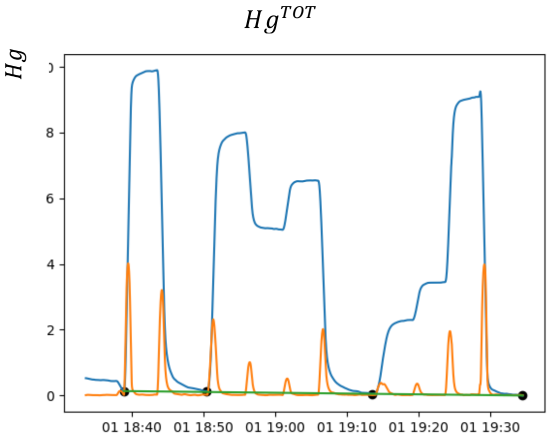
$$S_{res} = \sqrt{\frac{\sum(y - y_{est})^2}{n - 2}}$$

The drift was calculated by fitting a curve to the zero-level measurements points of the measurement. To reduce manual work, an algorithm was applied to automatically locate where these points were as well as when the standard deviation was low. The function that is studied at different intervals is the following:

$$f = w * \mu_{Hg^X} - (1 - w)\sigma_{Hg^X}$$

Examples of the automatized linear fit:





The blue lines are the values of the measurement (moving averages), the yellow ones are the standard deviations, and the green ones are the fitted curve based on the black points that correspond to the zero-level measurements.

The points were taken only per measurement and the number of points used differ greatly.

NOTE: This automatized script does not retrieve the exact zero-levels points. The Hg^0 were difficult for the script to retrieve accurately.

The repeatability terms were only considered as uncertainties and do not affect the absolute value of a measurement.

To calculate the combined standard uncertainty, the sensitivity coefficient, c_i, of each parameter was needed. According to the standard practice of the propagation of uncertainty, c_i of a parameter p_i is calculated as

$$\frac{\partial Hg^X}{\partial p_i}$$

The combined standard uncertainty can then be calculated as

$$u_c = \sqrt{\sum_{i=1}^{n} \left(c_i u(x_i)\right)^2}$$

where c_i is the sensitivity coefficient for the parameter in question and $u(x_i)$ is the same parameter's standard uncertainty.

The combined standard uncertainties for $\mathrm{Hg}_{\mathrm{Cal}}^{\mathrm{tot}}$ and $\mathrm{Hg}_{\mathrm{Cal}}^{0}$ were then used for determining the uncertainty of $\mathrm{Hg}^{\mathrm{II}}$.

$$Hg^{II} = Hg_{Cal}^{tot} - Hg_{Cal}^{0}$$

Parameter	Mean	Error	Sensitivity	Contribution
Hg_{Cal}^{tot}	$\mu_{Hg_{Cal}^{tot}}$	$u_c(Hg_{Cal}^{tot})$	1	$u_c(Hg_{Cal}^{tot})$
Hg_{Cal}^{0}	$\mu_{Hg_{Cal}^{0}}$	$u_c(Hg_{Cal}^{0})$	-1	$u_c(Hg_{Cal}^{0})$

The combined standard uncertainty is then be expressed as

$$u_c(Hg^{II}) = \sqrt{u_c(Hg_{Cal}^{TOT})^2 + u_c(Hg_{Cal}^{0})^2} \quad (10)$$

$\mathrm{Hg}^{\mathrm{TOT}}$

```
[[10.19003187  9.23206981]
 [ 9.23206981  8.38143877]]
```

Hg^{0}

```
[[7.02348881 7.6713485 ]
 [7.6713485  8.38143877]]
```

Following here is an example of the uncertainty budget of the two channels. The values are taken 10.2.2023, with the gas going through the analyser coming from HovaCAL gas generator. The theoretical value of the concentration from the generator is $\mathrm{Hg}^{\mathrm{II}} = 7.057 \frac{\mu g}{m^3}$.

	Contribution
Hg^0	0.004
a_{Hg^0}	0.00007
b_{Hg^0}	0.019
y^0_{drift}	0.005
$\delta^0_{ref.\ gas}$	-0.001
$\delta^0_{repeat.}$	0.045
$\delta^0_{repro.}$	0.045

$u_c\left(Hg^0_{cal}\right) \;=\; 0.066$

	Contribution
Hg^{tot}_{Lumex}	0.017
$P_{reaction}$	0.091
$a_{Hg^{tot}}$	0.045
$b_{Hg^{tot}}$	0.048
y^{tot}_{drift}	0.016
$\delta^{tot}_{ref.\ gas}$	0.114
$\delta^{tot}_{repeat.}$	0.042
$\delta^{tot}_{repro.}$	0.038

$u_c(Hg^{tot}_{cal}) \;=\; 0.172$

$Concentration$	$\frac{\mu g}{m^3}$
$Hg^{II}_{Lumex} + u_c(k=2)$	6.416 ± 0.368
$Hg^{II}_{Lumex} + u_c(k=2)_{\%}$	$6.416 \pm 5.7\%$

NOTE: $u_c(k=2)$ is calculated with 6 decimals in the $u_c(k=1)$ value, which is calculated with maximum decimals in $u_c\left(Hg^0_{cal}\right)$ and $u_c(Hg^{tot}_{cal})$ generated by the used software (see next section). The percentage is also calculated with $\mathrm{Hg}^{\mathrm{II}}_{\mathrm{Lumex}}$ having 6 decimals.

1.8.5 Calculation sequence

A data analysis program was developed at VTT MIKES with the programming language Python. The program enables automatic calculations and a more interactive display making it easier to analyse data.

The calculation of $\mathrm{Hg}^{\mathrm{II}}$ proceeds, with moving - average, in the following way:

1. Retrieval of $\mathrm{Hg}_{\mathrm{Lumex}}^{\mathrm{tot}}$ data
2. Correction of multiple timestamps
3. Applying linear regression model
4. Adding drift if applicable
    a. The drift values subtracted are subjected to the linear regression model
    b. The drift is calculated based on moving average
5. Applying moving average
6. Conversion to $\mathrm{Hg}^{\mathrm{II}} = \mathrm{Hg}_{\mathrm{Cal}}^{\mathrm{tot}} - \mathrm{Hg}_{\mathrm{Cal}}^{0}$, including steps 1-5 for Hg^{0}
7. Calculating combined standard uncertainty for $\mathrm{Hg}^{\mathrm{II}}$
8. Calculating mean and standard deviation for $\mathrm{Hg}^{\mathrm{II}}$, with specified time steps.

2. Calibration of a reference gas generator

The second part measurement of the output from selected dynamic Hg^{II} reference gas generators was performed using the calibrated analyser, i.e., calibration of a generator.

2.1 Traceability

The generator output needed to be calibrated against a traceable standard to ensure the traceability of the generated gas mixture. To confirm the output of oxidised mercury generator the output was measured using the calibrated analyser from previous Chapter 1. Further, for evaporative $HgCl_2$ gas generators, it was essential that the preparation and purity of the evaporated liquid mixtures obtained SI traceability.

In this work, the output of the liquid evaporative $HgCl_2$ gas generators developed by IAS (HovaCAL and HovaCAL SP, two separate models) and one developed in the EMPIR 16ENV01 MercOx project were calibrated using the calibrated two-channel Lumex analyser.

2.2 Measurement plan

A measurement plan for the generator output calibration was made. In the plan, the calibration range and the calibration points within the range were determined. Additionally, measurement sequences needed to investigate the repeatability and reproducibility, linearity, and hysteresis, were planned.

The selected calibration points should include at least points close to both minimum and maximum values of the generator's operational range, and enough points between those. It is highly recommended to include those concentration points, where the generator is most typically going to be used. This ensures to get enough information for linearity analysis and optimises the corrections and fitting curves used during the actual field usage of the analyser by avoiding large interpolations based on calibration data.

In this work, six different Hg^{II} concentrations were selected as calibration points in two different measurement ranges, 1 $\mu g/m^3$ and 10 $\mu g/m^3$. The selected percentages of the range were 0%, 75%, 45%, 60%, 0%, 15%, 30%, 90%, 0% and always at this same order. During the calibration each measurement point was measured at least three times, and the average of the recorded readings was used as a measured result for that point. Short term repeatability was calculated as a standard deviation from these. Linearity of the instrument were analysed from the results.

2.3 Generator preparation and generator details

Before starting the actual calibration measurements, the generator was allowed to warm-up according to the manufacturer's recommendation.

Specific properties of different types of generators, i.e., liquid-based gas generators and dry based gas generators, were considered according to the manufacturer's instructions. Typical warm-up times for liquid-based evaporative generators were a maximum of half an hour whereas for dry based gas generator stabilization overnight was recommended. The generators are left to run continuously during the measurements. During the warmup, a clean, dry air flow is running through the system. The warm-up time may change according to the set-up and/or the equipment.

Zero level (baseline) and its stability were checked after the warm-up time was completed. For an evaporative generator this was done using humid gas with water content set to value typical to measurement conditions since the actual calibration gas made through evaporation is humid gas as well. The humid and dry gases can detach mercury in different ways and in both cases, there is a specific equilibrium with mercury that may had adsorbed on the system surfaces in contact with the generated gas. Ultrapure water was dosed to the evaporator. As recommended, the zero level was also checked and measured during the calibration measurements.

2.4 Measurements

The generated gas mixture was supplied from the generator to the analyser. The analyser reading was monitored while it stabilized. After the stabilization period the analyser reading was recorded over a sufficient period that enough data for the result analysis was obtained considering the setup response time and measurement time.

In this work for the calibration of the liquid evaporative $HgCl_2$ generator in two different measurement ranges, two different liquid mixtures were used. The preparation of the liquid solution normally has two stages. The first stage is a base solution, which may be a commercial solution, or self-made solution prepared, e.g., by dissolving powder of pure solid chemical in water. The Hg concentration and purity analysis from the chemical supplier was used. It is also possible to analyse the solution concentration using atomic absorption spectrometry after $SnCl_2$ reduction or CV-AFS measurement according to EN ISO 17852 and to calibrate the measurement system using NIST Standard Reference Material (SRM) 3133. The uncertainty estimation for the self-made solutions can be calculated.

Selected different liquid flows were evaporated with selected fixed flow of carrier gas (air) to obtain six different Hg concentrations with varying water concentration. These outputs from the generator are analysed using the calibrated two-channel analyser with fixed gas flow through the analyser. In case of dry based generator concentration is determined by reservoir temperature and flowrates for gas flowing through Hg reservoir and the dilution gas flow.

2.5 Data analysis

The calibration data was analysed according to EN ISO 6143:2006 [4]. Based on the analysis, the generator's theoretical, calculated output concentration value was compared to the response from the analyser. The uncertainties of both the generator output and the analyser measurement capability needs to be considered when comparing these results. From these results, a calibration curve and uncertainty budget were calculated. These are specific values for the calibrated generator.

In this work, in the calibration of both liquid evaporative and dry based $HgCl_2$ generators, repeatability of the measurement data for the Hg^{tot} concentration was determined when using 1s sampling time in two-channel analytical system for consecutive measurement points. Averaging the measurement data gives even lower values for repeatability corresponding longer measurement time, e.g., 1 min.

The model equation of the generators was expressed as

$$Hg^{II} = aHg^{II} + b + u_{repeat.} + u_{repro.} + u_{ref} \ (11)$$

where a and b are the linear regression model coefficients obtained by using the formula

$$aHg^{II} + b = Hg^{II}_{Lumex_{Cal}}$$

The model's uncertainties were calculated according to equations 7 and 8.

The parameters $u_{repeat.}$, $u_{repro.}$ and u_{ref} are the repeatability, reproducibility, and reference gas uncertainties respectively. The values for $u_{repeat.}$ and $u_{repro.}$ were calculated when the concentration amount was 75% (except for HovaCal) of the measurement range. Considering the small amount of measurement points for the repeatability and reproducibility, the following formula was used:

$$u = \frac{max - min}{2\sqrt{3}}$$

which is the same as for a rectangular distribution.

The error of $\mathrm{Hg}^{\mathrm{II}}$ is already taken into consideration in u_{ref}, and therefore, it was assumed that it was not necessary to have a specific error for this term in the uncertainty budget.

The MercOx and HovaCal generators were tested with concentration ranges $1\frac{\mu g}{m^3}$ $\mathrm{Hg}^{\mathrm{II}}$ and $10\frac{\mu g}{m^3}Hg^{II}$, while the HovaCal SP generator was only with $10\frac{\mu g}{m^3}$ $\mathrm{Hg}^{\mathrm{II}}$. PSA generator was tested at one concentration point and with concentration range $10\frac{\mu g}{m^3}$ Hg^{II}.

Note: The standard deviation of the calculated $\mathrm{Hg}^{\mathrm{II}}$ can be lower than those of $\mathrm{Hg}_{\mathrm{Cal}}^{\mathrm{tot}}$ and $\mathrm{Hg}_{\mathrm{Cal}}^{0}$, however, by adding $\mathrm{u}_{\mathrm{ref}}$, the reference uncertainty comes into consideration.

Note that in the following sections, the calculations may be done with more decimals shown. This means that if eq. 10 is used, then the values may differ from the reported values.

2.6 Results

Reporting the results including measurement uncertainty for selected reference gas generators can be found on the 19NRM03 SI-Hg project Deliverable 6 document.

Conclusions

Traceability in detection of Hg^{tot} and accordingly Hg^{II} is a challenge with converter efficiency being an extra unknown when compared to detection of Hg^{0} only. The converter efficiency is challenging to determine and there is still significant uncertainty in the determined value. There are also other even more important sources of uncertainty and especially calibration of the two-channel dual analytical system using secondary elemental mercury generator turned out to be the largest single source of uncertainty in this work.

Determination of the converter efficiency within this project has been significant step forward and a great effort has been taken also in general by establishing the converter efficiency. This is a good starting point for future work and forthcoming research within this topic. Use of the calibrated secondary Hg^{0} gas generator also has influence on the uncertainty of the results. These are the major open actions for future research that need to be performed to secure the SI traceability chain for Hg^{II} measurement results with lower uncertainty.

References

[1] T. Rajamäki, S. Saxholm, W.T. Corns, C. Röllig, I. Živković, I. de Krom, Protocol for the SI-traceable calibration of oxidized mercury (HgII) gas generators used in the field, 2023, https://zenodo.org/records/10204408

[2] The European Parliament and the Council 2010 Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) OJ L334 17–119

[3] Petrov, P., Rajamäki, T., Corns, W.T., Goenaga-Infante, H. 2020. Evaluating the performance of oxidised Hg reference gas generators in the range ng m^{-3} to µg m^{-3} by improved coupling with ICP-MS. *Atmospheric Environment: X,* v. 8, doi.org/10.1016/j.aeaoa.2020.100090.

[4] EN ISO 6143:2006. Gas analysis. Comparison methods for determining and checking the composition of calibration gas mixtures.