D6: Report on the performance evaluation of at least three oxidised mercury gas generators on the market

19NRM03 SI-Hg D6

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Activity number	Activity description	Partners (Lead in bold)
A3.2.1 M20	VTT with support from JSI, TÜV Rheinland, VSL and LGC will define the test programme for the oxidised mercury generators by writing a protocol for the performance evaluation campaign for the assessment of the performance characteristics listed in A2.1.1. In order to get a comprehensive overview of the generator performance the evaluated performance characteristics include at least repeatability, reproducibility, accuracy, linearity, short term drift, bias as well as properties like robustness with respect to gas flow rate, gas pressure, line voltage and switching the system on and off.	**VTT**, JSI, TÜV Rheinland, VSL, LGC
A3.2.2 M26	VTT with support from JSI and TÜV Rheinland will invite participants (instrument manufactures who are collaborator and stakeholder) to make Hg^{II} gas generators available for the performance evaluation according to the test programme defined in A3.2.1 At least three Hg^{II} generators will be made available.	**VTT**, JSI, TÜV Rheinland
A3.2.3 M33	VTT, JSI, TÜV Rheinland and LGC with support from Lumex and PSA will perform measurements to assess the performance characteristics for the gas generators supplied by the participants in A3.2.2, according to test programme defined in A3.2.1.	**VTT**, JSI, TÜV Rheinland, LGC, Lumex, PSA
A3.2.4 M35	Using results from A3.2.1 – A3.2.3 VTT, JSI, TÜV Rheinland and LGC process data and produce a report on the performance evaluation for used Hg^{II} generators.	**VTT**, JSI, TÜV Rheinland, LGC
A3.2.5 M35	VTT with support from JSI, TÜV Rheinland, VSL and LGC, will review the report from A3.2.4 and will send it to the coordinator. The coordinator will then submit it to EURAMET as D6 *"Report on the performance evaluation of at least three oxidised mercury gas generators on the market"*.	**VTT**, JSI, TÜV Rheinland, VSL, LGC

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Introduction

This performance evaluation is based on the "Protocol for the performance evaluation of oxidised mercury gas generators on the market" that was written in the Activity 3.2.1 of the 19NRM03 SI-Hg project. The evaluation in designed to gather data to determine the performance and characteristics of at least three oxidised mercury (Hg^{II}) gas generators available on the market. This evaluation is part of the European Metrology for Innovation and Research Programme (EMPIR) project "Metrology for traceable protocols for elemental and oxidised mercury" (19NRM03 SI-Hg) and specifically its Work Package 3 (WP3) Task 3.2 *Performance evaluation of oxidised mercury generators on the market*.

Selected gas generator models for evaluation should be representative examples of applicable generation methods and generators available on the market. The evaluation work will take into account the corresponding preliminary calibration protocol developed in the EMPIR 16ENV01 MercOx project (project Deliverable no 2) and more recently in the 19NRM03 SI-Hg WP2 for Hg^{II} gas generators. The collected results are also used as an input to finalise the *Protocol for the SI-traceable calibration of oxidised mercury (Hg^{II}) gas generators used in the field* in SI-Hg WP2 [1]. Methods and good practices from EMRP ENV02 PartEmission, EMRP ENV51 MeTra, and EMPIR 16ENV01 MercOx and WP2 will be used in the evaluation work to measure output of the gas generators.

The aim of the performance evaluation is to evaluate the performance, characteristics and uncertainty of the selected Hg^{II} generators. The measurement methods based on Dual Channel Mercury Analysers (DCMA) with established converter efficiency and Hg^{II} solution purity from SI-Hg WP2 Task 2.1 are applied for direct real-time measurement of output concentration of the generators for Hg^{II} as well as possible residual elemental mercury (Hg^0). The dual analytical system is calibrated using a traceably calibrated Hg^0 gas generator.

The data obtained from the evaluation is essential for establishing a benchmark for equipment, understanding performance requirements for the protocols under development, encouraging the use of the best available techniques (BAT) and methods for generating Hg^{II} reference gas mixtures and making sure the developed protocol in SI-Hg WP2 is fit for purpose for equipment routinely used in the field. Based on the results *Report on the performance evaluation of at least three Hg^{II} gas generators on the market* will be produced as Deliverable no 6 of the 19NRM03 SI-Hg project.

2. Measurand and equipment of the experimental set-ups

Calibration gas mixtures of oxidised mercury will be generated by the gas generators under evaluation (hereinafter referred to as candidate generator) during the performance evaluation. The output of the generators will be determined by a calibrated dual mercury analyser capable to measure real time both elemental and oxidised mercury.

Carrier gas, e.g., instrument air, nitrogen (N_2) or argon (Ar), for the generated gas mixtures will be selected according to properties of measurement system. All measurements will be performed at standard conditions of temperature (293.15 K) and pressure (101.325 kPa). Gas mixtures will be transported from the generators to the dual analytical system using PFA or PTFE tubing. Tubing lengths are kept as short as possible to minimize adsorption to surfaces. Calibration gas flow ranges are defined for each generator listed in Chapter 4 according to their documented capabilities and suggestions.

2.1 Primary elemental mercury gas standard

The Van Swinden Laboratory (VSL) primary gas standard (hereinafter referred to as reference standard) has been developed as an Hg^0 gas generator that provides calibration gas mixtures to establish metrological traceability of mercury concentration measurement results, based on a gravimetric approach, for ambient air levels as well as higher concentrations [2-4]. The working principle of the primary mercury vapour generator is based on diffusion according to ISO 6145-8:2005 [5]. This is a dynamic gravimetric method to provide traceability to the International System of Units (SI) for concentration measurement results of mercury. Using specially designed diffusion cells, a mass flow of Hg^0 is created under well-controlled conditions (temperature, flow rate and pressure). By weighing the diffusion cells at regular time intervals with a high-resolution balance, an accurate mercury diffusion flow rate is obtained.

2.2 Secondary elemental mercury gas standard

The secondary elemental mercury generator is a transportable device that is shipped to other laboratories that make the performance evaluation of oxidised mercury gas generators. It is 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 is calibrated at VSL using the primary reference standard according to calibration proposal developed in SI-Hg WP1. The operation of the secondary mercury generator is furthermore established by recalibrating it after returning it to VSL after the performance evaluation campaign.

Results of the calibration of the PSA gas generator output for elemental mercury was determined in two ranges due to limitations of the VSL primary gas generator. The first range (Range 1) is 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	3046	3350	137	4.1
	2	6012	6415	262	4.1
	3	11493	12112	496	4.1
	4	15027	15971	652	4.1
	5	19977	21198	864	4.1

2	1	19977	21198	864	4.1
	2	40137	42820	1738	4.1
	3	60049	63182	2624	4.2
	4	80016	83282	3386	4.1
	5	99868	104885	4258	4.1

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

Deliverable no 4 of the 19NRM03 SI-Hg project shows how these results are used for the data processing [6].

2.3 Dual analytical system for mercury measurement

The performance evaluation experiments will be performed with a dual analytical system. Such a system typically consists of two gas channels, for determination of Hg^0 and total mercury (Hg^{tot}) concentration. The difference of the readings of these two analysers corresponds to the concentration of oxidised forms of mercury. The dual analytical system will be calibrated with the secondary elemental mercury gas standard during the performance evaluation. Output of the Hg^{tot} channel furthermore relies on a converter that converts oxidised mercury to elemental mercury as well as purity of the chemicals used to generate Hg^{II}. The converter efficiency and Hg^{II} solution purity are established at SI-Hg WP2 Task 2.1 and Task 2.2, respectively. More details of this kind of system can be found from the report written in the activity A2.1.1 of the 19NRM03 SI-Hg project SI-Hg *Literature Study on Dual Channel Mercury Analysers (DCMA)* [7].

The dual analytical system by Lumex Analytics GmbH, developed within the EMPIR 16ENV01 MercOx project, consists 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 is heated by an industrial heating blower up to 130 °C. The channel of Hg^0 consists of a heated cell, an atomic absorption spectrometer utilizing the Zeeman effect (Lumex RA-915F) and a pump. Temperature of the cell is kept at about 130 °C. To avoid catalytic reduction of Hg^{II} in the channel of Hg^0 all wetted parts are made of quartz, PTFE, PFA or similar plastic and no metal parts are used. The Hg^{tot} channel consists of an atomizer, a heated cell, the same spectrometer of the same type (RA-915F) and a pump. Temperature of the atomizer is 700 °C. Two manually operated valves on the input unit can direct ambient air in the channel via a Hg scrubber before entering the measurement cell for zeroing the equipment or analyte gas in the measurement cells for analysis. More details of the system can be found from EMPIR 16ENV01 MercOx project Deliverable no 1 [8].

Following result for converter efficiency was determined by LGC at SI-Hg WP2 Task 2.1:

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	

This correction is applied when calculating the following results.

3. Performance evaluation

3.1 Stability period, response time and recovery time

The candidate generator will be set-up and allowed to warm up according to operating instruction. Directly after warming up the output (with Hg^{II} concentration within the working range) of the candidate generator will be directed to the dual analytical system input. The output will be analysed for long enough time to determine period needed to obtain a stable response. The response is stable when the standard deviation between the measurements is < 1 %. Typically, for oxidised mercury this time can range from tens of minutes to several hours.

Due to the reactive nature of oxidised mercury gas, it is relevant to establish response time and recovery time for the measurement setup. Response time indicates how long it takes the measurement system to come to equilibrium measurement value (e.g., time to 95% full value) when a fixed concentration of oxidised mercury is introduced into the system. Recovery time indicates how long it takes the measurement system to register specific value over the limit of detection (LOD) (e.g., time to 5% full value) once the oxidised mercury is replaced with mercury free matrix gas. All parts of the measurement system contribute to response time and often it is not possibly to obtain an estimate for one specific system part only, e.g., for the candidate generator only. In case response time is significantly shorter for the measurement system than for the candidate generator, response time can be determined for the candidate generator. Experiments in the EMPIR 16ENV01 MercOx project revealed that response time of the Lumex dual analytical system is in the range of seconds even for Hg^{II} and this might enable determination of response time at least for some of the candidate generators.

3.2 Short term drift

Short term drift or span drift measurement quantifies the stability of measurement of a fixed Hg^{II} concentration (within the working range) over different time scales. This does not need to be a continuous, long-term measurement, although that would be ideal. In addition, measurements of baseline stability at same timescales will be performed.

The drift (d) is the difference between output of the candidate generator over a period of time. A single Hg^{II} concentration is continuously generated by the candidate gas generator, and it is sampled by the dual analytical system for at least 48 hours. At four times within those 48 hours the response (r_{c_i}) for the mercury concentration will be calculated to determine the drift (Equation (1)).

$$d = r_{c_2} - r_{c_1}$$
<div align="right">Eq. (1)</div>

The drift of the candidate generator will be corrected for drift of the dual analytical system if needed.

3.3 Calibration of output of the gas generator and working range

The candidate gas generator is calibrated according to the draft protocol developed in activity A2.3.1 of the 19NRM03 SI-Hg project [9]. The draft protocol is based on the calibration protocol developed within the EMPIR 16ENV01 MercOx project, which determines the output of liquid evaporative $HgCl_2$ gas generators. During the calibration the mercury concentration in a gas mixture prepared with a candidate generator is determined by the dual analytical system that is calibrated using the metrologically traceable secondary reference.

The concentration ranges to be investigated are defined for each generator listed in Chapter 4 according to their documented capabilities and within the limits of detection and measurement range of the measurement system. If the candidate generator is capable of multipoint operation, it

will be tested at six different Hg^{II} concentrations and at zero concentration level to ensure the number of data points is large enough to fit a cubic function. The set points are equally spaced between the lowest and highest Hg^{II} concentration in the range under test. The lowest and the highest set points are 10% and 90% of the investigated concentration ranges, respectively.

3.4 Precision: repeatability and reproducibility

To determine the precision of the output of the candidate generator the repeatability and reproducibility standard deviations are determined. The repeatability of the output is the closeness of the agreement between the results of successive individual measurements of Hg^{II} concentrations generated by the candidate generator carried out under the same conditions of measurement. The reproducibility of the output is the closeness of the agreement between the results obtained on three different days in a one-month period.

Data obtained during calibration of the candidate generator (Chapter 3.3) is used to determine the repeatability and within laboratory reproducibility standard deviations. The repeatability standard deviation (s_r, expressed as coefficient of variation in %) and within-laboratory reproducibility standard deviation (s_R, expressed as coefficient of variation in %) are calculated according to ISO 5725-2:2019 using one-way analysis of variance (ANOVA) [10].

3.5 Linearity

If the candidate generator is capable to multipoint operation over a range of Hg^{II} concentrations the linearity of the candidate generator is determined. To determine the linearity data obtained during calibration of the candidate generator (Chapter 3.3) will be used. The linearity assessment will be performed using ordinary least squares method. The residuals will be assessed considering the associated standard uncertainties. For a satisfactory fit of the data, it is required that the absolute value of the normalised residual will not exceed 2. The normalised residual is the residual divided by the standard uncertainty of the response.

3.6 Accuracy, Trueness and Precision

Measurement accuracy consist of systematic error, i.e. trueness, and random error, i.e. precision, of measurement. It is quantified by calculating measurement deviation whereas trueness only can be quantified by calculating bias of the repeated measurements. [11, 12] Systematic error may vary over the measurement range, and it is typically considered by correcting measurement results using the calibration curve resulting from the linearity measurement.

The measurement deviation (D_{c_i}) and relative measurement deviation (D_{rel}) are the closeness of the calibrated output of the candidate generator ($c_{i_{certified}}$) to the set point of the candidate generator ($c_{i_{set\,point}}$) (Equations (2) and (3)).

$$D_{c_i} = c_{i_{certified}} - c_{i_{set\,point}} \qquad\qquad \text{eq. (2)}$$

$$D_{rel} = \frac{D_{c_i}}{c_{i_{set\,point}}} \qquad\qquad \text{eq. (3)}$$

3.7 Sensitivity coefficient to sample gas pressure

The sensitivity coefficient to the output gas pressure of the candidate generator is determined by varying the output gas pressure within -0,1 bar and +0,1 bar around the ambient atmospheric pressure. Output concentration from the generator is measured at these pressures p_+ and p_- as c_+ and c_-, respectively. Sensitivity coefficient is determined using the equation 4.

$$S_p = \frac{c_+ - c_-}{p_+ - p_-}$$ <div style="text-align:right">eq. (4)</div>

The measurement is done at zero concentration and at a specific concentration that is between 70 - 90 % of the upper limit of the calibration range.

3.8 Sensitivity coefficient to the surrounding temperature

The sensitivity coefficient to the surrounding temperature of the candidate generator is determined by varying the ambient temperature within -15°C and +10°C around the normal temperature +20°C. Output concentration from the generator is measured at these temperatures t_+ and t_- as c_+ and c_-, respectively. Sensitivity coefficient is determined using the equation 5.

$$S_t = \frac{c_+ - c_-}{t_+ - t_-}$$ <div style="text-align:right">eq. (5)</div>

The measurement is done at zero concentration and at a specific concentration that is between 70 - 90 % of the upper limit of the calibration range.

3.9 Sensitivity coefficient to electrical voltage

The sensitivity coefficient to electrical voltage of the candidate generator is determined by varying the supply voltage within -10% and +10% around the nominal voltage defined by the manufacturer in the datasheet for the generator. Output concentration from the generator is measured at these voltages U_+ and U_- as c_+ and c_-, respectively. Sensitivity coefficient is determined using the equation 6.

$$S_U = \frac{c_+ - c_-}{U_+ - U_-}$$ <div style="text-align:right">eq. (6)</div>

The measurement is done at zero concentration and at a specific concentration that is between 70 - 90 % of the upper limit of the calibration range.

4. Participating oxidised mercury gas generators

The test protocol of the 19NRM03 SI-Hg project Deliverable 3 [1] is applicable to different types of oxidised mercury gas generators, e.g.:

- Liquid evaporative gas generators, working according to ISO 6145-4
- Saturation (mercury salt) gas generators, working according to ISO 6145-9
- Permeation gas generators, working according to ISO 6145-10
- Oxidative gas generators, based on oxidation of Hg^0 from a saturated source

4.1 IAS generators HovaCAL and HovaCAL SP

Inspire Analytical Systems GmbH (IAS, Germany) HovaCAL® calibration gas generator is a liquid evaporative gas generator. Separate models for high ($\mu g/m^3$) and low (ng/m^3) range oxidised mercury concentrations, typically met in process and ambient measurements, respectively, are available. Within this project two models, standard model HovaCAL and a new version HovaCAL SP were tested. Liquid solution dosing is using peristaltic pump in connection with balance in HovaCAL and using automatic syringe in HovaCAL SP. Carrier gas of the gas vapour mixture is freely chosen. Instrument air is used in this study. Generated test gas is humid and humidity level typically ranges between 0.1 to 30 vol-%. Temperature of the reference gas can be typically varied between 120°C and 180°C.

4.2 MercOx generator

MercOx reference gas generator developed in the EMPIR 16ENV01 MercOx project is based on liquid evaporation method [13]. The unit can be used in wide concentration range, from high ($\mu g/m^3$) to low (ng/m^3) oxidised mercury concentration ranges. Liquid solution dosing is using an automatic syringe. Humidity level of the generated gas typically ranges between 0.1 to some tens of vol-% and temperature of the reference gas can be typically varied between 100°C and 180°C.

5. Results

Results for different oxidised mercury calibrators are explained below.

5.1 Equations for Hg-Concentrations

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 Hg^{II} was obtained with $Hg^{II} = Hg^{TOT} - Hg^0$. The concentrations were obtained with the following formulas:

$$Hg^{TOT}_{Lumex} = P_{reaction} * Hg^{TOT}$$

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

$$Hg^{TOT}_{cal} = a_{Hg^{TOT}}Hg^{TOT} + b_{Hg^{TOT}} - y^{TOT}_{drift} + \delta^{TOT}_{ref.\ gas} + \delta^{TOT}_{repeat.} + \delta^{TOT}_{repro.} \ (7)$$

$$Hg^0_{cal} = a_{Hg^0}Hg^0 + b_{Hg^0} - y^0_{drift} + \delta^0_{ref.\ gas} + \delta^0_{repeat.} + \delta^0_{repro.} \ (8)$$

$$Hg^{2+} = Hg^{TOT}_{cal} - Hg^0_{cal}$$

$$Hg^{II} = \frac{a_{Hg^{TOT}}}{P_{react}}Hg^{TOT} + b_{Hg^{TOT}} - y^{TOT}_{drift} + \delta^{TOT}_{ref.\ gas} + \delta^{TOT}_{repeat.} + \delta^{TOT}_{repro.}$$
$$- \left(a_{Hg^0}Hg^0 + a_{Hg^0} - y^0_{drift} + \delta^0_{ref.\ gas} + \delta^0_{repeat.} + \delta^0_{repro.}\right) \ (9)$$

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.

Characterization of Lumex dual channel mercury analyser and explanation of the process of obtaining the different uncertainty terms is presented in 19NRM03 SI-Hg project Deliverable 4 document [6].

The model equation of the generators was expressed as

$$Hg^{II} = aHg^{II} + b + u_{repeat.} + u_{repro.} + u_{ref} \ (10)$$

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

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

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 Hg^{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 $1 \frac{\mu g}{m^3} Hg^{II}$ and $10 \frac{\mu g}{m^3} Hg^{II}$, while the HovaCal SP was only with $10 \frac{\mu g}{m^3} Hg^{II}$.

In the following tables, the value calc. Hg^{II} refers to the calculated Hg^{II} concentration based on the solution used by the generator. The value cal. Hg^{II} refers to the calibrated value, i.e., using a linear regression model on cal. Hg^{II}. The difference between the reference and the generator, $\Delta_{ref-gen}$, is always calculated with cal. Hg^{II} as the generator value, if present in the table. Otherwise, it is calculated with calc. Hg^{II}.
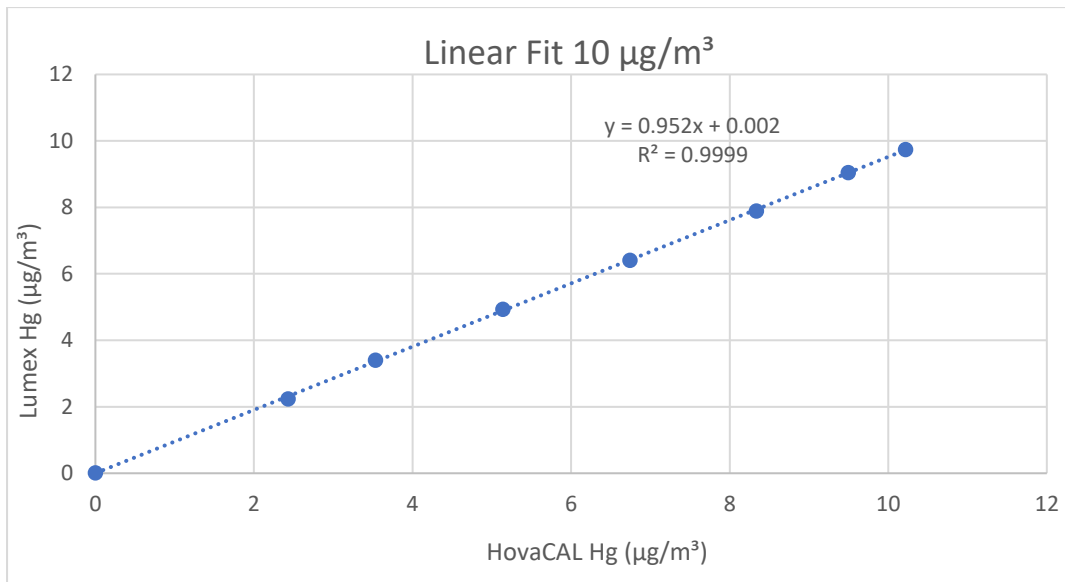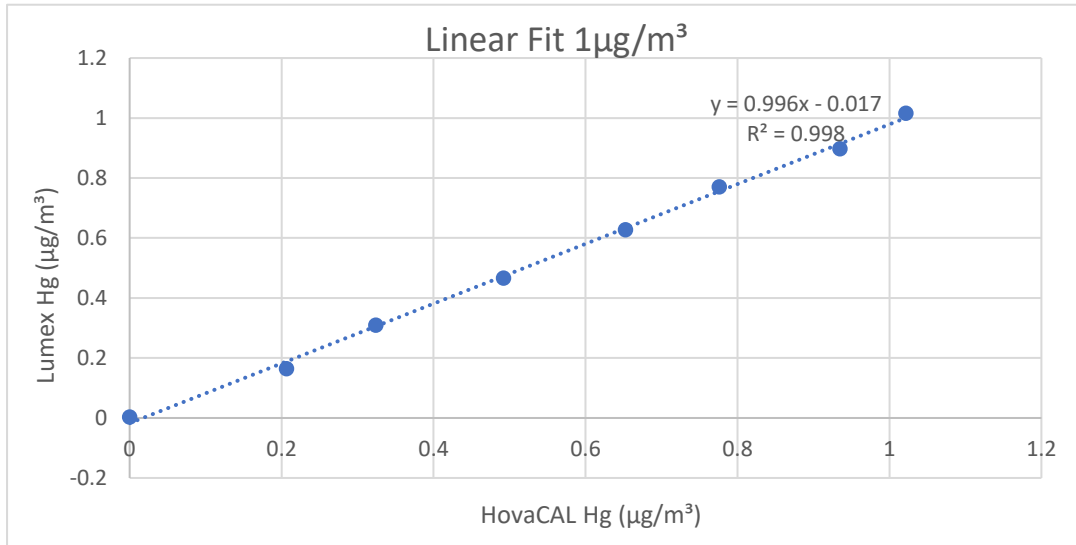
Note: The standard deviation of the calculated Hg^{II} can be lower than those of Hg_{Cal}^{TOT} and Hg_{Cal}^{0}, however, by adding u_{ref}, the reference uncertainty comes into consideration.

Note that in the following sections, the calculations may be done with more decimals shown and the values may differ slightly from the reported values.

5.2 HovaCAL generator
The following section shows the results obtained with the HovaCal generator. Here the reproducibility was determined when the flow was 45% of the range due to it being difficult to achieve the same liquid flow at 75% range. The reason behind this is the peristaltic liquid pump used by the generator.

The following plots were obtained for the linear regression model:

Linear Fit 1µg/m³

y = 0.996x - 0.017
R² = 0.998

Lumex Hg (µg/m³) vs HovaCAL Hg (µg/m³)

Linear Fit 10 µg/m³

y = 0.952x + 0.002
R² = 0.9999

Lumex Hg (µg/m³) vs HovaCAL Hg (µg/m³)

The values and errors for the parameters were obtained as following:

Parameter	Value		Error	
	$1\frac{\mu g}{m^3}$	$10\frac{\mu g}{m^3}$	$1\frac{\mu g}{m^3}$	$10\frac{\mu g}{m^3}$
a	0.996	0.952	0.018	0.005
b	-0.017	0.002	0.012	0.031
$u_{repeat.}$			0.031	0.030
$u_{repro.}$			0.033	0.169

The following table shows the contribution of the parameters to uncertainty budget. The values of Hg^{II} were theoretically calculated to be 0.776 and 8.338 respectively when the flow was at 75% of the range:

$Concentration\ range$	$1\frac{\mu g}{m^3}$	$10\frac{\mu g}{m^3}$
a	0.014	0.039
b	0.012	0.031
$u_{repeat.}$	0.031	0.030
$u_{repro.}$	0.033	0.169
u_{ref}	0.102	0.214
$u_c(k=1)$	0.113	0.279

This resulted in the following values:

$Concentration\ range$	$1\frac{\mu g}{m^3}$	$10\frac{\mu g}{m^3}$
$Hg^{II} + u_c(k=2)$	0.756 ± 0.226	7.939 ± 0.558
$Hg^{II} + u_c(k=2)_\%$	$0.756 \pm 29.2\%$	$7.939 \pm 6.7\%$

The following table shows the theoretical values, calibrated values, and uncertainties for different flow percentages with $1\frac{\mu g}{m^3}\ Hg^{II}$ and $10\frac{\mu g}{m^3}\ Hg^{II}$ concentration ranges respectively.

| g/min	$Hg\frac{\mu g}{l}$	gas l/min	$H_2O\ \%$	calc. $Hg^{II}\frac{\mu g}{m^3}$	cal. $Hg^{II}\frac{\mu g}{m^3}$	$\Delta_{ref-gen}$	$u_c(k=1)$	$u_c(k=2)$	$u_c(k=2)_\%$
0.070	103.437	7.087	1.228	1.022	1.000	-0.006	0.115	0.231	22.6
0.000	103.437	7.000	0.000	0.000	-0.017	0.003	0.111	0.222	-
0.053	103.437	7.066	0.933	0.776	0.756	-0.006	0.113	0.226	29.2
0.034	103.437	7.042	0.592	0.492	0.473	-0.026	0.112	0.223	45.4
0.045	103.437	7.055	0.784	0.652	0.633	-0.026	0.113	0.226	34.6
0.014	103.437	7.017	0.248	0.206	0.188	-0.043	0.111	0.222	107.6
0.022	103.437	7.027	0.389	0.324	0.305	-0.015	0.111	0.223	68.8
0.064	103.437	7.080	1.124	0.935	0.914	-0.038	0.114	0.229	24.5

g/min	$Hg\frac{\mu g}{l}$	gas l/min	$H_2O\ \%$	calc. $Hg^{II}\frac{\mu g}{m^3}$	cal. $Hg^{II}\frac{\mu g}{m^3}$	$\Delta_{ref-gen}$	$u_c(k=1)$	$u_c(k=2)$	$u_c(k=2)_\%$
0.070	1034.368	7.087	1.228	10.217	9.726	0.013	0.312	0.624	6.1
0.057	1034.368	7.071	1.003	8.338	7.939	-0.048	0.279	0.558	6.7
0.035	1034.368	7.044	0.618	5.140	4.894	0.045	0.235	0.470	9.2
0.046	1034.368	7.057	0.811	6.742	6.419	-0.006	0.256	0.511	7.6
0.000	1034.368	7.000	0.000	0.000	0.002	0.014	0.202	0.404	-
0.017	1034.368	7.021	0.292	2.431	2.316	-0.073	0.209	0.419	17.2

0.024	1034.368	7.030	0.425	3.531	3.363	0.045	0.219	0.437	12.4
0.065	1034.368	7.081	1.142	9.495	9.040	0.010	0.299	0.598	6.3

5.3 HovaCAL SP generator

The following section shows the results obtained with the HovaCal SP generator. Here only a concentration range of $10 \frac{\mu g}{m^3} Hg^{II}$ was used.

The following plots were obtained for the linear regression model:
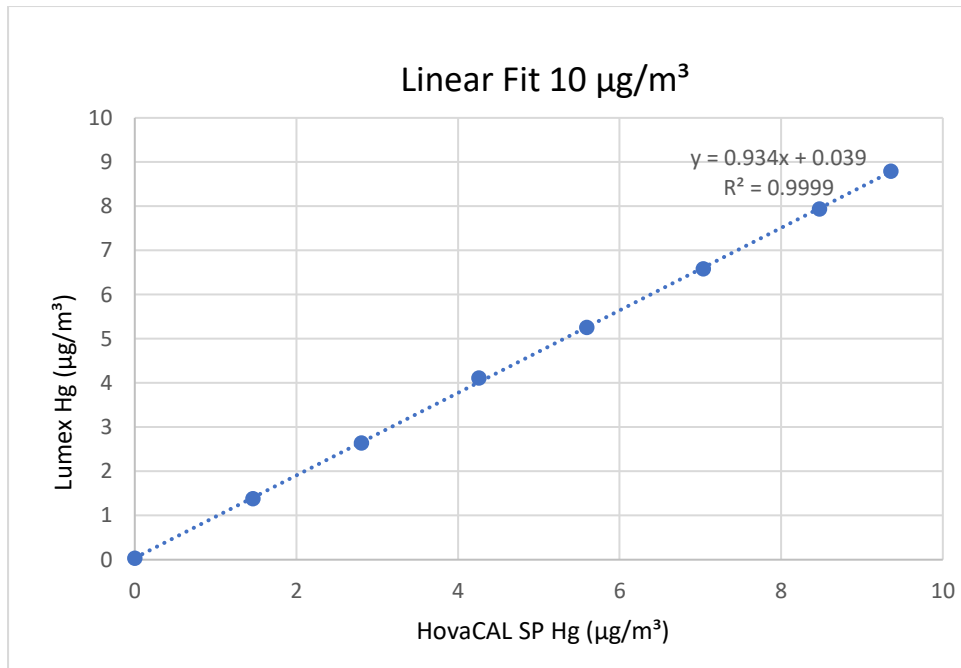
The values and errors for the parameters were obtained as following:

Parameter	Value	Error
a	0.934	0.005
b	0.039	0.027
$u_{repeat.}$		0.093
$u_{repro.}$		0.070

The following shows an example of the uncertainty budgets contributions with the theoretical value of the concentration to be $7.038 \frac{\mu g}{m^3} Hg^{II}$ and with a flow of 75% of the range:

Concentration range	$10\frac{\mu g}{m^3}$
a	0.033
b	0.027
$u_{repeat.}$	0.093
$u_{repro.}$	0.070
u_{ref}	0.200
$u_c(k=1)$	0.235

| Concentration range	$10\frac{\mu g}{m^3}$
$Hg^{II} + u_c(k=2)$	6.613 ± 0.470
$Hg^{II} + u_c(k=2)_\%$	$6.613 \pm 6.7\%$

The following table shows the theoretical values, calibrated values, and uncertainties for different flow percentages:

g/min	Hg $\frac{\mu g}{l}$	gas l/min	H_2O %	calc. Hg^{II} $\frac{\mu g}{m^3}$	cal. Hg^{II} $\frac{\mu g}{m^3}$	$\Delta_{ref-gen}$	$u_c(k=1)$	$u_c(k=2)$	$u_c(k=2)_\%$
0.069	1034.368	7.674	1.125	9.358	8.780	0.010	0.275	0.549	5.9
0.052	1034.368	7.653	0.846	7.038	6.613	-0.026	0.235	0.470	6.7
0.031	1034.368	7.627	0.512	4.260	4.018	0.091	0.199	0.399	9.4
0.041	1034.368	7.639	0.673	5.595	5.265	-0.008	0.214	0.429	7.7
0.000	1034.368	7.588	0.000	0.000	0.039	-0.009	0.172	0.344	-
0.011	1034.368	7.601	0.176	1.461	1.404	-0.021	0.175	0.350	23.9
0.021	1034.368	7.614	0.337	2.807	2.661	-0.017	0.183	0.366	13.1
0.063	1034.368	7.666	1.019	8.475	7.955	-0.020	0.259	0.517	6.1

5.4 MercOx generator

The following section shows the results obtained for the MercOx generator.

The following plots show the linear fits for the generator:
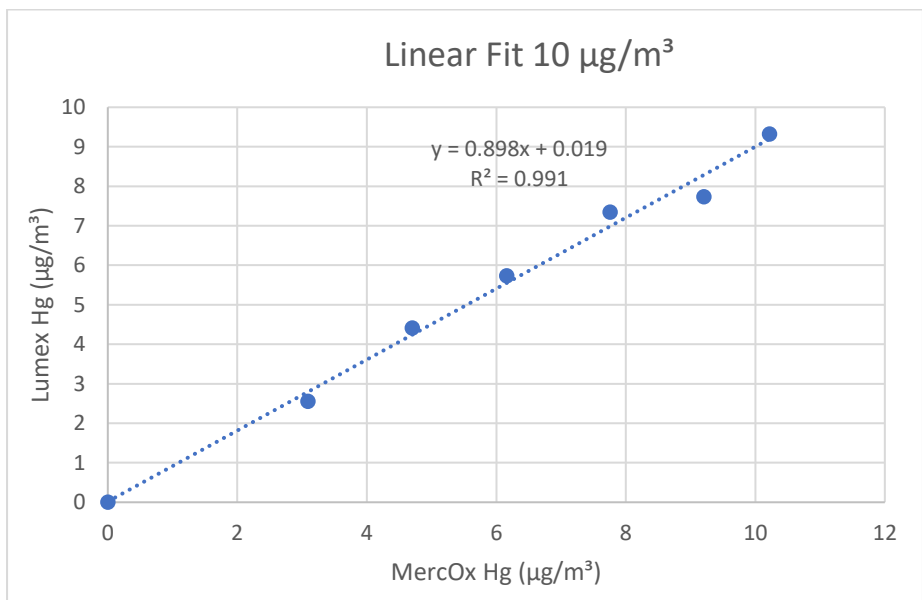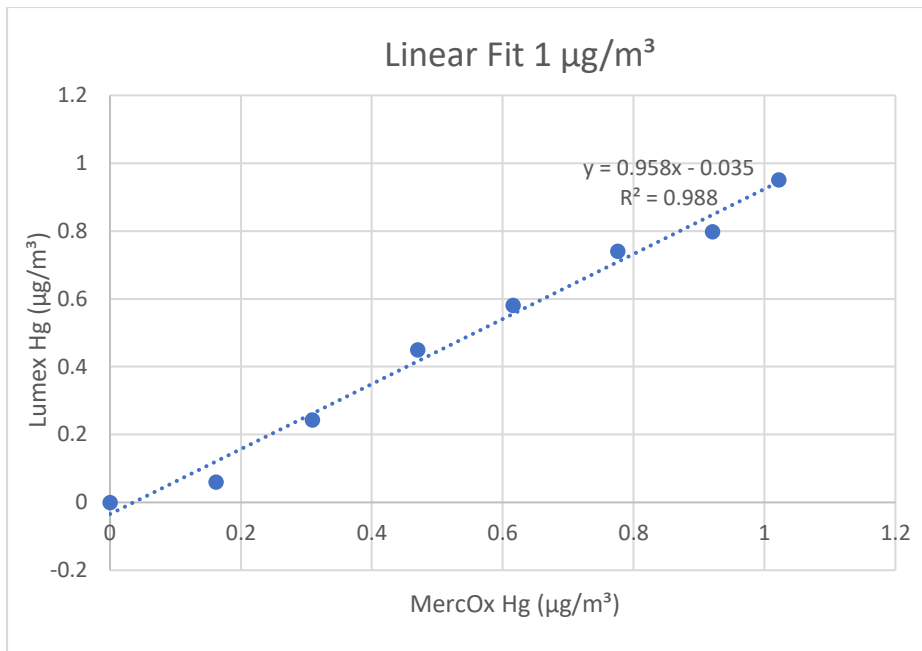
Linear Fit 1 μg/m³

$y = 0.958x - 0.035$
$R^2 = 0.988$

Linear Fit 10 μg/m³

$y = 0.898x + 0.019$
$R^2 = 0.991$

The values and errors for the parameters were obtained as following:

Parameter	Value		Error	
	$1\frac{\mu g}{m^3}$	$10\frac{\mu g}{m^3}$	$1\frac{\mu g}{m^3}$	$10\frac{\mu g}{m^3}$
a	0.958	0.898	0.043	0.038
b	-0.034	0.019	0.027	0.259
$u_{repeat.}$			0.048	0.289
$u_{repro.}$			0.038	0.049

The following table shows the contribution of the parameters to uncertainty budget. The values of Hg^{II} were theoretically calculated to be 0.776 and 7.759 respectively when the flow was at 75% of the range.

Concentration range	$1\frac{\mu g}{m^3}$	$10\frac{\mu g}{m^3}$
a	0.034	0.298
b	0.027	0.259
$u_{repeat.}$	0.048	0.289
$u_{repro.}$	0.038	0.049
u_{ref}	0.102	0.258
$u_c(k=1)$	0.127	0.555

This resulted in the following values:

Concentration range	$1\frac{\mu g}{m^3}$	$10\frac{\mu g}{m^3}$
$Hg^{II} + u_c(k=2)$	0.709 ± 0.253	6.988 ± 1.111
$Hg^{II} + u_c(k=2)_{\%}$	$0.709 \pm 32.6\%$	$6.988 \pm 14.3\%$

The following table shows the theoretical values, calibrated values, and uncertainties for different flow percentages with $1\frac{\mu g}{m^3}$ Hg^{II} and $10\frac{\mu g}{m^3} Hg^{II}$ concentration ranges respectively.

g/min	Hg $\frac{\mu g}{l}$	gas l/min	H_2O %	calc. $Hg^{II}\frac{\mu g}{m^3}$	cal. $Hg^{II}\frac{\mu g}{m^3}$	$\Delta_{ref-gen}$	$u_c(k=1)$	$u_c(k=2)$	$u_c(k=2)_{\%}$
0.070	103.437	7.087	1.228	1.022	0.945	0.006	0.131	0.261	25.6
0.000	103.437	7.000	0.000	0.000	-0.034	0.034	0.121	0.242	-
0.053	103.437	7.066	0.933	0.776	0.709	0.031	0.127	0.253	32.6
0.032	103.437	7.040	0.565	0.470	0.416	0.034	0.123	0.246	52.2
0.042	103.437	7.052	0.741	0.616	0.556	0.025	0.125	0.249	40.5
0.011	103.437	7.014	0.195	0.162	0.121	-0.061	0.124	0.248	152.8
0.021	103.437	7.026	0.372	0.309	0.262	-0.019	0.121	0.243	78.6
0.063	103.437	7.078	1.107	0.921	0.848	-0.050	0.128	0.257	27.9

g/min	Hg $\frac{\mu g}{l}$	gas l/min	H_2O %	calc. $Hg^{II}\frac{\mu g}{m^3}$	cal. $Hg^{II}\frac{\mu g}{m^3}$	$\Delta_{ref-gen}$	$u_c(k=1)$	$u_c(k=2)$	$u_c(k=2)_{\%}$
0.070	1034.368	7.087	1.228	10.217	9.196	0.123	0.626	1.252	12.3
0.053	1034.368	7.066	0.933	7.759	6.988	0.356	0.555	1.111	14.3
0.032	1034.368	7.040	0.565	4.702	4.242	0.166	0.482	0.964	20.5

0.042	1034.368	7.052	0.741	6.160	5.552	0.174	0.513	1.026	16.7
0.000	1034.368	7.000	0.000	0.000	0.019	-0.018	0.435	0.869	-
0.021	1034.368	7.026	0.372	3.092	2.796	-0.246	0.455	0.909	29.4
0.063	1034.368	7.078	1.107	9.206	8.288	-0.555	0.590	1.179	12.8

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/m3) studied. At lower concentration range (1 µg/m3) detection limit of the analyser system has an effect to that. Measured Hg^{II} concentrations are mostly below the calculated values, typically -4 % for the HovaCAL calibrators and -7 % for the MercOx calibrator.

5.5 Test with Hg^{tot} test gas generators on external disturbance values

In this part the performance of the test gas generators was investigated with respect to various environmental parameters. The following criteria have been checked during the tests:

- Influence of supply voltage on the produced test gas concentration.
- Influence of the ambient pressure on the produced test gas concentration
- Influence of the ambient temperature on the produced test gas concentration.

The investigations were carried out in each case with three test gas generators for the production of Hg^{tot} test gas.

The two-channel analyser system of Lumex described above, which can determine Hg^{tot} and Hg^0 in parallel, was used as a reference for determining the generated test gas concentration.

The investigations were carried out with the following test gas generators.

- IAS HovaCAL SP
- MercOx

Detailed description of these units is presented in Part 4.1 to 4.3 in the report in hand.

The tests were carried out in accordance with the requirements of standard EN 15267-3, which is the current standard for the qualification of continuous emission monitoring equipment (CEM). The use of suitable test gas sources is required as part of the quality assurance measures for these measuring devices used for official measurements prescribed in standard EN 14181. Based on the requirements of DIN EN 15267-3, the test criteria for the examination of the test gas generators for mercury were established. Details of the individual test points are presented below.

Table – Overview with the measurements performed at TÜV.

Time (date)	Characteristics
01-06-2023, 29-06-2023 and 05-07-2023	Line voltage

| 18 to 22-07-2023 | Temperature Test |
| 28-07- and 01-08-2023 | Pressure |

5.5.1 Influence of supply voltage variations

Test was conducted with a voltage supply variation to the test gas generators from 15 % from the nominal value below to +10 % from the nominal value above the nominal value of the supply voltage. Nominal Value is 230 V, maximum value in the test was 253 V and minimum value was 196 V.

Equipment

The test was carried out with each test gas generator, the Lumex two-channel analyser system, an isolating transformer (3 phases, 0 to 400 V) and a multimeter Type Fluke 85.

Method

The test gas generator to be tested was connected to the supply voltage using the isolating transformer. Output voltage was controlled by the multimeter. Test gas generators to be tested have been warmed according to manufacturer's specifications also the analyser system was warmed up according to relevant specifications.

The output of the generators at span point was determined at each voltage after a stabilisation period of the system, typically 12 min. Each value was averaged with a period of 3 min each. The deviations between the average readings at each voltage and the average reading at the nominal supply voltage were determined.

Evaluation

The deviations between the average readings at each voltage and the average reading at the beginning of the test were determined.

In addition, the sensitivity coefficient for the voltage dependence was calculated according to the following equation.

Where:

$$b_{sv} = \frac{(x_2 - x_1)}{(U_2 - U_1)}$$

b_{sv} is the sensitivity coefficient of supply voltage

x_1 is the average reading at voltage U_1

x_2 is the average reading at voltage U_2

U_1 is the minimum voltage (196 V)

U_2 is the maximum voltage (253 V)

Deviations have been related to the mean span value of each generators span reading at nominal voltage.

Presentation of test results

The individual results of the test on influence of voltage variations are presented in the following tables.

Table – results of line voltage test with IAS Generator for Hg^{tot}

| Voltage Volt | IAS | | |
	Reading µg/m³	Span point Deviation %MV$_{230V}$	b$_{SV}$
230	7.12	-	
242	7.10	-0.3	-0.002
253	7.04	-1.1	-0.005
219	7.04	-1.1	0.007
207	7.01	-1.5	0.003
196	7.00	-1.7	0.001
Maximum value	**-**	**-1.7**	**0.007**
b$_{SV}$ (253/196 Volt):			**0.001**
x$_{i,adj}$	7.12		
x$_{imax}$	7.10		
x$_{imin}$	7.00		
u	0.076		

Table – results of line voltage test with MercOx Generator for Hg^{tot}

Voltage Volt	MercOx		
		Span point	
	Reading	Deviation	b_{SV}
	µg/m³	%MV$_{230V}$	
230	7.58	-	
242	7.54	-0.5	-0.003
253	7.80	2.9	0.024
219	7.65	0.9	-0.006
207	7.70	1.6	-0.004
196	7.56	-0.3	0.013
Maximum value	**-**	**2.9**	**0.024**
b_{SV} (253/196 Volt)			**0.004**
$x_{i,adj}$	7.58		
x_{imax}	7.80		
x_{imin}	7.54		
u	0.117		

Assessment

The line voltage test of the generator showed a max. deviation of 2,9 % within the tested range at the MercOx generator and -1,7 % with IAS generator.

Basically, the deviations are high for all tested generators, but a tendency of deviation of the output value of the generator depending on the voltage was not observed. The found deviations are higher as the expected the uncertainty and repeatability of the relevant generators. Stability problems with the Hg(tot) chanel of the analyser system may have caused these problems. But the results of the pressure test show that better results can be obtained with this experimental setup, so there might be also a measurable influence of the line voltage to the performance of the generators.

5.5.2 Influence of ambient temperature

In accordance with the requirements of the standard EN 15267-3, an automatic measuring system intended for indoor-use use must be able to operate in the temperature range from 5 to 40 °C. The required temperature range for outdoor installations is -20 °C to 50 °C.

Since the available test gas generators are not suitable for outdoor operation, the temperature range for checking the test gas generators was accordingly also set to the range 5 to 40 °C.

Equipment

The test was carried out with each test gas generator, the Lumex two-channel analyser system and a climatic chamber with an adjustable temperature range from -40 °C to +80 °C and an adjustable moisture content. The moisture content in the climatic chamber was set to 50 % rel.

Method

The test gas generators were exposed to the following temperature sequence in the climatic chamber:

20 °C → 5 °C → 20 °C → 40 °C → 20 °C.

Test gas generators have been connected to the Lumex two-channel analyser system, during the entire period of the test program. The analyser system was placed outside of the climate chamber inside a temperature-controlled lab at 20 °C. An equilibration time of at least 6 h (typically one night) was included after the tests at each temperature change.

The tests at each temperature level test have been conducted with each test gas generator. The test gas generators as well as the analyser system were operating during the whole test. After a stabilisation period of the system, typically 12 min. Each value was averaged with a period of 3 min each.

The deviations between the average reading at each temperature and the average reading at 20 °C were determined. The three zero readings at the beginning, in the middle and at the end of the temperature cycle have been averaged to minimize possible drift effects of the analyser system in the calculation.

Evaluation

The deviations in the measurement signals were determined at each temperature.

The maximum sensitivity coefficient was calculated according to the following equation:

$$b_t = \frac{(x_i - x_{i-1})}{(T_i - T_{i-1})}$$

where:

b	is the sensitivity coefficient of ambient temperature
x_i	is the average reading at temperature T_n
x_{i-1}	is the average reading at temperature T_{n-1}
T_i	is the current temperature in the test cycle
T_{i-1}	is the previous temperature in the test cycle

Deviations have been related to the mean span value of each generators span reading at 20 °C.

Presentation of test results

The individual results of the test of the ambient temperature test are presented in the following table.

Table – results of ambient temperature test with IAS Generator for Hg^{tot}

Temperature	Reading	IAS	
		Span point	
		Deviation	b_t
°C	µg/m³	% MV (∅ 20°)	
∅ 20°	11.14	-	
20	11.14	0.0	-
5	11.25	1.0	-0.007
20	11.14	0.0	-0.007
40	11.69	4.9	0.027
20	11.14	0.0	0.027
Maximum value		**4.9**	**0.027**
$x_{i,adj}$	11.14		
x_{imax}	11.69		
x_{imin}	11.14		
u	0.318		

For MercOx generator temperature tests could not be conducted due to a transportation damage. When Generator was sent back from Tests in Italy in another working package the unit was damaged, so temperature tests have not been conducted for this generator.

Assessment

Major deviations of 4.9 % / -5.3 % occurred at 40 °C. We recommend to use the generator in a Temperature range close to 20 °C (-10°C/+10°C).

5.5.3 Influence of ambient pressure

Influence of ambient pressure was tested by adjusting pressure at the output of the generators. Test was conducted by increasing the sample gas pressure by 4 kPa above ambient pressure. Input pressure of carrier/dilution gas for the test gas generators is set according to manufacturer's specifications.

Equipment

The test was carried out with each test gas generator, the Lumex two-channel analyser system. For pressure measurement, a digital manometer was used.

Method

Tests have been conducted with constant input pressure of the carrier gas (dilution gas) according to manufacturer specifications. Pressure at output of generators has been adjusted with a needle valve and measured. The output of the generators at span point was determined at each pressure after a stabilisation period of the system, typically 12 min. Each value was averaged with a period of 3 min each. The deviations between the average readings at each pressure levels were determined. A

measurement at standard level was conducted before and after the measurement with the increased pressure. Mean value of the measurements at standard pressure was used as reference value.

Evaluation

The deviations between the average readings at both pressure levels and the average reading at standard level of the test were determined.

In addition, the sensitivity coefficient for the pressure dependence was calculated according to the following equation.

Where:

b_P is the sensitivity coefficient of supply voltage

x_1 is the average reading at standard pressure

$$B_P = \frac{(x_2 - x_1)}{(P_2 - P_1)}$$

x_2 is the average reading at increased pressure

P_1 is the standard pressure

P_2 is the increased pressure

Deviations have been related to the mean span value of each generator at standard pressure.

Presentation of test results

The individual results of the test of the ambient temperature test are presented in the following table

Table – results of ambient pressure test with IAS Generator for Hg^{tot}

	IAS		
Pressure	Reading	Deviation	b_f
kPa	µg/m³	%CR	
106,1	9.85	-0.40	-0.010
102,1	9.89	-	-
Maximum value		**-0.40**	**-0.010**
$x_{i,adj}$	9.89		
x_{imax}	9.89		
x_{imin}	9.85		
u	0.023		

For MercOx generator pressure tests could not be conducted due to a transportation damage. When Generator was sent back from tests in Italy in another working package the unit was damaged, so pressure tests have not been conducted for this generator.

Assessment

The generator showed a low-pressure influence on the generated test gas concentration (-0.4 %). The found deviation is within the uncertainty range and within the range of repeatability of the relevant generator in combination with the analyser system used. Voltage fluctuations in the typical range thus have no relevant influence on the performance of the test gas generator.

Conclusions

This performance evaluation indicated how the generators perform for the different characteristics that are most important considering their applicability. The results also showed that the two-step calibration protocol for the selected analyser and the candidate generator to be evaluated, explained in the 19NRM03 SI-Hg project Deliverable 3, is fit for purpose, but great care is needed in such performance evaluation process [1].

Traceability in detection of Hg^{tot} and accordingly Hg^{II} is a challenge with converter efficiency of the selected analyser being an extra unknown when compared to detection of Hg^0 only. The converter efficiency is not straightforward to determine and there is still considerable uncertainty in the determined value. However, its determination within this project has been significant step forward and a great effort has been taken by establishing the converter efficiency in general. Use of the calibrated secondary Hg^0 gas generator also influence on the uncertainty of the results. These two factors related to selected analyser that is used to monitor the calibrators output may create by far the greatest single source of uncertainty.

The results for tested generators compared mostly well but there were also some differences in the results considering sources of uncertainty for different evaluated generators. In part these differences are related to test method itself and for example a single measurement point may change the result considerably. One of the reasons for this may be the sticky nature of oxidised mercury. It easily adsorbs to any surfaces of the test setup, and this may cause the reading to deviate from expected results. For both analyser and generator fast response times are critical, and the response time used for the performance evaluation need to be selected carefully.

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