D5: Report on the performance evaluation of at least three elemental mercury gas generators on the market

19NRM03 SI-Hg D5

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Summary

During the performance evaluation of elemental mercury gas generators on the market three generators were tested, e.g., PSA 10.536 elemental Hg generator, bell-jar and Tekran Model 3425. Key characteristics were determined e.g.; the stabilisation period, short-term drift, precision, i.e., reproducibility and repeatability of the concentration generated, linearity, bias, sensitivity to sample gas pressure, sensitivity to surrounding temperature and sensitivity to electrical voltage. All three generators could be tested according to the calibration protocol developed within the project. The results obtained with the different gas generator clearly shows the importance of a metrological calibration. All three candidate generators show a different bias for the setpoint compared to the calibrated output.

Table of Contents

1. Introduction

Currently, mercury gas generators used in the field are not certified against primary standards and therefore lack traceability. The aim of the 19NRM03 SI-Hg project was to develop and validate metrological traceable protocols for the calibration of mercury gas generators used in the field (hereafter referred to as calibration protocol). In this way, the project will achieve significant improvements in the measurement comparability and uncertainty of mercury measurement results.

In the first year of the project a first draft of the protocol was developed for the calibration of elemental mercury (Hg^0) gas generators [1] and the first validation measurements were performed [2]. During the performance evaluation Hg^0 gas generators were tested according to the developed calibration protocol. With the performance evaluation data was gathered on the characteristics of three Hg^0 gas generators available on the market. This data is essential for a) establishing a benchmark for equipment, b) understanding performance requirements for the protocols under development, c) encouraging the use of the best available methods for generating Hg^0 gas mixtures and d) making sure the developed calibration protocol is fit for purpose for equipment routinely used in the field.

Before the start of the performance evaluation a protocol was set-up (Annex 1). This protocol was designed to determine key characteristics of off-the-shelf Hg^0 gas generators. These key characteristics include the stabilisation period, short-term drift, precision, i.e., reproducibility and repeatability of the concentration generated, linearity, bias, sensitivity to sample gas pressure, sensitivity to surrounding temperature and sensitivity to electrical voltage. The performance evaluation is based on the calibration protocol developed for these gas generators that enables them to provide calibration gas mixtures for Hg^0 concentration with traceability to the International System of Units (SI) and with a defined uncertainty [1]. Thereby, these off-the-shelf gas generators can fulfil requirements with respect to metrological traceability and measurement uncertainty, as required by, e.g., ISO/IEC 17025.

Three Hg^0 gas generators were tested 1) PSA 10.536 elemental Hg generator (Annex 1), 2) bell-jar (Annex 2) and 3) Tekran Model 3425 (Annex 3). All generators were saturation gas generators working according to ISO 6145-9 [3]. Generator 1 and 3 were continuously generating mercury concentrations, generator 2 requires manual injection of the mercury gas mixtures into an analyser. The measurements for the performance evaluation were performed at the Van Swinden Laboratory (VSL) in the Netherlands and Technischer Überwachungsverein Rheinland Energy GmbH (TÜV) in Germany (Table 1). All measurements were performed at standard conditions of temperature (293.15 K) and pressure (101.325 kPa).

Table 1 – Characteristics tested for each generator

Characteristic	**Generators tested**	**Determined at**
Stabilisation period	1, 2 and 3	VSL
Short-term drift	1, 2 and 3	VSL
Precision	1, 2 and 3	VSL
Linearity	1, 2 and 3	VSL
Bias	1, 2 and 3	VSL
Sensitivity coefficient to sample gas pressure	1 and 3	TÜV
Sensitivity coefficient to surrounding temperature	1 and 3	TÜV
Sensitivity coefficient to electrical voltage	1 and 3	TÜV

For each generator a separate report was written with the results obtained during the performance evaluation (Annex 2-4). In this report the results for the three generators are compared and a general conclusion about the performance evaluation is given. The bell-jar generator has not been tested at TÜV as the manual injection was not possible during these experiments.

2. Results

2.1 stabilisation period

The stabilisation period of the PSA generator is 24 minutes directly after setting up the generator and 9 minutes once the generator was running for a days. For the bell-jar generator the stabilisation period was only determined after it had been running for day's, the measurement showed the generator was stable at the first measurement. The stabilisation period of the Teran generator was only tested directly after setting up the generator and it took 15 minutes to obtain a stable signal.

The measurements for the stabilisation period were performed after the warm-up time. Once ready it takes 2.5 times longer to obtain a stable signal when the generator has just been started compared to when the generator was running for days. In general the stabilisation period takes at least half an hour once running it will take 10 to 15 minutes to obtain a stable signal.

In the calibration protocol a warm-up time specified by the manufacturer or a period of at least 30 minutes is recommended. Furthermore, a 15 minute stability check must be performed.

2.2 Short-term drift

The short-term drift for the PSA generator was 4%, for the bell-jar generator 1.7% and the Tekran generator has a short-term drift of 0.8%. The PSA generator is susceptible to influence from atmospheric pressure, these have not been included here.

The short-term drift of all the generators is below the uncertainty of the reference standards used with a relative expanded uncertainty of 4% in the µg m^{-3} range and 5% in the ng m^{-3} range. The uncertainty of the bell-jar generator and Tekran generator is also smaller than the measurement uncertainty of the analyser used (2% (k = 2)).

2.3 Calibration

All three calibrators were calibrated according to the calibration protocol [1]. A multipoint calibration was performed over a range of 5 mercury concentrations for the PSA generator and bell-jar generator and 3 for the Tekran generator (Table 2).

Table 2 – Mercury concentration ranges tested during the performance evaluation

Candidate generator	**Mercury concentration range (ng m^{-3})**	**Relative expanded uncertainty mercury concentrations from the reference generator (u(c_{ref})) (%)**
PSA	Range 1: 3000 – 20000 Range 2: 20000 – 100000	4 (for both ranges)
Bell-jar	50 – 300	5
Tekran	5000 – 25000	4

The calibration of the PSA generator was divided in two ranges. The calibration of the generators was repeated in 3 measurement series for the PSA generator and bell-jar generator and 4 measurement series for the Tekran generator.

The data obtained during the calibrations was processed according to the calibration protocol using software developed within the project [1, 4]. Based on the data the precision (section 2.4), interpolation function (section 2.5), bias (section 2.6) and uncertainty of the candidate generator was determined.

The uncertainty obtained after calculation according to the calibration protocol was between 4.0% and 4.3% for the PSA generator, 5.1% and 5.5% for the bell-jar generator and 4.0% and 4.3% for the Tekran generator.

The uncertainty sources are the uncertainty of the mercury concentration from the reference standard, u(c_{ref}) and the comparison uncertainty composed of the measurement stability and repeatability. The significance of the uncertainty sources depends on the stability and repeatability of the measurements performed for each mercury concentration. In general the significance of the uncertainty exists for 1% - 10% from the comparison uncertainty and 90% - 99% of the uncertainty of the mercury concentration from the reference standard.

2.4 Precision: Repeatability and reproducibility

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 %) were calculated according to ISO 5725-2:2019 using one-way analysis of variance (ANOVA) [5] for each candidate generator (Table 3).

Table 3 – Precision of the candidate generators

Generator	**s_r (%)**	**s_R (%)**
PSA	0.61	0.85
Bell-jar	1.03	2.28
Tekran	0.51	1.15

The precision of the bell-jar generator is highest this could be due to the manual injection needed for this generator. The measurement uncertainty of the analyser (2% (k = 2)) is probably the most important source for the precision.

2.5 Interpolation function

The best fit for the data for all three generators is a linear function, $c = b_0 + b_1 c_{cand}$. The data of all measurement series could be combined to obtain a single set of regressions coefficients for the interpolation function.

The generators can also be used at any setpoint within the range tested during the calibration. This can be done by using the interpolation function to calculate the output of the candidate generator at the chosen setpoint, in Annex 2 of the calibration protocol the procedure is explained [1].

2.6 Bias

Based on the output of the candidate generator, calculated according to the calibration protocol [1], the relative deviation (D_{rel}) compared to the setpoint was determined for all three candidate generators (Table 4).

Candidate generator	**(D_{rel}) (%)**	**Relative expanded uncertainty output candidate generator (u(c)) (%)**
PSA	Range 1: 7 Range 2: 5	4 (for both ranges)
Bell-jar	-5	5
Tekran	-0.5%	4

The deviations for each generator were comparable for the different setpoints and they were averaged for the overview in Table 4.

For each generator the data obtained with channel A and channel B of the analyser were comparable within the uncertainty and the data obtained in the different measurement series was also comparable. Therefore the data was averaged to obtain a single set of calibration results for each candidate generator tested (Annex 2 -4).

2.7 Sensitivity coefficient to sample gas pressure

The tests with pressure fluctuations for PSA generator and Tekran showed that pressure compensation is required. Tekran generator had only a deviation of 0.2 %.

2.8 Sensitivity coefficient to the surrounding temperature

Ambient temperature changes may have a significant influence to the generated test gas generation of PSA generator and Tekran. The tested generators should be used under laboratory conditions. For field application it is recommended to hold temperature conditions constant.

2.9 Sensitivity coefficient to electrical voltage

For both Generators a tendency of deviation of the output value of the generator depending on the voltage was not observed. Voltage fluctuations in the typical range thus have no relevant influence on the performance of the test gas generator.

3. Conclusion

Within the 19NRM03 SI-Hg project a metrological traceable calibration protocol was developed for the calibration of mercury gas generators. This protocol was validated and tested during a performance evaluation of three Hg^0 gas generators available on the market. Key characterises were determined e.g.; the stabilisation period, short-term drift, precision, i.e., reproducibility and repeatability of the concentration generated, linearity, bias, sensitivity to sample gas pressure, sensitivity to surrounding temperature and sensitivity to electrical voltage.

All three generators could be tested according to the calibration protocol developed within the project. Based on the validation measurements performed at the beginning of the project the protocol was already improved [2]. Based on the results of this performance evaluation no new improvements need to be suggested.

The data obtained is essential for a) establishing a benchmark for equipment, b) understanding performance requirements for the protocols under development, c) encouraging the use of the best available methods for generating Hg^0 gas mixtures and d) making sure the developed calibration protocol is fit for purpose for equipment routinely used in the field.

The results obtained with the different gas generator clearly shows the importance of a metrological calibration. All three candidate generators show a different bias for the setpoint compared to the calibrated output. Through calibration according to the SI-Hg protocol all measurement results become traceable to the SI units and comparable. This is essential to underpin global efforts to control and reduce the concentration of mercury in the environment, comply with legislation and protect human health.

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Annexes

Annex 1:	Protocol for the performance evaluation of elemental mercury gas generators on the market
Annex 2:	PSA 10.536 Elemental Hg generator performance evaluation report
Annex 3:	Bell-jar performance evaluation report
Annex 4:	Tekran Model 3425 performance evaluation report for elemental mercury

Protocol for the performance evaluation of elemental mercury gas generators on the market

19NRM03 SI-Hg A3.1.1

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Table of Contents

1. Introduction

This performance evaluation protocol is designed to determine key characteristics of off-the-shelf elemental mercury (Hg^0) gas generators. These key characteristics include the stabilisation period, short-term drift, precision, i.e., reproducibility and repeatability of the concentration generated, linearity, bias, sensitivity to sample gas pressure, sensitivity to surrounding temperature and sensitivity to electrical voltage. The performance evaluation is based on the calibration protocol developed for these gas generators that enables them to provide calibration gas mixtures for Hg^0 concentration with traceability to the International System of Units (SI) and with a defined uncertainty. Thereby, these off-the-shelf gas generators can fulfil requirements with respect to metrological traceability and measurement uncertainty, as required by, e.g., ISO/IEC 17025. The measurements for the performance evaluation will be conducted at the Van Swinden Laboratory (VSL) in the Netherlands and Technischer Überwachungsverein Rheinland Energy GmbH (TÜV) in Germany. All measurements will be performed at standard conditions of temperature (293.15 K) and pressure (101.325 kPa).

This evaluation is part of the project "Metrology for traceable protocols for elemental and oxidised mercury" (19NRM03 SI-Hg) in the European Metrology for Innovation and Research Programme (EMPIR). Selected gas generator models for evaluation are deemed representative for current applicable generation methods and generators available on the market. The evaluation work is based on the calibration protocol developed in WP1 of the project for Hg^0 gas generators, and the collected results are used as an input to finalise the protocol. Methods and good practices from the projects EMRP ENV02 PartEmission, EMRP ENV51 MeTra, and EMPIR 16ENV01 MercOx and WP1 will be used in the evaluation work to measure output of the gas generators.

The data obtained during this evaluation enables establishing a benchmark for equipment, understanding and setting performance requirements for the calibration protocols developed in WP1 of the SI-Hg project, encouraging the use of the best available techniques (BAT) and methods for generating Hg^0 gas mixtures and making sure the developed protocol in WP1 is fit for purpose for equipment routinely used in the field. Based on the performance evaluation results a will be produced as D5 of the 19NRM03 SI-Hg project "Report on the performance evaluation of at least three Hg^0 gas generators on the market".

2. Measurand and equipment

2.1 General

Calibration gas mixtures of elemental mercury (Hg^0) in air will be generated by the gas generators under evaluation (hereinafter referred to as candidate generator) during the performance evaluation key characteristics will be determined by a mercury analyser (Table 1). All measurements will be performed at standard conditions of temperature (273.15 K) and pressure (101.325 kPa).

Table 1: Key characteristics determined during the performance evaluation at VSL or TÜV

Characteristic	Determined at
Stabilisation period	VSL
Short-term drift	VSL
Precision	VSL
Linearity	VSL
Bias	VSL
Sensitivity coefficient to sample gas pressure	TÜV
Sensitivity coefficient to surrounding temperature	TÜV
Sensitivity coefficient to electrical voltage	TÜV

2.2 Primary mercury gas standard

The 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 [1-3].

The working principle of the primary mercury gas generator (hereinafter referred to as generator) is based on diffusion according to ISO 6145-8:2005 [4]. 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.

In the generator, the diffusion cells are housed in a diffusion chamber. The diffusion chamber is temperature (20.0 °C ± 0.1 °C) and pressure (105.0 kPa ± 0.1 kPa) controlled. At the bottom, a nitrogen flow of 500 mL min^{-1} enters the diffusion chamber. The complete gas flow, enriched by Hg^0 vapour from diffusion, is then guided to the outlet of the diffusion chamber through an aperture at the top. The desired Hg^0 concentrations are prepared by mixing the Hg^0-containing gas mixture from the diffusion system in a second step with a flow of the desired matrix gas, e.g., purified air. Volume flow rates of the matrix gas are typically between 1 L min^{-1} and 25 L min^{-1}.

The reference standard is used during the performance evaluation to calibrate the mercury analyser and ensure the measurement results are traceable to SI.

2.3 Mercury analyser

The experiments at VSL will be performed with a PSA Sir Galahad II mercury analyser (P S Analytical, UK). To monitor continuously for mercury in air or gas, two Amasil® traps are employed in parallel. While sample gas is directed over one trap, to absorb any mercury present, the second trap is analysed. The mercury concentration is measured using atomic fluorescence detection. The analyser is accompanied by a stream selector which can be used to connect 4 different mercury gas generators for alternating measurement.

The analyser is calibrated using a certified standard of own performance with an SI-traceable mercury concentration.

Gas mixtures will be transported from the generators to the analyser using PFA or PTFE tubing.

In case available for the performance evaluation, one or more commercial continuous emission measurement (CEM) systems will be used as well to perform measurements.

The performance evaluation experiments at TÜV have been 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 oxidized forms of mercury. The dual analytical system will be calibrated with the secondary elemental mercury gas standard during the performance evaluation. 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 or other 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 mercury scrubber before entering the measurement cell for zeroing the equipment or analyte gas in the measurement cells for analysis.

3. Performance evaluation

3.1 Stabilisation period

The candidate generator will be set-up and allowed to warm up according to operating instruction. Directly after warm up period, the output of the candidate generator will be directed to the analyser. The output will be continuously analysed for at least 2 hours to determine period needed to obtain a stable response. The response is stable when the standard deviation between the measurements is < 1 % or alternative until the signal has reached 95% of the expected value.

Furthermore, the period needed to shift from one concentration to a new concentration will be determined by changing the output of the candidate generator. The output will be continuously analysed for at least 2 hours to determine the period need to obtain a stable response. The response is stable when the standard deviation between the measurements is < 1 % or alternative until the signal has reached 95% of the expected value.

3.2 Short-term drift

The short-term drift (*d*) or span drift quantifies the stability of measurement of a fixed Hg^0 concentration over a period of time. A single nominal Hg^0 concentration is generated by the candidate gas generator and sampled by the analyser over a period of at least 48 hours. At 4 times within those 48 hours the mercury concentration (c_i) will be determined by performing measurements according to the calibration protocol for a single point. Based on the results the short-term drift can be calculated (Equation (1)).

$$d = c_2 - c_1 \quad \text{Eq. (1)}$$

The drift of the candidate generator will be corrected for drift of the analyser if needed.

3.3 Calibration output candidate generator

The candidate gas generator will be certified according to the protocol developed in activity A1.1.4 of the 19NRM03 SI-Hg project [5]. During the calibration the output of the candidate generator is determined by comparison with a metrologically traceable reference standard. The uncertainty of the mercury concentration generated with the candidate gas generator in relation to the known uncertainty of the reference standard will be calculated according to the calibration protocol. The concentrations to be investigated are defined separately for each candidate generator in Chapter 4. If possible the candidate generator will be tested at 6 different Hg^0 concentrations to ensure the number of data points is large enough to fit a cubic function. The setpoints are equally spaced between the lowest and highest Hg^0 concentration in the range under test.

The comparison is performed using a bracketing sequence in which the Hg^0 concentrations are analysed alternately from the reference standard and the candidate generator.

3.4 Precision: Repeatability and reproducibility

To determine the precision of the output of the candidate generator the repeatability and reproducibility standard deviations will be determined.

The repeatability of the output is the closeness of the agreement between the results of successive individual measurements of Hg^0 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) will be used to determine the repeatability and 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 %) will be calculated according to ISO 5725-2:2019 using one-way analysis of variance (ANOVA) [6].

3. 5 Interpolation function

If the candidate generator can be used over a range of mercury concentrations the interpolation function of the candidate generator will be determined. To determine the function, data obtained during calibration of the candidate generator (Chapter 3.3) will be used.

The assessment will be performed using weighted least squares [7]. The residuals will be assessed taking into account the associated standard uncertainties. For a satisfactory fit of the data, it is required that the absolute value of the normalised residuals will not exceed 2. The weighted residual is the residual divided by the standard uncertainty of the associated concentration.

3.6 Bias

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

$$D_{c_i} = c_i - c_{cand(i)} \quad \text{eq. (2)}$$

$$D_{rel} = \frac{D_{c_i}}{c_{cand(i)}} \quad \text{eq. (3)}$$

3. 7 Sensitivity coefficient to sample gas pressure

Influence of sample gas pressure was tested by adjusting pressure level at the output of the generators. The 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 generator is set according to manufacturer's specifications.

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

In addition, the sensitivity coefficient for the pressure dependence will be calculated according to Equation (4).

$$b_P = \frac{r_2 - r_1}{P_2 - P_1} \quad \text{eq. (4)}$$

Where:

b_P is the sensitivity coefficient to sample gas pressure

r_1 is the average reading at standard pressure

r_2 is the average reading at increased pressure

P_1 is the standard pressure (kPa)

P_2 is the increased pressure (kPa)

3. 8 Sensitivity coefficient to the surrounding 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 [9]. The required temperature range for outdoor installations is -20 °C to 50 °C.

The deviations in the measurement signals were determined at each temperature. The maximum sensitivity coefficient was calculated according Equation (5).

$$b_T = \frac{r_i - r_{i-1}}{T_i - T_{i-1}} \qquad \text{eq. (5)}$$

Where:

b_T is the sensitivity coefficient to surrounding temperature

r_1 is the average reading at temperature T_i

r_2 is the average reading at temperature T_{i-1}

P_1 is the current temperature in the test cycle (°C)

P_2 is the previous temperature in the test cycle (°C)

3. 9 Sensitivity coefficient to electrical voltage

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.

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 will be calculated according to Equation (6).

$$b_{sv} = \frac{r_2 - r_1}{U_2 - U_1} \qquad \text{eq. (5)}$$

Where:

b_{sv} is the sensitivity coefficient of supply voltage

r_1 is the average reading at voltage U_1

r_2 is the average reading at voltage U_2

U_1 is the minimum voltage (V)

U_2 is the maximum voltage (V)

4. Participating candidate generators

4.1 PSA

On behalf of P S Analytical (PSA, United Kingdom), the validation of the 10.536 elemental Hg generator will be performed for the measurement of elemental mercury in air in the concentration range to be determined at standard conditions of temperature (273.15 K and pressure (101.325 kPa).

The PSA 10.536 elemental Hg generator include a mercury reservoir. The unit operate on the principle of dilution a saturated source of mercury at a known temperature according to ISO 6145-9 [8]. A low flow rate is passed across the mercury reservoir ensuring that the gas becomes saturated with mercury. The mercury-saturated gas is then diluted into the concentration range of interest. The flow rates are controlled using two mass flow controllers. The mercury concentration can be adjusted by altering the temperature of the oven or by adjusting the reservoir or dilution flows. In the field the generator typically uses a fixed temperature and dilution flow and the reservoir flow is changed to provide different concentration outputs.

4.2 Bell-jar

VSL provided a Bell-jar for the validation. The Tekran® Model 2505 (Tekran, USA) mercury vapour calibration unit is based on the Bell-jar principle. A Bell-jar generates saturated mercury concentration in air, according to ISO 6145-9 [8]. Since the saturation vapour pressure of mercury is a function of temperature, the exact volume injected, and temperature of the mercury saturated air need to be set in order to determine the mercury injection mass based on the Dumarey equation [10-12]. The validation will be performed for the measurement of elemental mercury in air in the concertation range to be determined at standard conditions of temperature (273.15 K) and pressure (101.325 kPa).

4.3 Tekran

On behalf of Tekran (USA), the validation of the Tekran® Model 3425 will be performed for the measurement of elemental mercury in air in the concertation range to be determined at standard conditions of temperature (273.15 K) and pressure (101.325 kPa).

The Tekran® Model 3425 Elemental & Oxidized Mercury Generator provides NIST traceable calibration gas for system calibration. The 3425 is a saturation gas generator working according to ISO 6145-9 [8]. The generator can be set to automatically generate multi-point calibration gas. Elemental mercury gas is delivered using a NIST traceable, temperature controlled, saturated mercury vapor source. Precision mass flow controllers dilute the mercury source output to the desired value.

5. Schedule

The schedule for this performance evaluation reads as follows

Table 1: Performance evaluation schedule

Date	Activity
June 2022	Agreement protocol by supplier's candidate generators
August 2022	Shipment of candidate generators to VSL
December 2022	Calibration of candidate generators at VSL
April 2023	Shipment of candidate generators to TÜV Rheinland
August 2023	Return of candidate generators to suppliers
September 2023	Report available

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PSA 10.536 Elemental Hg generator performance evaluation report

19NRM03 SI-Hg Task 3.1

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Table of Contents

1. Introduction

The PSA 10.536 elemental mercury gas generator was tested during the performance evaluation. This evaluation was part of the project “Metrology for traceable protocols for elemental and oxidised mercury” (19NRM03 SI-Hg) in the European Metrology for Innovation and Research Programme (EMPIR). The aim of the performance evaluation was to gather data on the characteristics of at least three elemental mercury (Hg^0) gas generators on the market. Selected gas generator models for evaluation are representative examples of applicable generation methods and generators available on the market.

The PSA 10.536 elemental mercury gas generator includes a mercury reservoir. The unit operates on the principle of dilution of a saturated source of mercury at a known temperature according to ISO 6145-9 [1]. A low flow rate is passed across the mercury reservoir ensuring that the gas becomes saturated with mercury. The mercury-saturated gas is then diluted into the concentration range of interest. The flow rates are controlled using two mass flow controllers. The mercury concentration can be adjusted by altering the temperature of the oven or by adjusting the reservoir or dilution flows. In the field the generator typically uses a fixed temperature and dilution flow and the reservoir flow is changed to provide different concentration outputs.

The performance evaluation was performed according to the protocol [2]. The protocol was designed to determine key characteristics of off-the-shelf elemental mercury (Hg^0) gas generators. These key characteristics include the stabilisation period, short-term drift, precision, i.e., reproducibility and repeatability of the concentration generated, linearity, bias, sensitivity to sample gas pressure, sensitivity to surrounding temperature and sensitivity to electrical voltage. The performance evaluation was based on the calibration protocol developed for these gas generators that enables them to provide calibration gas mixtures for Hg^0 concentration with traceability to the International System of Units (SI) and with a defined uncertainty [3]. Thereby, these off-the-shelf gas generators can fulfil requirements with respect to metrological traceability and measurement uncertainty, as required by, e.g., ISO/IEC 17025. The measurements for the performance evaluation were performed at the Van Swinden Laboratory (VSL) in the Netherlands and Technischer Überwachungsverein Rheinland Energy GmbH (TÜV) in Germany. All measurements were performed at standard conditions of temperature (293.15 K) and pressure (101.325 kPa).

This report shows the results obtained during the performance evaluation of the PSA 10.536 elemental mercury gas generator. This report is part of D5 of the 19NRM03 SI-Hg project “Report on the performance evaluation of at least three Hg^0 gas generators on the market”.

2. Equipment

2.1 PSA 10.536 Elemental Hg Generator

Calibration gas mixtures of Hg^0 in air will be generated by the gas generator under evaluation (hereinafter referred to as candidate generator) during the performance evaluation key characteristics were determined according to the protocol [2]. All measurements will be performed at standard conditions of temperature (293.15 K) and pressure (101.325 kPa).

At VSL the candidate generator was tested in two ranges, 3000 ng m^{-3} – 20000 ng m^{-3} and 20000 ng m^{-3} – 100000 ng m^{-3} (Table 1).

Table 1 – Settings and setpoints ($c_{cand(i)}$) according to the equipment, of the candidate generator used during the performance evaluation measurements at VSL.

Range	Setpoint nr.	Reservoir Flow (mL min^{-1})	Dilution flow (L min^{-1})	$c_{cand(i)}$ (ng m^{-3})	$U(c_{(candi)})$ (ng m^{-3}) (k = 2) (= 4.81%)
1	1	1	14.9	3050	146
	2	2	15.1	6020	290
	3	3.9	15.4	11508	554
	4	5	15.1	15046	724
	5	7	15.9	20002	962
2	1	7	15.9	20002	962
	2	10	11.3	40189	1933
	3	15.1	11.4	60126	2892
	4	19.6	11.1	80119	3854
	5	18.3	8.3	99996	4810

During the measurements the backpressure at the output of the candidate generator was monitored with a GE Druck PACE 1000 pressure meter.

At TÜV the generator was tested at two setpoints Table 2).

Table 2 – Settings and setpoints ($c_{cand(i)}$) according to the equipment, of the candidate generator used during the performance evaluation measurements at VSL.

Setpoint nr.	Reservoir Flow (mL min^{-1})	Dilution flow (L min^{-1})	$c_{cand(i)}$ (µg m^{-3})	$U(c_{(candi)})$ (µg m^{-3}) (k = 2) (= 4.81%)
A	1.8	15.0	5.4	0.3
B	3.5	15.0	10.4	0.5

2.2 Primary mercury gas standard

The VSL primary gas standard (hereinafter referred to as reference standard) was 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 [4-6].

For the performance evaluation gas mixtures with different mercury concentrations (c_{ref}) were obtained with different settings of the reference standard (Table 3). For range 1, 1 diffusion cell with a capillary diameter of Ø33 mm was used with a diffusion rate of (72.3 ± 0.6) ng min^{-1} (k = 2) and purified air flow rates between 3 L min^{-1} and 24 L min^{-1}. For range 2, 3 diffusion cells with a capillary diameter of Ø33 mm were used with a diffusion rate of (216.1 ± 2.6) ng min^{-1} (k = 2) and purified air flow rates between 2 L min^{-1} and 11 L min^{-1}.

Table 3 – Mercury concentrations obtained with the reference standard during the performance evaluation.

Range	**Setpoint nr.**	c_{ref} **(ng m^{-3})**	$U(c_{ref})$ **(ng m^{-3}) (*k* = 2) (= 4%)**
1	1	3051	122
	2	5999	240
	3	11509	460
	4	14990	600
	5	20001	800
2	1	20014	801
	2	40025	1601
	3	59973	2399
	4	80041	3202
	5	99743	3990

2.3 Mercury analysers

The experiments at VSL were performed with a PSA Sir Galahad II mercury analyser (P S Analytical, UK) as explained in the protocol [2]. During the measurements in range 1 the gas mixtures were sampled 1 minute with a flow of 250 mL min^{-1} and a gain of 1. During the measurements in range 2 the gas mixtures were sampled 2 minutes with a flow of 350 mL min^{-1} and a gain of 1.

The performance evaluation experiments at TÜV were 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.

3. Measurements

During the performance evaluation different key characteristics will be determined (Table 4). Different measurements were performed to determine the characteristics of the candidate generator at VSL and TÜV (Table 5). Chapter 3 of the performance evaluation protocol explains how the characteristics were determined during the performance evaluation [2].

Table 4 – Key characteristics determined during the performance evaluation at VSL or TÜV

Characteristic	Determined at
Stabilisation period	VSL
Short-term drift	VSL
Precision	VSL
Linearity	VSL
Bias	VSL
Sensitivity coefficient to sample gas pressure	TÜV
Sensitivity coefficient to surrounding temperature	TÜV
Sensitivity coefficient to electrical voltage	TÜV

Table 5 – Overview with the measurements performed at VSL and TÜV.

Time (date)	Range	Setpoint(s)	Characteristics
12-08-2022	2	3	Stabilisation period
12-09-2022	1	3	Short-term drift
06-10-2022	2	1 – 5	Precision, linearity and Bias
11-10-2022	2	1 – 5	Precision, linearity and Bias
12-10-2022	2	1 – 5	Precision, linearity and Bias
18-10-2022	2	1, 5	Stabilisation period
28-11-2022	1	1 – 5	Precision, linearity and Bias
08-12-2022	1	1 – 5	Precision, linearity and Bias
14-12-2022	1	1 – 5	Precision, linearity and Bias
03-07-2023	1	A	Line voltage
18 to 22-07-2023	1	A	Temperature Test
28-07-2023	1	B	Pressure
15-09-2023	1	1 – 5	Recalibration
19-09-2023	1	1 – 5	Recalibration

The data obtained with the PSA analyser was downloaded. The file contains time stamps and peak areas for the measurements performed with channel A and channel B. The data was processed according to the calibration protocol using software [2, 7]. The data obtained with the candidate generator and the results of the data processing are available online [8].

The data obtained with the Lumex analyser at TÜV were downloaded. The file contains time stamps and concentration values (1s) with Hg(0) channel and Hg (tot) channel. All second values were first condensed to minute values. Then the minute values were used. First a stabilisation period, typically 12 minutes, was taken into account before taking the first reading. Three minute readings were used to process the data. These three readings were averaged.

4. Results

4.1 Stabilisation period

Two experiments were performed to determine the stabilisation period of the candidate generator. The first experiment was performed directly after setting up the generator (Figure 1).

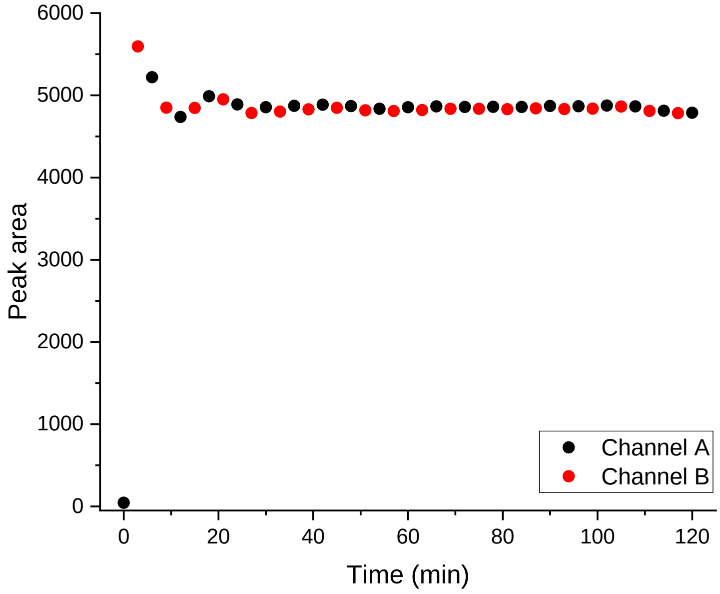

Figure 1 – Results stabilisation period directly after setting up the candidate generator.

The output of the candidate generator was stable after 8 measurements. Each measurement takes 3 minutes, giving a stabilisation period of 24 minutes.

During the second experiment the candidate generator was allowed to warm up and two different mercury concentrations were generated (Figure 2).

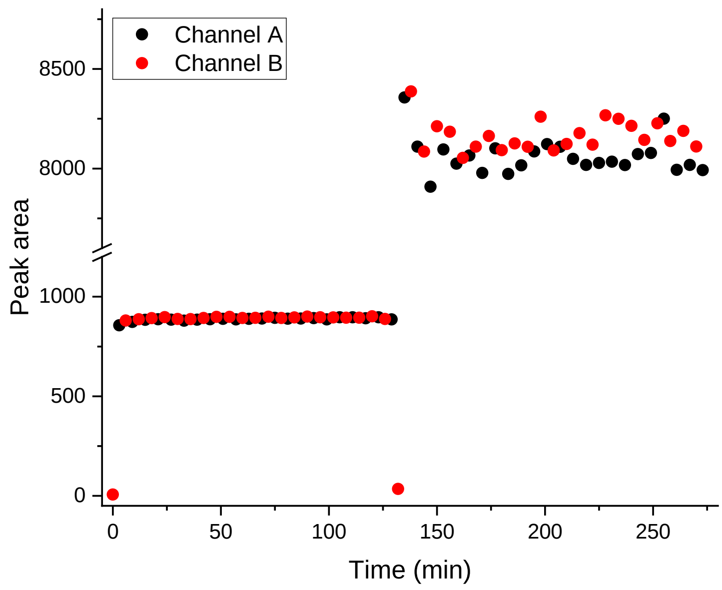

Figure 2 – Results stabilisation period after warm up of the candidate generator.

In this case for both mercury concentrations the stabilisation period was 3 measurements equal to 9 minutes.

4.2 Short-term drift

To determine the short-term drift (*d*) the output of the candidate generator was determined at t = 2, 8, 24 and 30 hours by comparison against the VSL reference standard (Table 6). The candidate output was determined and calculated according to the procedure described in the calibration protocol [2].

Table 6 – Candidate output (c_i) obtained during the short-term drift. The results from channel A and channel B were averaged.

Measurement (hours)	**c_i (ng m^{-3})**	**$U(c_i)$ (ng m^{-3}) (k = 2)**
2	12865	524
4	12612	531
24	12931	545
30	12405	528

The minimum c_i was 12405 ng m^{-3}, the maximum c_i was 12931 ng m^{-3} and the average $\overline{c_i}$ was 12704 ng m^{-3} with a standard deviation of 242 ng m^{-3}. The maximum difference between the candidate outputs obtained was 526 ng m^{-3} which is 4% of the average concentration. The average expanded uncertainty determined was 532 ng m^{-3} which is also a relative uncertainty of 4% (*k* = 2).

4.3 Calibration

Calibration of the candidate generator was performed for 2 concentration ranges. In each range 5 mercury concentrations are generated, and each concentration was measured in three measurement series. The output of the candidate generator and the uncertainty of the mercury concentration generated were calculated according to the protocol using the developed software (Table 7) [2,7].

Table 7 – Results calibrated output candidate generator and the calculated uncertainty of the mercury concentrations generated for channel A and channel B.

Range	Measurement series	Setpoint nr.	$c_{(i)}$ (ng m^{-3})	$U(c_{(i)})$ (ng m^{-3}) (k = 2)	$U(c_{(i)})$ (%) (k = 2)	$c_{(i)}$ (ng m^{-3})	$U(c_{(i)})$ (ng m^{-3}) (k = 2)	$U(c_{(i)})$ (%) (k = 2)
			Channel A			**Channel B**		
1	1	1	3326	138	4.2	3324	141	4.2
		2	6283	275	4.4	6320	262	4.2
		3	11827	489	4.1	11751	481	4.1
		4	15526	637	4.1	15560	633	4.1
		5	20963	846	4.0	20923	889	4.2
1	2	1	3337	138	4.1	3346	139	4.1
		2	6430	260	4.0	6400	260	4.1
		3	12295	496	4.0	12163	499	4.1
		4	15932	680	4.3	15991	663	4.1
		5	21455	878	4.1	21377	878	4.1
1	3	1	3383	140	4.1	3382	138	4.1
		2	6532	272	4.2	6522	267	4.1
		3	12315	520	4.2	12320	531	4.3
		4	16446	675	4.1	16373	674	4.1
		5	21415	910	4.2	21527	878	4.1
2	1	1	20976	874	4.2	20980	874	4.2
		2	42755	1738	4.1	42718	1756	4.1
		3	62770	2643	4.2	63696	2802	4.4
		4	83884	3401	4.1	83940	3387	4.0
		5	103023	4177	4.1	103298	4179	4.0
2	2	1	21169	865	4.1	21179	862	4.1
		2	42633	1734	4.1	42054	1780	4.2
		3	62338	2525	4.1	62725	2751	4.4
		4	82221	3374	4.1	82564	3399	4.1
		5	105498	4383	4.2	106152	4366	4.1
2	3	1	21180	865	4.1	21228	862	4.1
		2	43521	1734	4.1	43237	1780	4.2
		3	63645	2525	4.1	63919	2751	4.4
		4	83696	3374	4.1	83386	3399	4.1
		5	105625	4383	4.2	105714	4366	4.1

The relative expanded uncertainty of the mercury concentrations generated with the candidate generator ranges between 4.0% and 4.4%.

4.4 Precision: Repeatability and reproducibility

All mercury concentrations obtained with the candidate generator in range 1 and range 2 were analysed and repeated three times in different measurement series according to the calibration protocol [2]. Based on the responses of channel A the repeatability standard deviation (s_r, expressed as coefficient of variation in %) and reproducibility standard deviation (s_R, expressed as coefficient of variation in %) were determined (Table 8).

Table 8 – repeatability standard deviation (s_r) and reproducibility standard deviation (s_R).

Setpoint nr.	$c_{cand(i)}$ (ng m^{-3})	s_r (%)	s_R (%)
1	3046	0.68	1.29
2	6012	0.70	1.02
3	11493	0.69	1.18
4	15027	0.68	0.93
5	19977	0.55	0.71
1	19977	0.47	0.62
2	40137	0.65	0.65
3	60049	0.52	0.57
4	80016	0.49	0.84
5	99868	0.69	0.69

The average s_r was 0.61 % and the average s_R was 0.85%. The candidate generator has a precision of 0.85%, the uncertainty of the PSA SG analyser (2 %) is probably the most important source for the precision.

4.5 Interpolation function

The interpolation function of the candidate generator was determined for the two different ranges based on the three-measurement series performed for each range. The interpolation function for each measurement was determined using the software according to the protocol [2,7]. The software calculates the interpolation function for the data obtained with channel A and channel B separately (Figure 3). Based on the Akaike Information Criterion for small sample size (AICc) (Table 9) the interpolation function with the best fit for the data was determined. As an example, the interpolation function of range 1 measurement series 1 is shown.

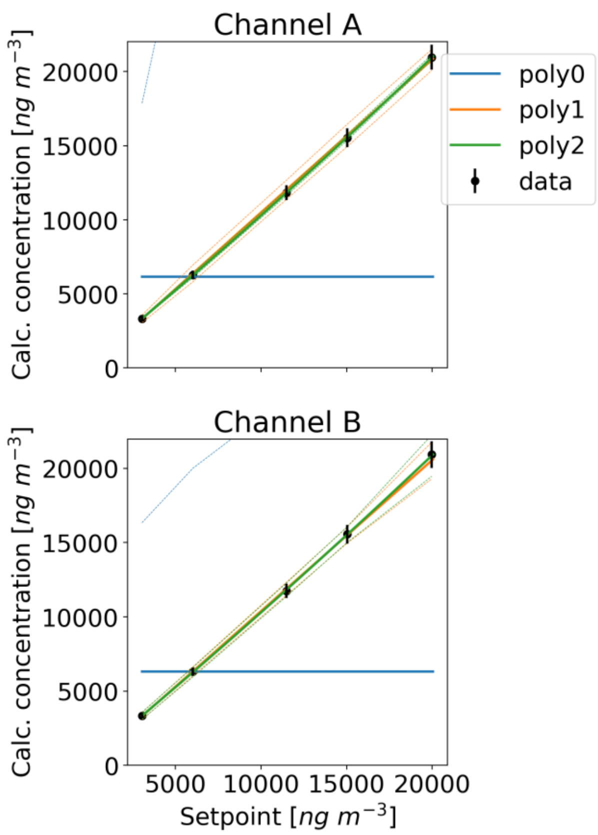

Figure 3 – Interpolation functions determined for channel A and channel B for range 1 measurement series 1.

Table 9 – AICc determined for channel A and channel B for range 1 measurement series 1. The smallest value indicates the best fit for the data.

Polynomial	Channel A	Channel B
Poly0 (non-zero constant)	107	104
Poly1 (linear)	*72*	*70*
Poly2 (quadratic)	73	84

The smallest value for the AICc indicates the best fit for the data which is the linear function. The linear function, $c = b_0 + b_1 c_{cand}$, is the optimal function for channel A and channel B of all measurement series (Table 10).

Table 10 – Regression coefficients for the interpolation function of Channel A and Channel B of range 1 measurement series 1.

	Parameters	Standard error
Channel A		
b_0	159	72
b_1	1.032	0.009
Channel B		
b_0	210	71
b_1	1.017	0.010

Due to the different intercept of all the interpolation functions, the slope of the functions was also different. To determine if the regression coefficients are comparable for Channel A and Channel B the functions can be averaged and a value for the comparability can be calculated (Chi squared). When they are comparable they can be combined (Figure 4).

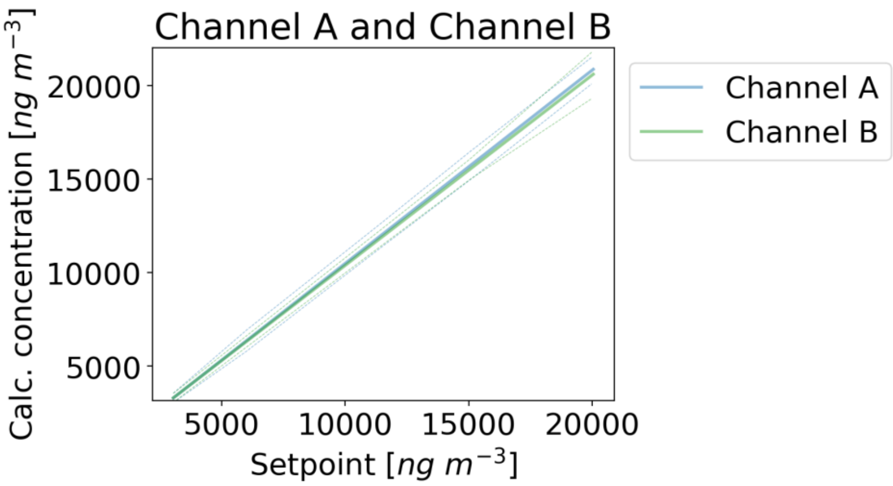

Figure 4 – Overlay interpolation functions channel A and channel B range 1 measurement series 1.

In this example the average regressed polynomial is acceptable with a Chi squared value of 2.5 and the probability that such a chi squared value should occur by chance was 0.96. The average regression coefficients and a covariance matrix were calculated (Table 11 and Table 12). The covariance matrix explains how the two data sets (b_0, b_1) are correlated. This correlation should be included in the calculation of the total uncertainty associated to the interpolation function.

Table 11 – Coefficients interpolation function obtained for range 1 measurement series 1

	Parameters	**Standard error**
$\boldsymbol{b_0}$	173	50
$\boldsymbol{b_1}$	1.027	0.007

Table 12 – Covariance matrix range 1 measurement series 1

	$\boldsymbol{b_0}$	$\boldsymbol{b_1}$
$\boldsymbol{b_0}$	2469	-0.251
$\boldsymbol{b_1}$	-0.251	0.0000426

For both ranges and all measurement series the optimal interpolation function poly 1 ($c = b_0 + b_1 c_{cand}$) and for all measurements the functions for channel A and channel B were comparable.

4.6 Bias

Based on the setpoint of the candidate generator (c_{cand}) the deviation (D_{c_i}) and relative deviation (D_{rel}) were determined for channel A and channel B (Table 13, Figure 5).

Table 13 – Deviation between the setpoint and the calibrated output of the candidate gas generator channel A and channel B.

Range	**Measurement series**	**Setpoint nr.**	$\boldsymbol{c_i}$ **(ng m^-3^)**	$\boldsymbol{D_{c_i}}$ **(ng m^-3^)**	$\boldsymbol{D_{rel}}$ **(%)**	$\boldsymbol{c_i}$ **(ng m^-3^)**	$\boldsymbol{D_{c_i}}$ **(ng m^-3^)**	$\boldsymbol{D_{rel}}$ **(%)**
			Channel A			**Channel B**		
1	1	1	3326	280	9.2	3324	278	9.2
		2	6283	271	4.5	6320	308	4.5
		3	11827	334	2.9	11751	258	2.9
		4	15526	499	3.3	15560	533	3.3
		5	20963	986	4.9	20923	946	4.9
1	2	1	3337	291	9.6	3346	300	9.6
		2	6430	418	7.0	6400	388	7.0
		3	12295	802	7.0	12163	670	7.0
		4	15932	905	6.0	15991	964	6.0
		5	21455	1478	7.4	21377	1400	7.4
1	3	1	3383	337	11.1	3382	336	11.1
		2	6532	520	8.7	6522	510	8.7
		3	12315	822	7.2	12320	827	7.2
		4	16446	1419	9.4	16373	1346	9.4
		5	21415	1438	7.2	21527	1550	7.2
2	1	1	20976	999	5.0	20980	1003	5.0
		2	42755	2618	6.5	42718	2581	6.5
		3	62770	2721	4.5	63696	3647	4.5
		4	83884	3868	4.8	83940	3924	4.8
		5	103023	3155	3.2	103298	3430	3.2

2	2	1	21169	1192	6.0	21179	1202	6.0
		2	42633	2496	6.2	42054	1917	6.2
		3	62338	2289	3.8	62725	2676	3.8
		4	82221	2205	2.8	82564	2548	2.8
		5	105498	5630	5.6	106152	6284	5.6
2	3	1	21180	1192	6.0	21228	1202	6.0
		2	43521	2496	6.2	43237	1917	6.2
		3	63645	2289	3.8	63919	2676	3.8
		4	83696	2205	2.8	83386	2548	2.8
		5	105625	5630	5.6	105714	6284	5.6

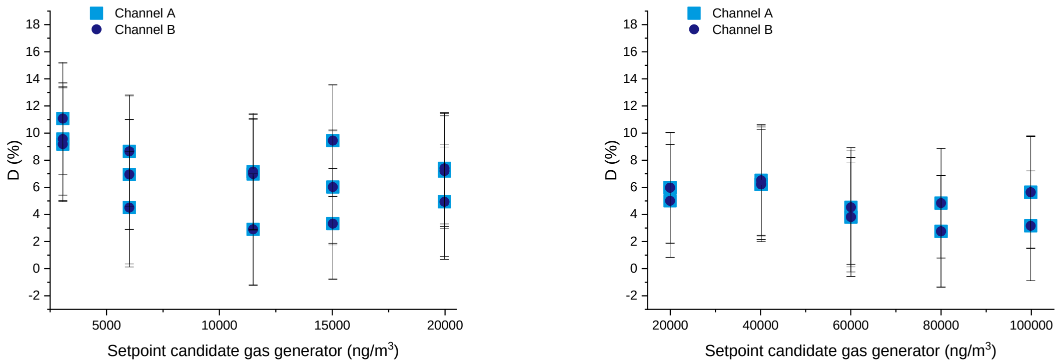

Figure 5 – Relative deviation of channel A and channel B for the measurement series. The uncertainty bars reflect the uncertainty calculated according to the calibration protocol [2].

The average relative deviation for range 1 was 7% and for range it was 2 5%. The relative deviations of channel A and channel B and the results of the different measurement series are comparable within the uncertainty determined according to the calibration protocol [2]. As the results for channel A and channel B and the different measurement series are comparable within the uncertainty they can be averaged to obtain the final calibration results.

4.7 Recalibration

After measurements at TÜV the generator was returned to VSL for a recalibration, to determine the stability of the generator over time and after transport and use. This was preformed 11 months after the first calibration measurements. Two measurements were performed in range 1 (Table 14, Figure 6).

Table 14 – Summary of the recalibration results obtained for the mercury concentration, c, from the candidate generator, the uncertainty, U(c), of the concentration and the deviation, D_c and D_{rel}, compared to the setpoint for channel A and channel B.

Measurement series	**Setpoint nr.**	c_{ref} **± U** (ng m^{-3}) (k = 2)	$c_{cand} \pm U$ (ng m^{-3}) (k=2)	c (ng m^{-3})	**U(c) (k = 2)** (ng m^{-3})	(%)	**Deviation** (ng m^{-3})	(%)
				Channel A				
4	1	3043 ± 122	3046 ± 146	3188	136	4.3	142	4.7
	2	5985 ± 239	6012 ±290	6150	295	4.8	138	2.3
	3	11482 ± 459	11493±554	11781	496	4.2	288	2.5
	4	14955 ± 598	15027±724	15749	654	4.2	722	4.8
	5	19954 ± 798	19977±962	20095	839	4.2	118	0.6

5	1	3043 ± 122	3046±146	3152	158	5.0	106	3.5
	2	5985 ± 239	6012±290	5766	251	4.4	-246	-4.1
	3	11482 ± 459	11493±554	11924	563	4.7	431	3.8
	4	14955 ± 598	15027±724	15843	649	4.1	816	5.4
	5	19954 ± 798	19977±962	20720	887	4.3	743	3.7
Measurement series	**Setpoint nr.**	c_{ref} **± U** (ng m^{-3}) (k = 2)	$c_{cand} \pm U$ (ng m^{-3}) (k=2)	c (ng m^{-3})	**U(c) (k = 2)** (ng m^{-3})	(%)	**Deviation** (ng m^{-3})	(%)
Channel B								
4	1	3043 ± 122	3046±146	3251	140	4.3	205	4.7
	2	5985 ± 239	6012±290	6215	282	4.5	203	2.3
	3	11482 ± 459	11493±554	11894	498	4.2	401	2.5
	4	14955 ± 598	15027±724	15721	660	4.2	694	4.8
	5	19954 ± 798	19977±962	20209	841	4.2	232	0.6
5	1	3043 ± 122	3046±146	3206	131	4.1	160	3.5
	2	5985 ± 239	6012±290	6172	263	4.3	160	-4.1
	3	11482 ± 459	11493±554	12082	516	4.3	589	3.8
	4	14955 ± 598	15027±724	15906	656	4.1	879	5.4
	5	19954 ± 798	19977±962	20673	907	4.4	696	3.7

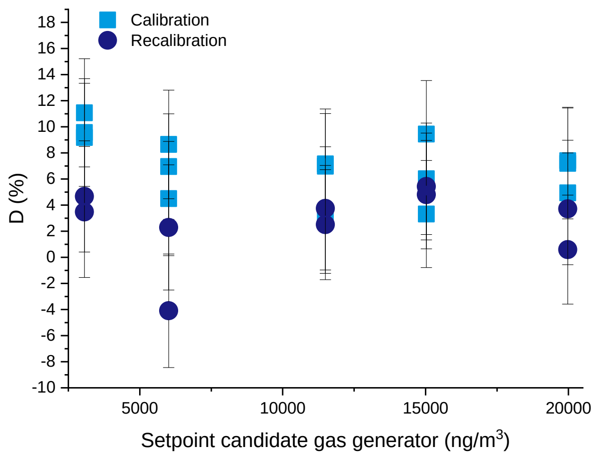

Figure 6 – Relative deviation of the calibration measurements. Only the results for Channel A are shown. The calibration results are measurement series 1, 2 and 3. The recalibration results are measurement series 4 and 5. The uncertainty bars reflect the uncertainty calculated according to the calibration protocol [2].

There was more deviation in the results obtained during the recalibration measurements than during the first three calibration measurements, the measurements obtained for setpoint 2 are not comparable for measurement series 4 and 5, within the obtained uncertainty. The results obtained during the recalibration for setpoint 1 are not comparable with the results obtained during the calibration. For setpoint 2 only the result in measurement series 4 is comparable and for setpoint 5 only the result in series 5 is comparable within the obtained uncertainty. For setpoint 3 and 4 the results of the calibration and recalibration are comparable. More calibration measurements are needed in the future to give a conclusion about the deviations obtained and about the recalibration period of the gas generator. Overall a closer agreement was found between the candidate generator and reference generator was obtained for the second set of data.

4.8 Sensitivity coefficient to sample gas pressure

Influence of sample gas pressure was tested by adjusting pressure level at the output of the generators. The 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 generator was set according to the manufacturer specifications.

Tests were conducted with constant input pressure of the carrier gas (dilution gas) according to manufacturer specifications. Pressure at output of generators was adjusted with a needle valve and measured. 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.

Deviations were related to the mean response of the candidate generator at standard pressure (Table 15).

Table 15 - Results of pressure test

	PSA 10.536		
Pressure kPa	**Reading µg/m³**	**Deviation %MV**	**b_P**
108.8	9.69	-4.12	-0.100
104.7	10.10	-	-
Maximum value		**-4.12**	**-0.100**
x_1	10.10		
x_2	9.69		
u	0.231		

The pressure test showed a maximum deviation of 4.12 % of the set point at a pressure difference of 4 kPa without pressure compensation. Data for pressure compensation can be set into the system to reduce the influence. The software provided with the generator has a pressure correction which equated to setpoint offset of -9.03% so the deviation measured was lower than expected.

4.9 Sensitivity coefficient to the surrounding 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 [9]. The required temperature range for outdoor installations was -20 °C to 50 °C.

Since the 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.

The test gas generator was exposed to the following temperature sequence in the climatic chamber:

20 °C → 5 °C → 20 °C → 40 °C → 20 °C.

The candidate gas generator was 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 were conducted with the candidate gas generator. The candidate gas generator as well as the analyser system was operating during the whole test.

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 were averaged to minimize possible drift effects of the analyser system in the calculation.

Deviations are related to the mean response of the candidate generator at 20 °C (Table 16).

Table 16 - Results of temperature test

Temperature °C	PSA 10.536 Reading µg/m³	Deviation % MV (∅ 20°)	B_t
(∅ 20°)	10.4	-	
20	10.4	0.0	-
5	10.5	1.0	-0.007
20	10.3	-1.0	-0.013
40	18.0	72.9	0.385
20	10.6	1.9	0.370
maximum value		**72.9**	**0.385**
$x_{i,adj}$	10.4		
x_{imax}	18.0		
x_{imin}	10.3		
u	4.359		

The temperature test demonstrated, that the generator cannot be used in the complete range of EN 15267-3 [9]. Especially with high temperatures the internal temperature of the mercury reservoir will rise and so output concentration of the generator will be out of range. It is recommended to use the unit in a temperature range close to 20 °C (+5 °C/-10 °C). The setpoint of the generator was 35 °C. For installations that exceed 40 °C a higher temperature setpoint is normally used.

4.10 Sensitivity coefficient to electrical voltage

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 was 230 V, maximum value in the test was 253 V and minimum value was 196 V.

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

The candidate gas generator to be tested was connected to the supply voltage using the isolating transformer. Output voltage was controlled by the multi meter. The candidate gas generator was warmed up according to manufacturer's specifications also the analyser system was warmed up according to relevant specifications.

The deviations between the average readings at each voltage and the average reading at the nominal supply voltage were determined.

Deviations were related to the mean response of the candidate generator at a nominal voltage of 230 V (Table 17).

Table 17 - Results of line voltage test

Voltage Volt	PSA 10.536 Span point Reading µg/m³	Deviation %MV	b_{sv}
230	5.66	-	
242	5.70	0.7	0.003
253	5.64	-0.4	-0.005
219	5.63	-0.5	0.003
207	5.64	-0.4	-0.001
196	5.63	-0.5	0.001
Maximum value-		**0.7**	**-0.005**
b_{sv} (253/196 Volt)			**0.000**
$x_{i,adj}$	5.66		
x_{imax}	5.70		
x_{imin}	5.63		
u	0.021		

The line voltage test showed a max. deviation of -0,7 % within the tested range. A tendency of deviation of the output value of the generator depending on the voltage was not observed. The found deviations of max. 0.7 % are within the uncertainty range and within the range of repeatability of the generator in combination with the measuring device used. Voltage fluctuations in the typical range thus have no relevant influence on the performance of the test gas generator.

5. Conclusion

The candidate generator (PSA 10.536) was tested under the performance evaluation by determining the stabilisation period, short-term drift, calibration and uncertainty of the mercury concentration generator, linearity, bias and sensitivity coefficient to sample gas pressure, surrounding temperature and electrical voltage. Two mercury concentration ranges were investigated, range 1 3000 ng m^{-3} – 20000 ng m^{-3} and range 2 20000 ng m^{-3} – 100000 ng m^{-3}.

The stabilisation period of the candidate generator was 24 minutes after the first start-up. Once running the stabilisation period was 9 minutes. The short-term drift of the candidate generator was 4%, which is equal to the measurement and generator uncertainty. Based on the calibration measurements the repeatability standard deviation and reproducibility standard deviation were determined to be 0.61% and 0.85 % respectively. The gas generator can be used over a range of mercury concentrations with a linear function for the two ranges investigated. The deviation between the setpoint of the candidate generator and the calibrated mercury concentration was 7% for range 1 and 5% for range 2.

Based on the performance evaluation the calibration results of the measurement series and channel A and channel B were averaged to provide results for the output and uncertainty of candidate generator (Table 18).

Table 18 – Averaged calibration results measurement series 1, 2 and 3.

Range	Setpoint nr.	$c_{cand(i)}$ (ng m^{-3})	$U(c_{(candi)})$ (ng m^{-3}) (k = 2) (= 4.81%)	c_i (ng m^{-3})	$U(c_i)$ (ng m^{-3}) (k = 2)	$U(c_i)$ (%) (k = 2)
1	1	3046	146	3350	139	4.2
	2	6012	290	6415	266	4.1
	3	11493	554	12112	502	4.1
	4	15027	724	15971	660	4.1
	5	19977	962	21109	867	4.1
2	1	19977	962	21109	867	4.1
	2	40137	1933	42475	1754	4.1
	3	60049	2892	62765	2666	4.2
	4	80016	3854	82899	3389	4.1
	5	99868	4810	104937	4309	4.1

The relative expanded uncertainty of the mercury concentration generated was 4.1% for the setpoints save from setpoint number 3 in range 2 which has a relative expanded uncertainty of 4.2%.

The regression coefficients for the linear function, $c = b_0 + b_1 c_{cand}$, were also calculated based on the results of the different measurement series (Table 19 and Table 20).

Table 19 – Coefficients interpolation function obtained for range 1 and range 2

	Range 1		Range 2	
	Parameters	Standard error	Parameters	Standard error
b_0	142	34	295	151
b_1	1.049	0.006	1.043	0.004

Table 20 – Covariance matrix for range 1 and range 2

	Range 1		Range 2	
	b_0	b_1	b_0	b_1
b_0	1182	-0.16	22885	-0.52
b_1	-0.16	0.000034	-0.52	0.000017

Recalibration of the generator after a period of 11 months showed mixed results. Half of the recalibrated setpoints showed comparable results with the calibration results, the other half of the deviations larger than the obtained uncertainty for the recalibration. More calibration measurements are needed in the future to give a conclusion about the recalibration period of the gas generator.

The sensitivity coefficient for sample gas pressure is larger than the uncertainty, however data for pressure compensation can be set into the system to reduce the influence. The results for the temperature sensitivity showed a large influence at high temperatures the internal temperature. It is recommended to use the unit in a temperature range close to 20 °C (+5 °C/-10 °C). No influence was found for the sensitivity coefficient for electrical voltage.

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Bell-jar performance evaluation report

19NRM03 SI-Hg Task 3.1

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Table of Contents

1. Introduction

An automatic bell-jar from the Van Swinden Laboratory (VSL) was tested during the performance evaluation. This evaluation was part of the project "Metrology for traceable protocols for elemental and oxidised mercury" (19NRM03 SI-Hg) in the European Metrology for Innovation and Research Programme (EMPIR). The aim of the performance evaluation was to gather data on the characteristics of at least three elemental mercury (Hg^0) gas generators on the market. Selected gas generator models for evaluation are representative examples of applicable generation methods and generators available on the market.

VSL provided a Bell-jar for the validation. The Tekran® Model 2505 (Tekran, USA) mercury vapour calibration unit is based on the Bell-jar principle. A Bell-jar generates saturated mercury concentration in air, according to ISO 6145-9 [1]. Since the saturation vapour pressure of mercury is a function of temperature, the exact volume injected, and temperature of the mercury saturated air need to be set in order to determine the mercury injection mass based on the Dumarey equation [2-4].

The performance evaluation was performed according to the protocol [5]. The protocol was designed to determine key characteristics of off-the-shelf elemental mercury (Hg^0) gas generators. These key characteristics include the stabilisation period, short-term drift, precision, i.e., reproducibility and repeatability of the concentration generated, linearity and bias. The performance evaluation was based on the calibration protocol developed for these gas generators that enables them to provide calibration gas mixtures for Hg^0 concentration with traceability to the International System of Units (SI) and with a defined uncertainty [6]. Thereby, these off-the-shelf gas generators can fulfil requirements with respect to metrological traceability and measurement uncertainty, as required by, e.g., ISO/IEC 17025. The measurements for the performance evaluation were performed at VSL in the Netherlands. All measurements were performed at standard conditions of temperature (293.15 K) and pressure (101.325 kPa).

This report shows the results obtained during the performance evaluation of the Bell-jar elemental mercury gas generator. This report is part of D5 of the 19NRM03 SI-Hg project "Report on the performance evaluation of at least three Hg^0 gas generators on the market".

2. Equipment

2.1 Bell-jar

Calibration gas mixtures of Hg^0 in air were be generated by the bell-jar under evaluation (hereinafter referred to as candidate generator). The bell-jar was set at a temperature of 18 °C and a calibrated digital syringe (Hamilton) was used with a volume between 5 and 25 µl to remove a known mass of mercury from the Bell-jar and inject the volume in the analyser. To obtain metrological traceable calibration standards the temperature sensor inside the Bell-jar and the syringe used to transfer the gas mixture were calibrated. The mass inside the syringe is calibrated according to the Dumarey equation [2-4]. The mercury mass is injected into the sample stream of the analyser, the mercury concentration is calculated by dividing the mercury mass by the total sample flow used. The sample flow used for all experiments was 1L. During the performance evaluation key characteristics were determined according to the protocol [5]. All measurements will be performed at standard conditions of temperature (293.15 K) and pressure (101.325 kPa).

The candidate generator was tested in the range 50 ng m^{-3} – 300 ng m^{-3} (Table 1).

Table 1 – Settings and setpoints ($c_{cand(i)}$) according to the equipment, of the candidate generator used during the performance evaluation.

Setpoint nr.	**Volume (µL)**	**Mercury mass* (ng)**	$c_{cand(i)}$ **(ng m^{-3})**
1	5.1	0.05634	56.34
2	10.2	0.11047	110.47
3	15.2	0.16791	167.91
4	20.3	0.22425	224.25
5	25.4	0.28059	280.59

* According to Dumarey.

2.2 Primary mercury gas standard

The VSL primary gas standard (hereinafter referred to as reference standard) was 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 [7-9].

For the performance evaluation gas mixtures with different mercury concentrations (c_{ref}) were obtained with different settings of the reference standard (Table 2). For these experiments 3 diffusion cells with a capillary diameter of Ø1 mm were used with a total diffusion rate of (0.583 ± 0.015) ng min^{-1} (k = 2) and purified air flow rates between 1 L min^{-1} and 9 L min^{-1}.

Table 2 – Mercury concentrations obtained with the reference standard during the performance evaluation.

Setpoint nr.	c_{ref} **(ng m^{-3})**	$U(c_{ref})$ **(ng m^{-3}) (*k* = 2) (= 5%)**
1	56.1	2.8
2	110	6
3	168	8
4	228	11
5	275	14

2.3 Mercury analysers

The experiments at VSL were performed with a PSA Sir Galahad II mercury analyser (P S Analytical, UK) as explained in the protocol [5]. During the measurements the gas mixtures were sampled 2 minutes with a flow of 500 mL min^{-1} and a gain of 100.

3. Measurements

During the performance evaluation different key characteristics will be determined, e.g.: stabilisation period, short-term drift, precision, linearity and bias. Different measurements were performed to determine the characteristics of the candidate generator (Table 3). Chapter 3 of the performance evaluation protocol explains how the characteristics were determined during the performance evaluation [5].

Table 3 – Overview with the measurements performed.

Time (date)	**Setpoint(s)**	**Characteristics**
14-02-2023	1	Short-term drift
20-02-2023	1 – 5	Precision, linearity and Bias
28-02-2023	1 – 5	Precision, linearity and Bias
09-03-2023	1 – 5	Precision, linearity and Bias
14-03-2023	1, 5	Stabilisation period

The data obtained with the PSA analyser was downloaded. The file contains time stamps and peak areas for the measurements performed with channel A and channel B. The data was processed according to the calibration protocol using software [5, 10]. The data obtained with the candidate generator and the results of the data processing are available online [11].

4. Results

4.1 Stabilisation period

An experiment was performed to determine the stabilisation period of the candidate generator (Figure 1). In the period before this measurement the generator was turned on and stabilised. The syringe used for the injection had been used in the period before as well and was flushed at least three times with the mercury gas mixture from the bell jar before injection.

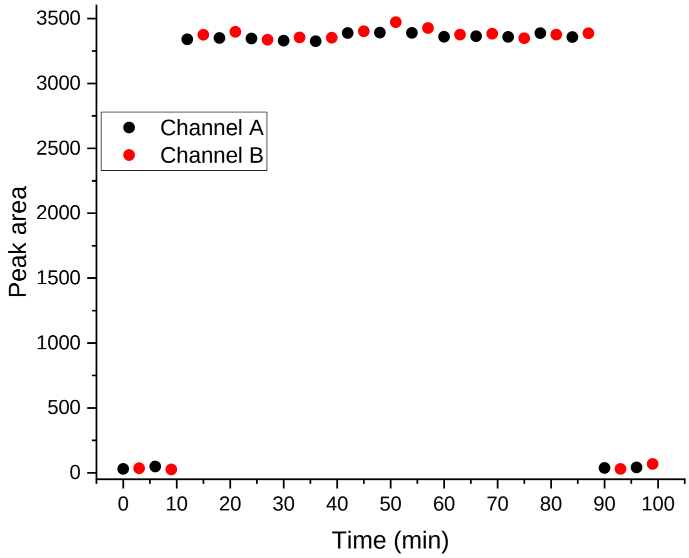

Figure 1 – Results stabilisation period of the candidate generator.

Before and after the experiment 4 zero air measurements were performed, the output of the candidate generator was stable at the first measurements.

4.2 Short-term drift

To determine the short-term drift (*d*) the output of the candidate generator was determined at t = 2, 6, 24 and 30 hours by comparison against the VSL reference standard (Table 4). The candidate output was determined and calculated according to the procedure described in the calibration protocol [5,10].

Table 4 – Candidate output (c_i) obtained during the short-term drift. The results from channel A and channel B were averaged.

Measurement (hours)	**c_i (ng m^{-3})**	**$U(c_i)$ (ng m^{-3}) (k = 2)**
2	51.6	2.8
6	51.8	3.2
24	51.9	3.0
30	52.5	2.9

The minimum c_i was 51.6 ng m^{-3}, the maximum c_i was 52.5 ng m^{-3} and the average $\overline{c_i}$ was 51.9 ng m^{-3} with a standard deviation of 0.4 ng m^{-3}. The maximum difference between the candidate outputs obtained was 0.9 ng m^{-3} which is 1.7% of the average concentration. The average expanded uncertainty determined was 2.8 ng m^{-3} which is a relative uncertainty of 6% (*k* = 2).

4.3 Calibration

Calibration of the candidate generator was performed over concentration range for which 5 mercury concentrations are generated, and each concentration was measured in three measurement series. The output of the candidate generator and the uncertainty of the mercury concentration generated were calculated according to the protocol using the developed software (Table 5) [5,10].

Table 5 – Results calibrated output candidate generator and the calculated uncertainty of the mercury concentrations generated for channel A and channel B.

Measurement series	**Setpoint nr.**	$c_{(i)}$ **(ng m^{-3})**	$U(c_{(i)})$ **(ng m^{-3}) (k = 2)**	$U(c_{(i)})$ **(%) (k = 2)**	$c_{(i)}$ **(ng m^{-3})**	$U(c_{(i)})$ **(ng m^{-3}) (k = 2)**	$U(c_{(i)})$ **(%) (k = 2)**
		Channel A			**Channel B**		
1	1	50.5	3.1	6.2	53.2	3.1	5.8
	2	105.3	5.5	5.3	104.0	5.4	5.2
	3	161.8	8.3	5.1	158.6	8.6	5.4
	4	216.4	11.0	5.1	216.6	11.2	5.2
	5	271.3	14.2	5.2	270.1	14.4	5.3
2	1	53.4	3.0	5.7	50.8	2.8	5.5
	2	105.6	5.4	5.1	105.7	5.6	5.3
	3	160.6	8.2	5.1	159.7	8.2	5.1
	4	215.7	10.9	5.1	215.5	11.0	5.1
	5	272.3	13.7	5.0	272.0	13.8	5.1
3	1	50.5	3.0	5.9	50.6	3.0	6.0
	2	103.3	5.7	5.5	102.4	5.4	5.2
	3	158.9	8.1	5.1	158.6	8.0	5.0
	4	214.7	11.0	5.1	214.0	11.3	5.3
	5	270.5	13.6	5.0	269.8	13.6	5.0

The relative expanded uncertainty of the mercury concentrations generated with the candidate generator ranges between 5.0% and 6.2%.

4.4 Precision: Repeatability and reproducibility

All mercury concentrations obtained with the candidate generator were analysed and repeated three times in different measurement series according to the calibration protocol [5]. Based on the responses of channel A the repeatability standard deviation (s_r, expressed as coefficient of variation in %) and reproducibility standard deviation (s_R, expressed as coefficient of variation in %) were determined (Table 6).

Table 6 – repeatability standard deviation (s_r) and reproducibility standard deviation (s_R).

Setpoint nr.	$c_{cand(i)}$ **(ng m^{-3})**	**s_r (%)**	**s_R (%)**
1	56.34	1.53	3.08
2	110.47	1.32	1.32
3	167.91	0.96	4.50
4	224.25	0.67	0.73
5	280.59	0.65	1.75

The average s_r was 1.03% and the average s_R was 2.28%. The spread in s_R is large with an absolute standard deviation of 1.5%. The Bell-jar generator has a precision of 2.3%, the uncertainty of the PSA SG analyser (2 %) is probably the most important source for the precision.

4.5 Interpolation function

The interpolation function of the candidate generator was determined based on the three-measurement series performed for each range. The interpolation function for each measurement was determined using the software according to the protocol [5,10]. The software calculates the interpolation function for the data obtained with channel A and channel B separately (Figure 3). Based on the weighted squared deviation (Figure 4) and Akaike Information Criterion for small sample size (AICc) (Table 7) the interpolation function with the best fit for the data was determined. As an example, the interpolation function of measurement series 1 is shown.

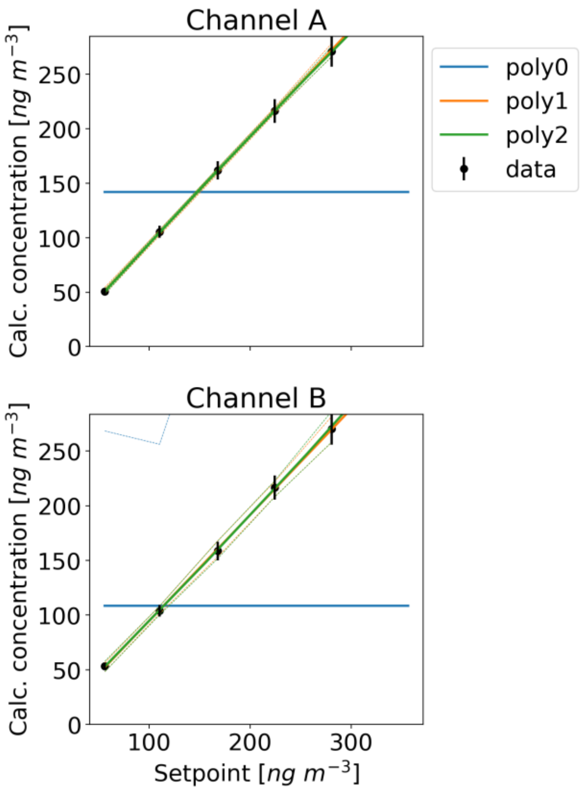

Figure 3 – Interpolation functions determined for channel A and channel B for measurement series 1.

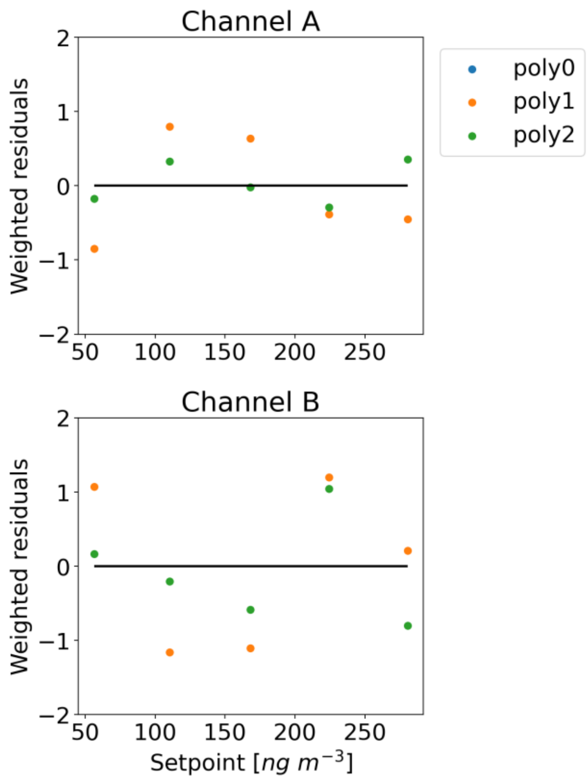

Figure 4 – Weighted residuals determined for channel A and channel B for measurement series 1.

Table 7 – AICc determined for channel A and channel B for measurement series 1. The smallest value indicates the best fit for the data.

Polynomial	**Channel A**	**Channel B**
Poly0 (non-zero constant)	60	60
Poly1 (linear)	*20*	*27*
Poly2 (quadratic)	31	42

A function is acceptable if the weighted residual is in absolute value ≤ 2. For both poly1 and poly2 the weighted residuals are in absolute value ≤ 2. The best fit for the data is the straight line as the data will be overfitted when using poly2. The smallest value for the AICc indicates the best fit for the data which is also the linear function. The linear function, $c = b_0 + b_1 c_{cand}$, is the optimal function for channel A and channel B of all measurement series (Table 8).

Table 8 – Regression coefficients for the interpolation function of Channel A and Channel B of range 1 measurement series 1.

	Parameters	**Standard error**
Channel A		
$\boldsymbol{b_0}$	-4.2	0.9
$\boldsymbol{b_1}$	0.985	0.005
Channel B		
$\boldsymbol{b_0}$	-2.2	1.3
$\boldsymbol{b_1}$	0.969	0.010

Due to the different intercept of all the interpolation functions, the slope of the functions is also different. To determine if the regression coefficients are comparable for Channel A and Channel B the functions can be averaged and a value for the comparability can be calculated (Chi squared). If they are comparable they can be combined (Figure 5).

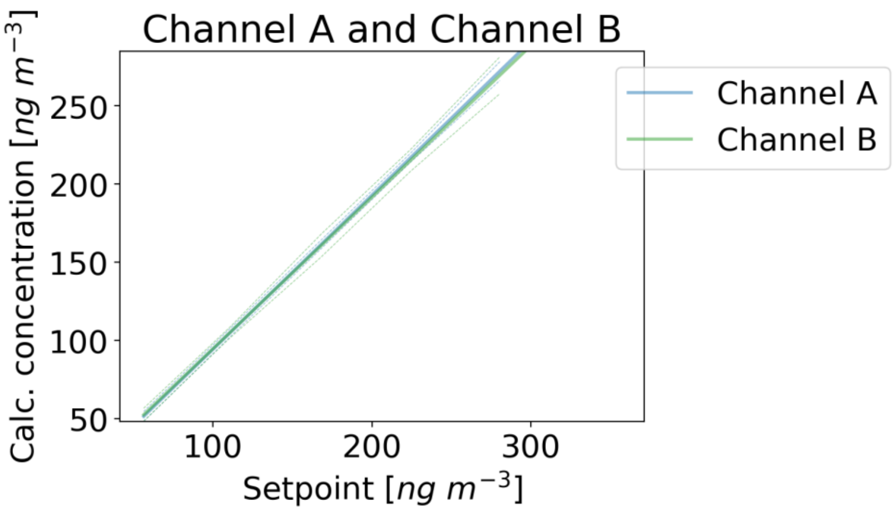

Figure 5 – Overlay interpolation functions channel A and channel B measurement series 1.

In this example the average regressed polynomial is acceptable with a Chi squared value of 2.0 and the probability that such a chi squared value should occur by chance was 0.98. The average regression coefficients and a covariance matrix were calculated (Table 7 and Table 8). The covariance matrix explains how the two data sets (b_0, b_1) are correlated. This correlation should be included in the calculation of the total uncertainty associated to the interpolation function.

Table 7 – Coefficients interpolation function obtained for measurement series 1

	Parameters	**Standard error**
b_0	-3.3	0.8
b_1	0.979	0.005

Table 8 – Covariance matrix range 1 measurement series 1

	b_0	b_1
b_0	0.62	-0.0037
b_1	-0.0037	0.000028

For both ranges and all measurement series the optimal interpolation function poly 1 ($c = b_0 + b_1 c_{cand}$) and for all measurements the functions for channel A and channel B were comparable.

4.6 Bias

Based on the setpoint of the candidate generator (c_{cand}) the deviation (D_{c_i}) and relative deviation (D_{rel}) were determined for channel A and channel B (Table 9, Figure 6).

Table 9 – Deviation between the setpoint and the calibrated output of the candidate generator channel A and channel B.

Measurement series	Setpoint nr.	c_{cand} (ng m-3)	c_i (ng m-3)	D_{c_i} (ng m-3)	D_{rel} (%)	c_i (ng m-3)	D_{c_i} (ng m-3)	D_{rel} (%)
			Channel A			Channel B		
1	1	56.34	50.5	-5.8	-10.4	53.2	-3.2	-10.4
	2	110.47	105.3	-5.2	-4.7	104.0	-6.5	-4.7
	3	167.91	161.8	-6.1	-3.6	158.6	-9.3	-3.6
	4	224.25	216.4	-7.8	-3.5	216.6	-7.6	-3.5
	5	280.59	271.3	-9.2	-3.3	270.1	-10.5	-3.3
2	1	56.34	53.4	-2.9	-5.2	50.8	-5.5	-5.2
	2	110.47	105.6	-4.9	-4.4	105.7	-4.8	-4.4
	3	167.91	160.6	-7.3	-4.3	159.7	-8.2	-4.3
	4	224.25	215.7	-8.6	-3.8	215.5	-8.7	-3.8
	5	280.59	272.3	-8.3	-3.0	272.0	-8.6	-3.0
3	1	56.34	50.5	-5.8	-10.3	50.6	-5.8	-10.3
	2	110.47	103.3	-7.2	-6.5	102.4	-8.1	-6.5
	3	167.91	158.9	-9.0	-5.4	158.6	-9.3	-5.4
	4	224.25	214.7	-9.6	-4.3	214.0	-10.2	-4.3
	5	280.59	270.5	-10.0	-3.6	269.8	-10.8	-3.6

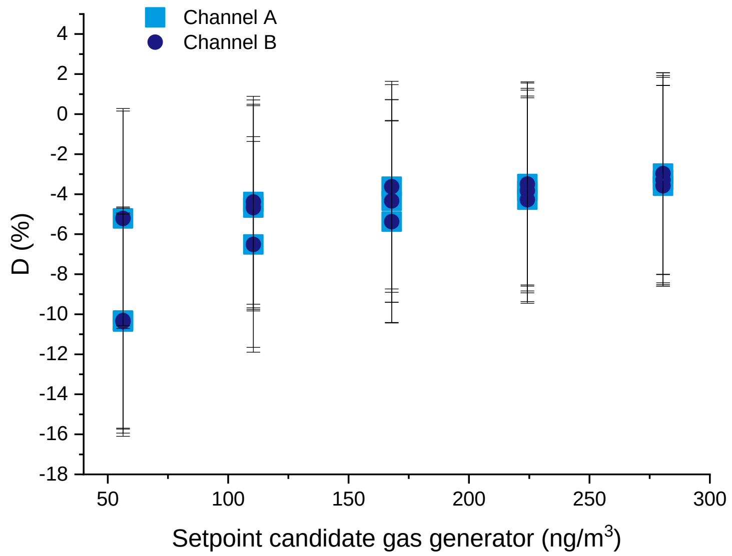

Figure 6 – Relative deviation of channel A and channel B for the measurement series. The uncertainty bars reflect the uncertainty calculated according to the calibration protocol [5].

The average relative deviation was -5%. The relative deviations of channel A and channel B and the results of the different measurement series are comparable within the uncertainty determined according to the calibration protocol [5]. As the results for channel A and channel B and the different measurement series are comparable within the uncertainty they can be averaged to obtain the final calibration results.

5. Conclusion

The candidate generator (Bell-jar) was tested under the performance evaluation by determining the stabilisation period, short-term drift, calibration and uncertainty of the mercury concentration generator, linearity and bias. A range of mercury concentrations was tested 50 ng m^{-3} – 300 ng m^{-3}.

The stabilisation period of the candidate generator once running the stabilisation period was 0 minutes. The short-term drift of the candidate generator was 1.7%, which is within the measurement uncertainty. Based on the calibration measurements the repeatability standard deviation and reproducibility standard deviation were determined to be 1.0% and 2.5 % respectively. The gas generator can be used over a range of mercury concentrations with a linear function for the range investigated. The deviation between the setpoint of the candidate generator and the calibrated mercury concentration was -5%.

Based on the performance evaluation the calibration results of the measurement series and channel A and channel B were averaged to provide results for the output and uncertainty of candidate generator (Table 10).

Table 10 – Averaged calibration results

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	56.3	51.5	3.0	5.8
2	111	104	6	5.3
3	168	160	8	5.2
4	224	216	11	5.1
5	281	271	14	5.1

The relative expanded uncertainty of the mercury concentration generated ranges from 5.1% to 5.8% for the lower mercury concentrations. The higher uncertainty is caused by the larger spread in the measurement data leading to a larger stability uncertainty and repeatability uncertainty contribution. The regression coefficients for the linear function, $c = b_0 + b_1 c_{cand}$, were also calculated based on the results of the different measurement series (Table 11 and Table 12).

Table 11 – Regression coefficients for the linear function, $c = b_0 + b_1 c_{cand}$

	Parameters	**Standard error**
b_0	-3.3	0.8
b_1	0.979	0.005

Table 12 – Covariance matrix

	b_0	b_1
b_0	0.62	-0.0037
b_1	-0.0037	0.000028

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Tekran Model 3425 performance evaluation report for elemental mercury

19NRM03 SI-Hg Task 3.1

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Table of Contents

1. Introduction

The Tekran® Model 3425 Elemental & Oxidized Mercury Generator was tested during the performance evaluation. In this report results for elemental mercury are shown. This evaluation was part of the project "Metrology for traceable protocols for elemental and oxidised mercury" (19NRM03 SI-Hg) in the European Metrology for Innovation and Research Programme (EMPIR). The aim of the performance evaluation was to gather data on the characteristics of at least three elemental mercury (Hg^0) gas generators on the market. Selected gas generator models for evaluation are representative examples of applicable generation methods and generators available on the market.

The Tekran® Model 3425 Elemental & Oxidized Mercury Generator provides NIST traceable calibration gas for system calibration. The 3425 is a saturation gas generator working according to ISO 6145-9 [1]. The generator can be set to automatically generate multi-point calibration gas. Elemental mercury gas is delivered using a NIST traceable, temperature controlled, saturated mercury vapor source. Precision mass flow controllers dilute the mercury source output to the desired value. A low flow rate is passed across the mercury reservoir ensuring that the gas becomes saturated with mercury. The mercury-saturated gas is then diluted into the concentration range of interest. The flow rates are controlled using two mass flow controllers. The mercury concentration can be adjusted by altering the temperature of the oven or by adjusting the reservoir or dilution flows. The Tekran 3425 and earlier models have been in use and performing under the strict United States Environmental Protection Agency (US EPA) National Institute of Standards and Technology (NIST) traceability protocols since 2009 (~200 units) [2]. Therefore, this is the first comparison between the VSL primary mercury gas standard and a NIST calibrated gas generator.

The performance evaluation was performed according to the protocol [3]. The protocol was designed to determine key characteristics of off-the-shelf elemental mercury (Hg^0) gas generators. These key characteristics include the stabilisation period, short-term drift, precision, i.e., reproducibility and repeatability of the concentration generated, linearity, bias, sensitivity to sample gas pressure, sensitivity to surrounding temperature and sensitivity to electrical voltage. The performance evaluation was based on the calibration protocol developed for these gas generators that enables them to provide calibration gas mixtures for Hg^0 concentration with traceability to the International System of Units (SI) and with a defined uncertainty [4]. Thereby, these off-the-shelf gas generators can fulfil requirements with respect to metrological traceability and measurement uncertainty, as required by, e.g., ISO/IEC 17025. The measurements for the performance evaluation were performed at the Van Swinden Laboratory (VSL) in the Netherlands and Technischer Überwachungsverein Rheinland Energy GmbH (TÜV) in Germany. All measurements were performed at standard conditions of temperature (293.15 K) and pressure (101.325 kPa).

This report shows the results obtained during the performance evaluation of the Tekran® Model 3425 gas generator for elemental mercury. This report is part of D5 of the 19NRM03 SI-Hg project "Report on the performance evaluation of at least three Hg^0 gas generators on the market".

2. Equipment

2.1 Tekran® Model 3425

Calibration gas mixtures of Hg^0 in air were generated by the Tekran Model 3425 candidate gas generator under evaluation (hereinafter referred to as Tekran generator) during the performance evaluation key characteristics were determined according to the protocol [3]. All measurements will be performed at standard conditions of temperature (293.15 K) and pressure (101.325 kPa).

At VSL the Tekran generator was tested in the range 5000 ng m^{-3} – 25000 ng m^{-3} and at TÜV two setpoints were used (Table 1).

Table 1 – Settings and setpoints ($c_{cand(i)}$) according to the equipment, of the Tekran generator used during the performance evaluation experiments.

Setpoint nr.	**Tekran generator setpoint**	$c_{cand(i)}$ **(ng m^{-3})**	Partner
1	P20L	5590	VSL & TÜV
2	P20M	12220	VSL & TÜV
3	P40M	24130	VSL

The setpoints of the Tekran generator have been calibrated against the Tekran Vendor Prime generator which has in turn been calibrated against the NIST Prime generator [2].

2.2 Primary mercury gas standard

The VSL primary gas standard (hereinafter referred to as reference standard) was 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 [5-7].

For the performance evaluation gas mixtures with different mercury concentrations (c_{ref}) were obtained with different settings of the reference standard (Table 2). One diffusion cell with a capillary diameter of Ø33 mm was used with a diffusion rate of (72.1 ± 0.4) ng min^{-1} (k = 2) and purified air flow rates between 1 L min^{-1} and 5 L min^{-1}.

Table 2 – Mercury concentrations obtained with the reference standard during the performance evaluation.

Setpoint nr.	c_{ref} **(ng m^{-3})**	$U(c_{ref})$ **(ng m^{-3}) (k = 2) (= 4%)**
1	5553	222
2	12259	490
3	23718	949

2.3 Mercury analysers

The experiments at VSL were performed with a PSA Sir Galahad II mercury analyser (P S Analytical, UK) as explained in the protocol [3]. During the measurements the gas mixtures were sampled 1 minute with a flow of 140 mL min^{-1} and a gain of 10.

The performance evaluation experiments at TÜV were 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 oxidized forms of mercury. The dual analytical system will be calibrated with the secondary elemental mercury gas standard during the performance evaluation.

3. Measurements

During the performance evaluation different key characteristics will be determined (Table 3). Different measurements were performed to determine the characteristics of the Tekran generator at VSL and TÜV (Table 4). Chapter 3 of the performance evaluation protocol explains how the characteristics were determined during the performance evaluation [3].

Table 3 – Key characteristics determined during the performance evaluation at VSL or TÜV

Characteristic	Determined at
Stabilisation period	VSL
Short-term drift	VSL
Precision	VSL
Linearity	VSL
Bias	VSL
Sensitivity coefficient to sample gas pressure	TÜV
Sensitivity coefficient to surrounding temperature	TÜV
Sensitivity coefficient to electrical voltage	TÜV

Table 4 – Overview with the measurements performed at VSL and TÜV.

Time (date)	Setpoint(s)	Characteristics
09-06-2023	2	Stabilisation period
12-06-2023	1 – 3	Precision, linearity and Bias
19-06-2023	1 – 3	Precision, linearity and Bias
21-06-2023	2	Short-term drift
26-06-2023	1 – 3	Precision, linearity and Bias
29-06-2023	1 – 3	Precision, linearity and Bias
14.07.2023	2	Line voltage
18 to 22-07-2023	1-2	Temperature Test
28-07-2023	2	Pressure

The data obtained with the PSA analyser was downloaded. The file contains time stamps and peak areas for the measurements performed with channel A and channel B. The data was processed according to the calibration protocol using software [3, 8]. The data obtained with the Tekran generator and the results of the data processing are available online [9].

The data obtained with the Lumex analyser at TÜV were downloaded. The file contains time stamps and concentration values (1s) with Hg(0) channel and Hg (tot) channel. All second values were first condensed to minute values. Then the minute values were used. First a stabilisation period, typically 12 minutes, was taken into account before taking the first reading. Three minute readings were used to process the data. These three readings were averaged.

4. Results

4.1 Stabilisation period

An experiment was performed to determine the stabilisation period of the Tekran generator. The experiment was performed directly after setting up the generator (Figure 1).

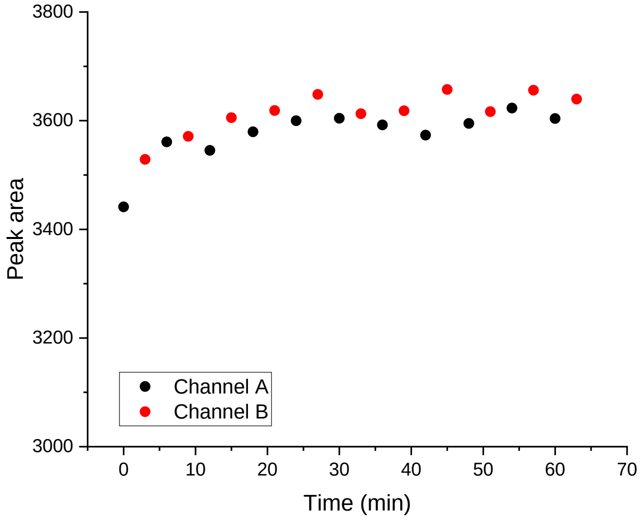

Figure 1 – Results stabilisation period directly after setting up the Tekran generator.

The output of the Tekran generator was stable after 5 measurements. Each measurement takes 3 minutes, giving a stabilisation period of 15 minutes.

4.2 Short-term drift

To determine the short-term drift (*d*) the output of the Tekran generator was determined at t = 2, 7, 26 and 31 hours by comparison against the VSL reference standard (Table 5). The Tekran generator output was determined and calculated according to the procedure described in the calibration protocol [3].

Table 5 – Tekran generator output (c_i) obtained during the short-term drift. The results from channel A and channel B were averaged.

Measurement (hours)	**c_i (ng m^{-3})**	**$U(c_i)$ (ng m^{-3}) (k = 2)**
2	11959	488
7	12004	498
26	11979	485
31	12049	498

The minimum c_i was 11959 ng m^{-3}, the maximum c_i was 12049 ng m^{-3} and the average $\overline{c_i}$ was 11998 ng m^{-3} with a standard deviation of 39 ng m^{-3}. The maximum difference between the Tekran generator outputs obtained was 90 ng m^{-3} which was 0.8% of the average concentration. The average expanded uncertainty determined was 492 ng m^{-3} which is also a relative uncertainty of 4% (k = 2).

4.3 Calibration

Calibration of the Tekran generator was performed over a range of mercury concentrations. Three mercury concentrations are generated, and each concentration was measured in four measurement series. The output of the Tekran generator and the uncertainty of the mercury concentration generated were calculated according to the protocol using the developed software (Table 6) [3, 8].

Table 6 – Results calibrated output Tekran generator and the calculated uncertainty of the mercury concentrations generated for channel A and channel B.

Measurement series	Setpoint nr.	$c_{(i)}$ (ng m^{-3})	$U(c_{(i)})$ (ng m^{-3}) (k = 2)	$U(c_{(i)})$ (%) (k = 2)	$c_{(i)}$ (ng m^{-3})	$U(c_{(i)})$ (ng m^{-3}) (k = 2)	$U(c_{(i)})$ (%) (k = 2)
		Channel A			**Channel B**		
1	1	5777	233	4.03	5916	241	4.08
	2	12040	489	4.06	12172	499	4.10
	3	24276	975	4.01	24642	999	4.05
2	1	5708	233	4.08	5813	241	4.15
	2	11854	478	4.04	11974	485	4.05
	3	23942	1034	4.32	24191	1002	4.14
3	1	5783	236	4.08	5926	253	4.27
	2	11833	486	4.10	12015	497	4.14
	3	23557	962	4.09	23831	975	4.09
4	1	5597	240	4.28	5757	240	4.16
	2	11885	478	4.02	12049	488	4.05
	3	23725	974	4.11	24014	988	4.12

The relative expanded uncertainty of the mercury concentrations generated with the Tekran generator ranges between 4.01% and 4.28%.

4.4 Precision: Repeatability and reproducibility

All mercury concentrations obtained with the Tekran generator were analysed and repeated four times in different measurement series according to the calibration protocol [3]. Based on the responses of channel A the repeatability standard deviation (s_r, expressed as coefficient of variation in %) and reproducibility standard deviation (s_R, expressed as coefficient of variation in %) were determined (Table 7).

Table 7 – repeatability standard deviation (s_r) and reproducibility standard deviation (s_R).

Setpoint nr.	$c_{cand(i)}$ (ng m^{-3})	s_r (%)	s_R (%)
1	5590	0.84	1.18
2	12220	0.37	1.08
3	24130	0.33	1.21

The average s_r was 0.51% and the average s_R was 1.15%. The Tekran generator has a precision of 1.2%, the uncertainty of the PSA SG analyser (2 %) is probably the most important source for the precision.

4.5 Interpolation function

The interpolation function of the Tekran generator was determined based on the three-measurement series performed for each range. The interpolation function for each measurement was determined using the software according to the protocol [3, 8]. The software calculates the interpolation function for the data obtained with channel A and channel B separately (Figure 2). Based on the Akaike Information Criterion for small sample size (AICc) (Table 8) the interpolation function with the best fit for the data was determined. As an example, the interpolation function of range 1 measurement series 1 is shown.

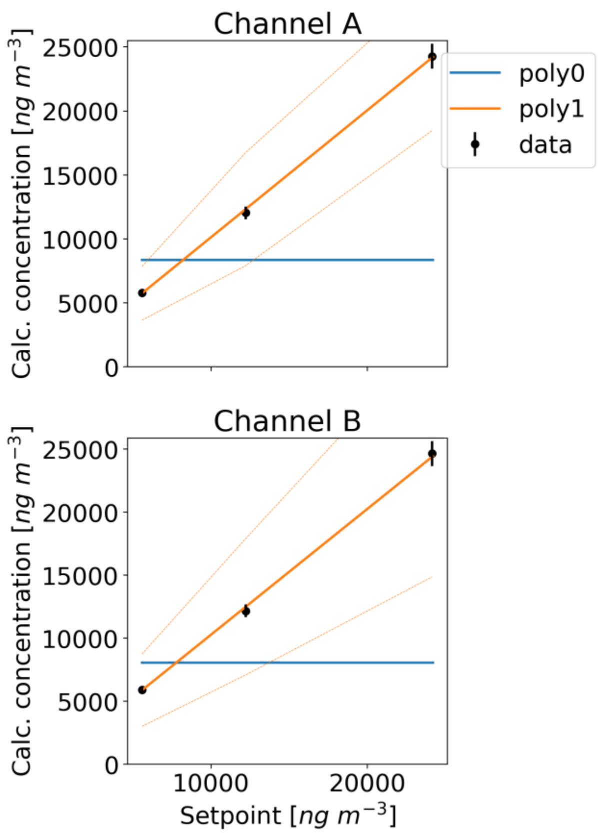

Figure 2 – Interpolation functions determined for channel A and channel B for measurement series 1.

Table 8 – AICc determined for channel A and channel B for range 1 measurement series 1. The smallest value indicates the best fit for the data.

Polynomial	**Channel A**	**Channel B**
Poly0 (non-zero constant)	68	67
Poly1 (linear)	*42*	*44*

The smallest value for the AICc indicates the best fit for the data which is the linear function. The linear function, $c = b_0 + b_1 c_{cand}$, is the optimal function for channel A and channel B of all measurement series (Table 9).

Table 9 – Regression coefficients for the interpolation function of Channel A and Channel B of range 1 measurement series 1.

	Parameters	**Standard error**

Channel A		
b_0	199	183
b_1	0.993	0.018
Channel B		
b_0	296	269
b_1	0.998	0.029

Due to the different intercept of all the interpolation functions, the slope of the functions is also different. To determine if the regression coefficients are comparable for Channel A and Channel B the functions can be averaged and a value for the comparability can be calculated (Chi squared). When they are comparable they can be combined (Figure 3).

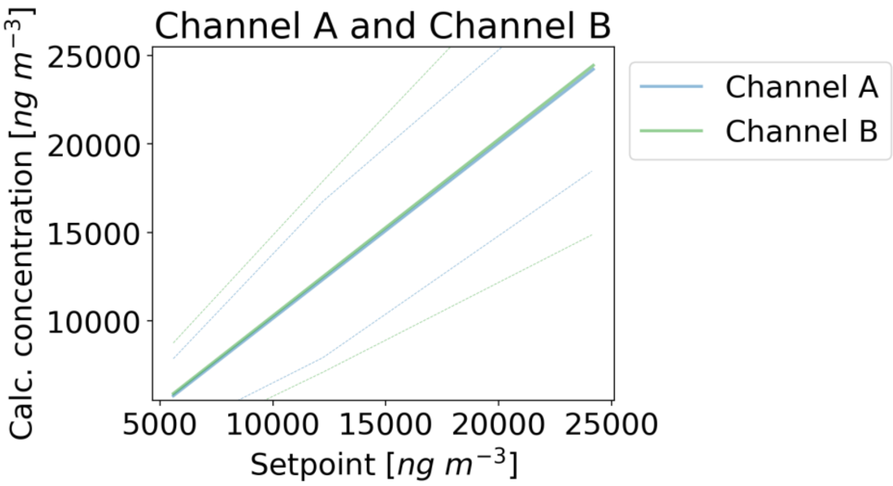

Figure 3 – Overlay interpolation functions channel A and channel B range 1 measurement series 1.

In this example the average regressed polynomial is acceptable with a Chi squared value of 4.5 and the probability that such a chi squared value should occur by chance was 0.34. The average regression coefficients and a covariance matrix were calculated (Table 10 and Table 11). The covariance matrix explains how the two data sets (b_0, b_1) are correlated. This correlation should be included in the calculation of the total uncertainty associated to the interpolation function.

Table 10 – Coefficients interpolation function obtained for measurement series 1

	Parameters	**Standard error**
b_0	233	118
b_1	0.994	0.012

Table 11 – Covariance matrix measurement series 1

	b_0	b_1
b_0	14015	-1.179
b_1	-1.179	0.000146

For all measurement series the optimal interpolation function poly 1 ($c = b_0 + b_1 c_{cand}$) and for all measurements the functions for channel A and channel B were comparable.

4.6 Bias

Based on the setpoint of the Tekran generator (c_{cand}) the deviation (D_{c_i}) and relative deviation (D_{rel}) were determined for channel A and channel B (Table 12, Figure 4).

Table 12 – Deviation between the setpoint and the calibrated output of the Tekran generator channel A and channel B.

Measurement series	Setpoint nr.	c_{cand} (ng m^{-3})	c_i (ng m^{-3})	D_{c_i} (ng m^{-3})	D_{rel} (%)	c_i (ng m^{-3})	D_{c_i} (ng m^{-3})	D_{rel} (%)
			Channel A			Channel B		
1	1	5590	5777	187	3.3	5916	326	3.3
	2	12220	12040	-180	-1.5	12172	-48	-1.5
	3	24130	24276	146	0.6	24642	512	0.6
2	1	5590	5708	118	2.1	5813	223	2.1
	2	12220	11854	-366	-3.0	11974	-246	-3.0
	3	24130	23942	-188	-0.8	24191	61	-0.8
3	1	5590	5783	193	3.4	5926	336	3.4
	2	12220	11833	-387	-3.2	12015	-205	-3.2
	3	24130	23557	-573	-2.4	23831	-299	-2.4
4	1	5590	5597	7	0.1	5757	167	0.1
	2	12220	11885	-335	-2.7	12049	-171	-2.7
	3	24130	23725	-405	-1.7	24014	-116	-1.7

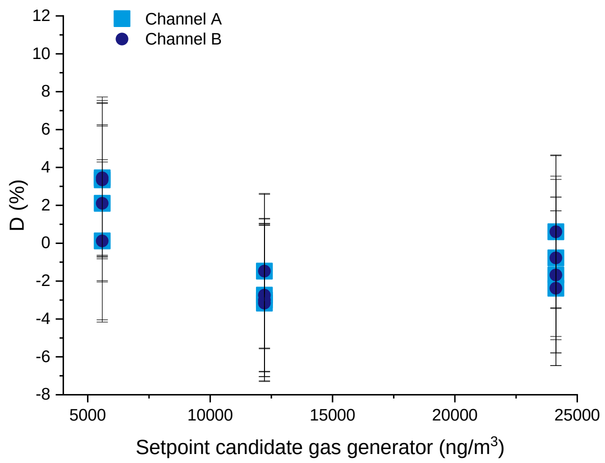

Figure 4 – Relative deviation of channel A and channel B for the measurement series. The uncertainty bars reflect the uncertainty calculated according to the calibration protocol [3].

The average relative deviation was -0.5%. The relative deviations of channel A and channel B and the results of the different measurement series are comparable within the uncertainty determined according to the calibration protocol for each setpoint [3]. As the results for channel A and channel B and the different measurement series are comparable within the uncertainty they can be averaged to obtain the final calibration results. Furthermore, these results show comparability between the VSL primary mercury gas standard and NIST calibrated gas generator for the first time. This confirms the results obtained in earlier studies where a comparison was performed using gold sorbent tubes sampled with the VSL primary mercury gas standard and NIST liquid standard reference materials (SRM) 3133 [7].

4.7 Sensitivity coefficient to sample gas pressure

Influence of sample gas pressure was tested by adjusting pressure level at the output of the generators. The 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 generator was set according to the manufacturer specifications.

Tests were conducted with constant input pressure of the carrier gas (dilution gas) according to manufacturer specifications. Pressure at output of generators was adjusted with a needle valve and measured. 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.

Deviations were related to the mean response of the Tekran generator at standard pressure (Table 13).

Table 13 - Results of pressure test

	Tekran generator		
Pressure kPa	**Reading µg/m³**	**Deviation %MV**	**b_P**
110.3	9.94	-0.20	-0.005
106.4	9.96	-	-
Maximum value		**-0.20**	**-0.005**
$x_{i,adj}$	9.96		
x_{imax}	9.96		
x_{imin}	9.94		
u	0.012		

The pressure test showed a maximum deviation of -0.2 % of the set point at a pressure different of 4 kPa.

4.8 Sensitivity coefficient to the surrounding 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 [10]. The required temperature range for outdoor installations was -20 °C to 50 °C.

Since the 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.

The test gas generator was exposed to the following temperature sequence in the climatic chamber:

20 °C → 5 °C → 20 °C → 40 °C → 20 °C.

The Tekran generator was 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 were conducted with the Tekran generator. The Tekran generator as well as the analyser system was operating during the whole test.

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 were averaged to minimize possible drift effects of the analyser system in the calculation.

Deviations are related to the mean response of the Tekran generator at 20 °C (Table 14 and Table 15).

Table 14 - Results of temperature test setpoint 1

Temperature °C	**Tekran generator Reading µg/m³**	**Deviation % MV (Æ 20°)**	**B_t**
(Æ 20°)	5.18	-	
20	5.12	-1.2	-
5	5.34	3.1	-0.015
20	5.13	-1.0	-0.014
40	5.04	-2.7	-0.004
20	5.29	2.1	-0.013
Maximum value		**3.1**	**-0.015**
$x_{i,adj}$	5.18		
x_{imax}	5.34		
x_{imin}	5.04		
u	0.087		

Table 15 - Results of temperature test setpoint 2

Temperature °C	**Tekran generator Reading µg/m³**	**Deviation % MV (Æ 20°)**	**B_t**
(Æ 20°)	10.89	-	
20	10.87	-0.2	-
5	11.18	2.7	-0.021
20	10.84	-0.5	-0.023
40	10.70	-1.7	-0.007
20	10.97	0.7	-0.014
maximaler Wert		**2.7**	**-0.023**
$x_{i,adj}$	10.89		
x_{imax}	11.18		
x_{imin}	10.70		
u	0.147		

The temperature test demonstrated, that the generator is basically suitable to be used in the complete range of EN 15267-3 with an maximum deviation of 3.1 % at setpoint 1 and 2,7 % at setpoint 2 [10]. Maximum deviations occurred at the temperature point of 5 °C but also at 40 °C relevant deviations occurred. We recommend to use the unit in a Temperature range close to 20 °C (-10 °C/+10 °C).

4.9 Sensitivity coefficient to electrical voltage

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 was 230 V, maximum value in the test was 253 V and minimum value was 196 V.

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

The Tekran generator to be tested was connected to the supply voltage using the isolating transformer. Output voltage was controlled by the multi meter. The Tekran generator was warmed up according to manufacturer's specifications also the analyser system was warmed up according to relevant specifications.

The deviations between the average readings at each voltage and the average reading at the nominal supply voltage were determined.

Deviations were related to the mean response of the Tekran generator at a nominal voltage of 230 V (Table 16).

Table 16 - Results of line voltage test

Voltage	Tekran generator		
	Reading	Deviation	b_{SV}
Volt	µg/m³	%MV	
230	8.16	-	
242	8.16	0.0	0.000
253	8.16	0.0	0.000
219	8.15	-0.1	0.001
207	8.14	-0.2	0.001
196	8.13	-0.4	0.001
maximum value-		**-0.4**	**0.001**
$x_{i,adj}$	8.16		
x_{imax}	8.16		
x_{imin}	8.13		
u	0.017		

The line voltage test showed a maximum deviation of -0,4 % within the tested range. A tendency of deviation of the output value of the generator depending on the voltage was not observed. The found deviations of max. 0.4 % are within the uncertainty range and within the range of repeatability of the generator in combination with the measuring device used. Voltage fluctuations in the typical range thus have no relevant influence on the performance of the test gas generator.

5. Conclusion

The candidate generator (Tekran Model 3425) was tested under the performance evaluation by determining the stabilisation period, short-term drift, calibration and uncertainty of the mercury concentration generator, linearity, bias and sensitivity coefficient to sample gas pressure, surrounding temperature and electrical voltage. A mercury concentration range was investigated between 5000 ng m^{-3} and 25000 ng m^{-3}.

The stabilisation period of the Tekran generator was 15 minutes after the first start-up. The short-term drift of the Tekran generator was 0.8%. Based on the calibration measurements the repeatability standard deviation and reproducibility standard deviation were determined to be 0.51% and 1.15% respectively. The gas generator can be used over a range of mercury concentrations with a linear function. The deviation between the setpoint of the Tekran generator and the calibrated mercury concentration was -0.5%. These results show that the output of the VSL primary mercury gas standard and NIST calibrated gas generator are comparable within the relative expanded uncertainty of 4% (k = 2).

Based on the performance evaluation the calibration results of the measurement series and channel A and channel B were averaged to provide results for the output and uncertainty of Tekran generator (Table 12).

Table 12 – Averaged calibration results

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	5590	5784	240	4.14
2	12220	11978	487	4.07
3	24130	24022	989	4.12

The relative expanded uncertainty of the mercury concentration generated are 4.1%.

The regression coefficients for the linear function, $c = b_0 + b_1 c_{cand}$, were also calculated based on the results of the different measurement series (Table 13 and Table 14).

Table 13 – Coefficients interpolation function obtained

	Parameters	**Standard error**
b_0	332	70
b_1	0.969	0.008

Table 14 – Covariance matrix

	b_0	b_1
b_0	4861	-0.48
b_1	-0.48	0.000062

During the experiments to determine the sensitivity coefficient for sample gas pressure and for electrical voltage not influence was found. The results for the temperature sensitivity showed a higher influence with a surrounding temperature of 5 °C and 40 °C. It is recommended to use the unit in a temperature range close to 20 °C (-10 °C/+10 °C).

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