Dynamic calibration method for reactive gases

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Abstract

In this study an evaporation method is applied to dynamically generate reference gas mixtures with an accurately known concentration of reactive compounds. As a representative application, the method is used to generate several reference gas mixtures for oxidized mercury. The reliability of online monitoring of gases is dependent on the availability of accurate and metrologically traceable calibration standards. For reactive gases this is a challenge since these sticky gases easily adsorb to surfaces, which complicates and can even prevent the use of traditional static tools. In the evaporation method, a solution with well-known concentration is dosed using, e.g. an automatic syringe pump or a peristaltic pump, and mixed with the carrier gas flow. Mixing and evaporation are key parts of this process, along with temperatures and materials in different parts of the system and gas flow rate, which play an important role in the response time optimization. To estimate the applicability of this method we test its operation in the case of oxidized mercury by investigating the key operational parameters: calibrator response time and stability, possible non-linear behaviour of selected molecules, and also sensitivity to interference caused by other reactive gas compounds. We also compare its outcome to a traceable source for Hg⁰. Based on the achieved results the evaporation method technique is both a potential and feasible tool for the dynamic preparation of calibration gas mixtures for reactive components, in both laboratory and field conditions.

Keywords: evaporation, traceability, reference gas, gas generator, gas flow, reactive compounds, mercury

(Some figures may appear in colour only in the online journal)

1. Introduction

The reliability of online monitoring of gases is dependent on the availability of accurate and metrologically traceable calibration standards. Metrological traceability of gravimetrically generated static gas mixtures [1, 2] is generally well-known and several operators can provide bottled gas standards with high accuracy and long term stability. For reactive compounds like water soluble inorganic acids and bases this is often not the case. These sticky gases easily adsorb to surfaces, which complicates and can even prevent the use of traditional static tools.

The evaporation method is a potential method to improve measurement comparability and uncertainties, and to achieve metrological traceability [3–5]. In this method a solution with well known concentration is dosed and mixed with the carrier gas flow [6–9]. Mixing and optimized evaporation are key parts of this process as are temperatures and materials in different parts of the system and gas flow, which play an important role in response time optimization.

In this study, an evaporation method is applied to dynamically generate reference gases with an accurately known concentration of oxidized mercury. Mercury (Hg) emitted by both natural and anthropogenic sources is highly toxic to humans, animals and ecosystems, and as such is regulated by numerous...
EU Directives [10–13]. In addition to its elemental form, mercury also occurs in reactive oxidized forms that can be transformed into other species, such as methylmercury—the most toxic mercury species and the one most prone to bioaccumulation in aquatic systems.

Half of the atmospheric mercury emissions are of natural origin while the remaining half are from anthropogenic sources. The latter is primarily from the burning of fossil fuels and other high temperature industrial processes, such as cement clinker production, waste incineration, ore roasting and steel production.

Currently, traceable calibration methods only exist for elemental mercury (Hg0), however such measurements are also needed for oxidized Hg species, i.e. Hg2+ [14]. When applying the evaporation method to oxidized mercury, key parameters studied are calibrator response time and stability, investigation of possible non-linear behaviour of selected molecules, and also sensitivity to interference caused by other reactive gas compounds.

2. Liquid evaporative method

Reference gases of water soluble chemical compounds can be generated by liquid evaporative generators. These generators are capable of generating calibration gas mixtures in a wide range of total gas flow rates and chemical concentrations. The method is especially suitable for chemically active water-soluble compounds, which are reactive and easily stick to surfaces, and for which it is challenging to produce traceable, long-lived static reference gas mixtures or bottled gas standards using static calibration methods. Typical examples of these compounds are ammonia (NH3), hydrogen fluoride (HF), hydrogen chloride (HCl), oxidized forms of mercury, especially mercury chloride (HgCl2) and some organic compounds, e.g. formaldehyde (CH2O). It is also possible to make these generators portable, enabling dynamic reference gas generation in both laboratory and field conditions.

In the liquid evaporative generators the reference gas is generated by mixing a liquid solution with a known concentration of a target chemical into a carrier gas, e.g. air, nitrogen or methane. It is also possible to stabilize the generated gases, e.g. by using suitable acids or bases to control the pH of the solution. The mixture is then evaporated in a special evaporator unit to create the reference gas. The evaporation of the gas–liquid mixture has to be complete and the adsorption on the generator’s surfaces minimized.

When all the parameters are known, the concentration of the component of interest in the generated gas mixture \( c_{\text{gen}} \) can be calculated as:

\[
c_{\text{gen}} = \frac{c_{\text{sol}}}{q_{v,g} + q_{v,w}} \cdot q_{v,sol}
\]

where \( c_{\text{gen}} \) is the concentration of the target chemical in the generated gas, \( c_{\text{sol}} \) is the concentration of the target chemical in solution, \( q_{v,g} \) is the volume flow rate of the carrier gas, \( q_{v,w} \) is the volume flow rate of the evaporated water in gas phase, and \( q_{v,sol} \) is the flow rate of the liquid solution. Now \( q_{v,g} + q_{v,w} \) is the total wet volumetric gas flow from the generator.

In this work two different types of portable and field deployable gas generators that produce trace level concentrations of reference gases in a traceable manner were investigated.

2.1. HovaCAL

HovaCAL is a commercial gas generator by IAS GmbH [15]. It is a commonly used tool for testing and quality assurance of continuous emission measurement systems (CEMS) applied in the process and stack gas monitoring applications, in both laboratory and field conditions. It is commonly used for water, ammonia, hydrogen chloride, hydrogen fluoride as well as HgCl2. A flowchart of the HovaCAL principle is shown in
In this version liquid is dosed with a peristaltic pump and liquid flow is measured using a scale.

2.2. Optoseven

This gas generator is developed by Optoseven Ltd together with VTT Ltd within the EMPIR Metrology for Oxidized Mercury (MercOx) project [14]. The newly developed generator is portable.

The main design goals for this system were a fast response time through minimization of adsorption to surfaces and stable operation in wide concentration ranges for carrier gas, water content of the generated gas and the concentration of the studied chemical. The starting point for the setup has been evaporation of the liquid samples in standard laboratory analysers, based on, e.g. inductively coupled plasma spectrometry (ICP) [16]. Especially in case of mercury, a minimal amount of adsorption and use of inert surfaces at the same time effectively prevent unwanted reduction of $\text{Hg}^{2+}$ to $\text{Hg}^0$ in the generated calibration gas mixture. An automatic, stepper motor controlled, syringe pump is used for accurate chemical solution dosing. A displaceable evaporation unit enables the use of different surface coatings (e.g. glass is not a suitable material with its high HF content), and it is also possible to apply different nebulizer [17, 18] types for different chemicals. The flowchart of the generator principle is shown in figure 2.

3. Operational principles of gas generator system components

It is possible to achieve metrological traceability [5] for the generated gas mixture through traceable system components [6, 8, 19]. The generator itself consists of different physical and chemical components, the traceability of which are carefully considered one by one. In practice, the traceability is achieved through a chain of calibrations, where all the calibration results are linked to the international system of units (SI).

The generator system components and their traceability through calibration (when relevant) are explained in the following sections.

3.1. Preparation of the liquid solutions

Usually, the preparation is performed in two stages. The first one is the preparation of a stock solution, which may be commercial or self-made from pure chemical. The second stage is the dilution of that base solution to the desired working concentration.

The self-made base solution can be prepared, e.g. by dissolving powder in water. A known amount of powder is measured using a calibrated weighing instrument. A known amount of distilled water is measured using, e.g. a measuring flask. The subsequent dilution of the base solution can be done gravimetrically or volumetrically. A small amount of strong acids (e.g. concentrated high purity hydrochloric acid or nitric acid) can be added to stabilize the final solution.

3.2. Carrier gas conditioning

Clean, dry gas, e.g. air, nitrogen or methane, is used as carrier gas. Pressure needs to be reduced to the desired level by using a pressure regulator equipped with an integrated pressure gauge having a suitable accuracy class. Also, the thermal mass flow controller included in the generator system requires an uncontaminated gas stream for reliable performance.

A gas stream free of moisture, oil and particles is ensured by suitable filters along the supply line. The carrier gas should not contain any components of the target component, therefore a special filter, e.g. activated carbon, is used.

3.3. Carrier gas dosing

A thermal mass flow controller supplies a known mass flow rate of carrier gas into the system. Alternatively, critical flow

![Flow chart of the gas generator developed by Optoseven Ltd together with VTT Ltd.](image-url)
orifices [20] can be used. To ensure that the evaporator unit operates properly, the carrier gas flow rate should be within the specified range.

The thermal mass flow controller should be calibrated for specific gases against national or international reference standards, which are traceable to international system of units (SI) [21]. The measurement standards need to be internationally recognized and approved to be equal (e.g. accredited calibration laboratory or CMCs approved in BIPM database). The calibration should be performed in conditions similar to the typical conditions during usage.

3.4. Liquid solution dosing

A special automatic syringe pump or a peristaltic pump with a weighing instrument is used for liquid solution dosing. Both pump types can produce a very small liquid flow rate with good precision. It should be noted that the syringe pump is semi-continuous as the liquid flow is stopped during the refill of the liquid container. This effect can be further minimized by using two syringe pumps in parallel or by selecting a sufficiently large volume with respect to the desired liquid flow. The plunger or piston of the syringe can be accurately controlled, e.g. with a stepper motor.

A stepper motor driven syringe pump has to be calibrated regularly by using a calibrated weighing instrument to achieve traceability for the pump flow rate. As a result, the pump output portion per one stepper motor step is known. During normal operation it is sufficient to calculate the number of steps to calculate the flow rate. Due to the peristaltic pump’s operation principle, a calibrated weighing instrument needs to be used continuously to ensure a known and metrologically traceable liquid flow rate when the pump is running.

Special care should be taken when handling highly volatile substances due to the evaporation effect from containers before the pumps. This practical challenge becomes greater during long measurement periods.

The calibration of the liquid flow output of both pump types is done by weighing the amount of liquid it either takes in or outputs in a certain duration of time. A calibrated weighing instrument [22] is used.

3.5. Evaporator

Optimum evaporation of the mixture of carrier gas and liquid solution as well as response time of the system are critical to minimize the losses, and accordingly the uncertainty in gas concentration, caused by adsorption of the chemicals to system surfaces. Several details need to be taken into account during the design and construction phase of the evaporator.

The evaporator consists of a nozzle to mix and spray the liquid solution with carrier gas, and the heated evaporation chamber. Only inert materials should be used for the inner parts of the nozzle, the evaporator chamber and all subsequent parts that are in contact with the humid gas. Proven good choices for reactive chemicals easily adsorbing to surfaces are, e.g. polytetrafluoroethylene (PTFE a.k.a. Teflon), perfluoroalkoxy alkanes (PFA) and glass. Metal (e.g. stainless steel or aluminium) parts coated with these materials as well as pure metal surfaces with stainless steel (e.g. Hastelloy) are also possible. The surface quality of the evaporator’s inner parts needs to be very fine.

The evaporator chamber must be well heated, depending on water content and chemical a temperature of at least 120 °C is recommended. A stable temperature ensures optimum evaporation conditions and prevents fluctuations.

The flow rate of the generated gas into and through the evaporator needs to be high enough to ensure a short exchange time of gas inside the evaporator chamber.

The geometry of the evaporation chamber is designed to be the optimum for the evaporation process when used with the selected nozzle: there needs to be enough free space for the generated spray profile to evaporate before reaching the walls of the chamber. This design ensures that no liquid droplets are attached to the wall surfaces before evaporation takes place.

4. Metrological traceability and measurement uncertainty

Metrological traceability is a cornerstone of all reliable methods and measurement results. Measurement uncertainty needs to be reported together with measurement results, because without knowledge of uncertainty the reliability is not known.

An overall measurement uncertainty analysis requires a list of relevant uncertainty components. These are all the components and effects, which are present during the operation. The role and magnitude of each component is analysed separately. As an example, in the following an uncertainty calculation is presented for the generated reference gas, in the defined circumstances, according to the principles of [23].

4.1. Model equation

Each uncertainty component’s role in the model equation defines how this component affects the overall uncertainty. All the needed terms must be added to the basic equation (1) to get all the recognized corrections and uncertainty components involved, resulting in equation (2):

\[
\delta c_{\text{gen}} = \left( \frac{c_{\text{sol}}}{q_{v,g}} \right) \cdot \delta c_{\text{sol}} + c_{\text{eva}} + \delta c_{\text{rep}}
\]

where \( c_{\text{gen}} \) is the concentration of the target chemical in the generated gas, \( c_{\text{sol}} \) is the concentration of the target chemical in solution, \( q_{v,g} \) is the volume flow rate of the carrier gas, \( q_{v,w} \) is the flow rate of the evaporated water in gas phase, \( q_{v,sol} \) is the flow rate of the liquid solution, \( \delta c_{\text{eva}} \) is correction/effect of the evaporator (due to adsorption losses), and \( \delta c_{\text{rep}} \) is overall repeatability of the gas generator.

The total uncertainty of the concentration of the component in the generated calibration gas mixture consists of the mentioned uncertainty components, explained in the following sections. Finally, the uncertainty values with assumed distributions and related contributions to the uncertainty of
the concentration of the component of interest in the calibration gas mixture are listed in table 3. Sensitivity coefficients and contributions are calculated according to [23] based on equation (2).

4.1.1. Uncertainty of concentration of the target chemical in solution. The uncertainty due to the concentration of the target chemical in solution, \( c_{\text{std}} \), consists of the uncertainties of the base solution and working solution. For example, when the base solution for oxidized mercury is prepared, the uncertainties due to Hg-powder, weighing instrument and laboratory flask need to be taken into account, as described in [24].

Additionally, uncertainty caused by adding the stabilizers to the solution is taken into account based on the calculated estimation.

As an example, the uncertainty components with assumed distributions and related contributions to the oxidized mercury base solution uncertainty are listed in table 1.

In this example the base solution uncertainty for the self-prepared solution is approximately 0.08% \((k = 2)\). The presented uncertainty estimation does not include the long-term stability of the solution.

The uncertainty of the working solution consists of uncertainties due to the base solution, pipetting and laboratory flask and these need to be taken into account, as described in [24]. Additionally, the uncertainty caused by adding the stabilizers to the solution is taken into account based on the calculated estimation.

As an example, the uncertainty components with assumed distributions and related contributions to the working solution uncertainty are listed in table 2. Sensitivity coefficients and contributions are calculated according to equation (3)

where \( c_{\text{ws}} \) is the mercury concentration of the working solution, \( m_{\text{std}} \) is the weight of standard solution, \( c_{\text{std}} \) is the mercury concentration of the standard solution, and \( V_{\text{total}} \) is the final volume of working solution.

From the above, the working solution \( (c_{\text{ws}}) \) uncertainty is approximately 0.11% \((k = 2)\). It should be noted that the long-term stability of the solution depends on the chemical, and is not included in the presented uncertainty calculation. Fresh, newly prepared solutions are used whenever possible.

In the examples, listed in tables 1 and 2, repeatability of filling the flask is assumed to be inside the flask tolerance. A stabilized laboratory room condition is assumed for solution preparation and due to this an additional component for temperature effects was not added.

4.1.2. Uncertainty of flow rate of the carrier gas. The uncertainty of the flow rate of the carrier gas, \( q_{\text{carrier}} \), is due to mass flow controlling. The mass flow controller calibration uncertainty needs to be taken into account. Due to the fact that during the normal operation the mass flow controller is not used at exactly the same flow rates, pressure levels and temperatures compared to those during calibration, an uncertainty level of approximately 1% \((k = 2)\) is chosen. The mass flow controller calibration was done using the same gas as that used as the carrier gas.

The effect of the carrier gas conditioning (pressure regulator) on the carrier gas dosing (thermal mass flow controller) may be considered insignificant when a precision pressure regulator with an integrated pressure gauge are used.

4.1.3. Uncertainty of flow rate of the evaporated water in total gas flow. The uncertainty due to the flow rate of the evaporated water, \( q_{\text{w,v}} \), is calculated based on the amount of evaporated water in the gas phase. The dosed liquid solution is evaporated, and the resulting volume of water in the gas phase
is calculated with the help of the molar mass of the water and using the molar volume of the ideal gas. The uncertainty of the evaporated water in gas phase is (in practice) dependent on the uncertainty of the liquid solution dosing: accuracy of the dosing does have a direct effect on the evaporated amount of water and its volume in gas phase.

4.1.4. Uncertainty of flow rate of the solution. The uncertainty due to the volume flow rate of the solution, \( q_{\text{v,sol}} \), is estimated based on the liquid solution dosing: the uncertainty of the weighing instrument (peristaltic pump with balance) or pump volume (syringe pump), and repeatability. The uncertainty value for the syringe pump total volume varies and depends on manufacturer and model of the pump.

4.1.5. Uncertainty of evaporator. The uncertainty due to the evaporator (due to adsorption losses), \( \delta c_{\text{eva}} \), is estimated to be, e.g. 1% of the generated gas, based on the repeatability tests. Short-term repeatability is tested by performing replicate measurements over a short period of time. These measurements are all done under the same conditions including, e.g. the same measurement procedure, operator, measuring system, operating conditions and location. Long-term reproducibility is tested by performing replicate measurements under different conditions including, e.g. different locations and operators.

4.1.6. Overall repeatability of the gas generator. The uncertainty due to the overall repeatability of the gas generator, \( \delta c_{\text{rep}} \), is estimated to be, e.g. 1% of the generated gas, based on the repeatability tests. Short-term repeatability is tested by performing replicate measurements over a short period of time. These measurements are all done under the same conditions including, e.g. the same measurement procedure, operator, measuring system, operating conditions and location. Long-term reproducibility is tested by performing replicate measurements under different conditions including, e.g. different locations and operators.

4.2. Estimation of total uncertainty

The uncertainty components affecting generated gas uncertainty are listed in table 3. Standard uncertainties are calculated for each component separately according to their assumed distribution. Standard uncertainty components are combined and finally the expanded uncertainty for the generated gas is achieved, with the coverage factor \( k = 2 \), which corresponds to a probability of 95% for a normal distribution. The uncertainty calculation is performed according to the rules of GUM [23]. From the above, the uncertainty of the generated gas is approximately 2.02% (\( k = 2 \)).

Table 3. The overall uncertainty of the generated gas concentration, at room temperature (20 °C ± 0.5 °C) and at ambient pressure. The presented numerical values are examples only.

| Term   | Average value | Standard uncertainty | Distribution | Sensitivity coefficient | Contribution | Relative contribution |
|--------|---------------|----------------------|--------------|-------------------------|--------------|----------------------|
| \( c_{\text{sol}} \) | 1000 \( \mu g \) \( l^{-1} \) | 0.55 \( \mu g \) \( l^{-1} \) | Norm. | 0.01 | 0.01 \( \mu g \) \( m^{-3} \) | 0.05% |
| \( q_{\text{v,g}} \) | 71 \( l \) \( min^{-1} \) | 0.041 \( l \) \( min^{-1} \) | Norm. | -1.4 | -0.05 \( \mu g \) \( m^{-3} \) | -0.49% |
| \( q_{\text{v,w}} \) | 0.09 \( l \) \( min^{-1} \) | 0.00031 \( l \) \( min^{-1} \) | Rect. | -1.4 | -0.0004 \( \mu g \) \( m^{-3} \) | -0.004% |
| \( \delta c_{\text{eva}} \) | 0 \( \mu g \) \( m^{-3} \) | 0.06 \( \mu g \) \( m^{-3} \) | Rect. | 1 | 0.06 \( \mu g \) \( m^{-3} \) | 0.58% |
| \( \delta c_{\text{rep}} \) | 0 \( \mu g \) \( m^{-3} \) | 0.06 \( \mu g \) \( m^{-3} \) | Rect. | 1 | 0.06 \( \mu g \) \( m^{-3} \) | 0.58% |
| \( c_{\text{gen}} \) | 10 \( \mu g \) \( m^{-3} \) | | | | | |

From \( k = 1 \): 0.10 \( \mu g \) \( m^{-3} \), 1.01%

From \( k = 2 \): 0.20 \( \mu g \) \( m^{-3} \), 2.02%

Figure 3. Water content measurement. The difference between measured and generated water content is shown with the observed noise marked by error bars. Measurement range is 1.5%.
Values used in the uncertainty estimation in table 3 are examples for one specified case only. Uncertainties, their sensitivity coefficients and contributions may vary, if different flow rates and concentrations are used.

4.2.1. Estimation of total uncertainty for water concentration. The total uncertainty for water concentration of the generated gas mixture can be determined following the principles explained in the previous sections of chapter 4. In practice, the uncertainty components related to the concentration of the target chemical in the generated gas and in the solution are left out.

The water content of the generated gas can be traceable calibrated against national reference measurement standards. With this the correctness of the generated water content can be ensured. Successful calibration results give strong support to the overall operational capability of the gas generator already covering the main components from equation (2).

5. Results

5.1. Water evaporation test

Water content measurements were performed at the National Metrology Institute VTT MIKES using a Dew Point Mirror as the measurement standard. This is calibrated against the dew point generator to get metrological traceability through the national humidity and temperature standards to the SI. By calibrating generator output (with pure water solution, generated gas mixture containing only water) against the Dew Point Mirror, metrological traceability is achieved for water vaporization, i.e. those parts of the generator that are relevant.
in water gas mixture generation. These are everything but the chemical Hg-solution and the evaporator behaviour related to Hg-solution vaporization.

During the water content measurements the clean gas generated by the HovaCAL and Optoseven generators containing only water vapour was supplied to the Dew Point Mirror. The test results showed that the water content generated by the generators agrees with the water content measured by the measurement standard, within the estimated uncertainty level. The results are shown in figure 3.

5.2. HgCl$_2$ evaporation tests

The liquid evaporative HgCl$_2$ generators (HovaCAL and Optoseven) were tested at the National Metrology Institute VTT MIKES using the dual analytical system by Lumex Analytics GmbH, developed within the EMPIR MercOx project to compare the outputs. In this system the input gas is driven to two separate analysers; one with a sample cell at room temperature to measure elemental mercury (Hg$^0$) and another with a hot catalytic converter oven and a sample cell at elevated temperature to measure total gaseous mercury (Hg$_{tot}^+$). The difference of the readings of these two analysers corresponds to the concentration of oxidized forms of mercury.

The concentration of the liquid HgCl$_2$ solution in all of these tests was selected in order to produce a Hg$^{2+}$ reference gas concentration of 0.1 µg m$^{-3}$–10 µg m$^{-3}$ (at room temperature (20 °C ± 0.5 °C) and at ambient pressure) with typical solution and carrier gas flow rates. To reach a water concentration of maximum 1–2 Vol% typically the mercury standard solution volume flow rate is 0.01 ml min$^{-1}$–0.1 ml min$^{-1}$ and carrier gas flow rate is 5 l min$^{-1}$–10 l min$^{-1}$. This derives to have a mercury solution with concentration
100 µg l\(^{-1}\)–1000 µg l\(^{-1}\). The typical HCl concentration in generated gas was 0.25 ppm to stabilize the generated gas.

Results from these tests for system response time, noise or sensitivity, linearity and cross-sensitivity are explained in the following sections.

5.2.1. Response time. For sticky gases like HgCl\(_2\) the system response time reveals losses due to adsorption to surfaces. With inert materials and fast flow rates with respect to surface areas this effect can be minimized. In the HovaCAL calibrator used in this study, an evaporator made from stainless steel without a coating was used. In the Optoseven calibrator the PFA-coated evaporator was in use.

Tubing length between evaporator output and analytical system input was minimized. No heated hoses were used since the water dew point in generated gas was well below room temperature. The typical evaporator temperature was approximately 125 °C. Compressed air was used as a carrier gas.

The system was heated up and allowed to stabilize at least 2h before starting the measurements.

Figure 4 shows a typical response time for the Hg\(^{tot}\) reading when HgCl\(_2\) is generated with HovaCAL by switching the solution from pure water to a HgCl\(_2\) containing solution. The response time is typically some tens of minutes. The response time can be shortened significantly by letting the generator stabilize with constant HgCl\(_2\) containing gas flow for more than an hour, as shown in figure 5.

As the response of the analytical system is a couple of seconds, as shown in figure 6, it is also possible to detect even fast oscillations in concentration of the generated gas, e.g. the oscillation due to the peristaltic pump operation principle can be seen according to figure 7.

5.2.2. Sensitivity and noise. Standard deviation of the signal gives an estimate of analyser sensitivity and noise. Figures 8(a) and (b) show the response of the analytical

Figure 8. (a) Measurement signal with clean air. Raw data (blue line) and ten point moving average (red line) are shown. (b) Measurement signal with HgCl\(_2\) concentration. Raw data (blue line) and ten point moving average (red line) are shown.
system with clean air and with 5 μg m⁻³ HgCl₂ concentration (at room temperature (20 °C ± 0.5 °C) and at ambient pressure) as an example. Standard deviation calculated from some tens of consecutive points is 0.02 μg m⁻³–0.03 μg m⁻³ in all cases and the standard deviation three times multiplied is 0.06 μg m⁻³–0.08 μg m⁻³. The latter value is often depicted as lower detection limit (LDL).

The sensitivity of the analytical system is analysed to be better than 0.1 μg m⁻³. This result coincides with the zero point stability of the analytical system; during several hour measurement periods drift of the analysers zero was less than or equal to 0.1 μg m⁻³, both for Hg⁰ and Hgtot readings.

5.2.3. Linearity. The linearity of the dual analytical system and evaporative generators was tested by changing the liquid flow in a sequence of 100%/0%/70%/40%/0%/60%/10%/30%

![Figure 9. Linearity test results with analytical system and Optoseven generator.](image)

![Figure 10. Signal of analytical system with three HgCl₂ solutions used with HovaCAL generator.](image)

| Response (μg m⁻³) | Hg⁰ corrected value (μg m⁻³) | Hgtot corrected value (μg m⁻³) |
|-------------------|------------------------------|-------------------------------|
| 1.000             | 1.099                        | 0.994                         |
| 2.000             | 2.036                        | 2.011                         |
| 3.000             | 3.062                        | 3.028                         |
| 4.000             | 4.089                        | 4.045                         |
| 5.000             | 5.116                        | 5.062                         |
| 6.000             | 6.143                        | 6.079                         |
| 7.000             | 7.170                        | 7.096                         |
| 8.000             | 8.196                        | 8.113                         |
| 9.000             | 9.223                        | 9.130                         |
| 10.000            | 10.250                       | 10.147                        |
%90%/0% of selected concentration ranges for HgCl₂ and water by keeping the carrier gas flow constant. As an example, results from the test with the Optoseven generator in a lower mercury concentration range (approximately 1 \(\mu\)g m\(^{-3}\)) are shown in figure 9.

Even at the lower concentration range for HgCl₂ the response is very linear. Point wise error in the linear fit of the results is less than 1% of the concentration range (1 \(\mu\)g m\(^{-3}\)).

### 5.2.4 Cross-sensitivity and other parameters

The linearity test gives strong evidence on interference free operation of the system with respect to water and HCl concentrations. Another test was conducted in the wider HCl concentration range, approximately at the levels 0.025 ppm/0.25 ppm/2.5 ppm, using three different HgCl₂ solutions while all other parameters were kept constant. Measurement results using the analytical system are shown in figure 10.

| \(x_{Hg}\) solution (\(\mu\)g l\(^{-1}\)) | Liquid flow (g min\(^{-1}\)) | \(N_2\) flow (l min\(^{-1}\)) | Total gas flow (l min\(^{-1}\)) | \(x_{Hg(ref)}\) (\(\mu\)g m\(^{-3}\)) | \(x_{HCl}\) (mg m\(^{-3}\)) | \(x_{H_2O}\) (%) | Response \(Hg^{tot}\) (\(\mu\)g m\(^{-3}\)) | Stdev. \(Hg^{tot}\) (\(\mu\)g m\(^{-3}\)) |
|---------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 870.22                          | 0.1158               | 6.9947               | 7.1387               | 14.1163              | 0.8193               | 1.9974               | 12.86               | 0.08                 |
| 870.22                          | 0.0819               | 6.9947               | 7.0966               | 10.0431              | 0.5829               | 1.4210               | 9.00                | 0.04                 |
| 870.22                          | 0.0641               | 6.9947               | 7.0744               | 7.8849               | 0.4576               | 1.1157               | 7.05                | 0.05                 |
| 870.22                          | 0.0525               | 6.9947               | 7.0600               | 6.4712               | 0.3756               | 0.9156               | 5.61                | 0.09                 |
| 870.22                          | 0.0381               | 6.9947               | 7.0421               | 4.7082               | 0.2733               | 0.6662               | 4.07                | 0.11                 |
| 870.22                          | 0.0141               | 6.9947               | 7.0122               | 1.7498               | 0.1016               | 0.2476               | 1.26                | 0.03                 |
| 870.22                          | 0.0113               | 6.9947               | 7.0088               | 1.4030               | 0.0814               | 0.1985               | 0.98                | 0.03                 |
| 870.22                          | 0.0086               | 6.9947               | 7.0054               | 0.6083               | 0.0620               | 0.1512               | 0.78                | 0.03                 |

Table 6. Concentrations (at room temperature (20 °C ± 0.5 °C) and at ambient pressure) generated by Optoseven and responses obtained by the Lumex analyser.

Table 5. Concentrations (at room temperature (20 °C ± 0.5 °C) and at ambient pressure) generated by HovaCAL and responses obtained by the Lumex analyser.
Lower HCl concentration does not have an effect on Hg\text{tot} readings as was concluded previously in section 5.2.3 in the linearity test. However, with ten times higher HCl concentration the mercury reading drops almost 10%. This may indicate that the high temperature converter in the analytical system no longer works properly and all Hg\text{2+} is not converted to elemental form, but almost 10% remains oxidized and is accordingly not detectable with Zeeman Hg\text{0} absorption spectroscopy. When switching back to a HCl concentration of 0.25 ppm mercury concentration recovers to the original reading. The Hg\text{0} channel reading of the analytical systems also remains constant during the whole of this test.

Evaporator temperature may have an effect on the Hg\text{0} share of Hg\text{tot} concentration in the liquid evaporative generator’s output due to possible reduction in evaporator surfaces. This was tested at four different temperature levels with the Optoseven generator: 125 °C/140 °C/160 °C/125 °C. From this test, no difference was seen in the Hg\text{0} or Hg\text{tot} readings.

In the case that some reactions occurred at a higher temperature, the Hg\text{0} concentration should have increased.

5.3. HgCl\text{2} evaporation generators comparison tests

The Lumex analyser was calibrated using a traceable source for Hg\text{0} by the Dutch National Metrology Institute VSL, and after that the liquid evaporative HgCl\text{2} generators were tested using the Lumex analyser to compare the outputs. These are explained in the following sections.

5.3.1. Calibration of the analytical system. The Lumex analytical system and its analysers were calibrated at VSL using the primary Hg\text{0} vapour generator. The working principle is based on diffusion according to [25], to establish metrological traceability of the Hg\text{0} concentration measurement results, based upon a gravimetric approach, for ambient air levels as well as higher concentrations [26]. The calibration results obtained for both channels, Hg\text{0} and Hg\text{tot}, are reproducible within the uncertainty of the calibration gas mixtures used. New calibration coefficients were determined based on the results. The regression coefficients in combination with the model equation can be used to interpolate responses of unknown samples, e.g. for the measurements of Hg\text{0} and Hg\text{2+} generators. Alternatively, the response of both channels can be corrected according to table 4.

Thus, the traceability of Hg\text{2+} concentration measurements is established. However, it was not possible to determine the converter efficiency of the Hg\text{tot} channel of the Lumex analyser. More tests will be needed for this. The same is concluded in [27].

5.3.2. Comparison tests. The liquid evaporative HgCl\text{2} generators (HovaCAL and Optoseven) were tested using the calibrated Lumex analyser by comparing the outputs of these generators to analyser results from elemental and total channels.

The concentrations (at room temperature (20 °C ± 0.5 °C) and at ambient pressure) of liquid HgCl\text{2} solutions were 1.2 µg m⁻³ for the HovaCAL generator, and 1.4 µg m⁻³ for the Optoseven generator. The Hg\text{2+} reference gas concentrations produced (at room temperature (20 °C ± 0.5 °C) and at ambient pressure) were 0.9 µg m⁻³, 1.0 µg m⁻³ and 0.1 µg m⁻³, respectively. The stock solutions used were further analysed against traceable standard solutions to check the actual concentrations were within the stated uncertainties.

For the HovaCAL, the mercury standard solution flow rates used were between 0.009 ml min⁻¹–0.12 ml min⁻¹ and the carrier gas flow rate was fixed at 7 l min⁻¹. This resulted in mercury gas mixtures with concentrations between 1 µg m⁻³–14 µg m⁻³, as shown in table 5.

For the Optoseven, the mercury standard solution flow rates used were between 0.03–0.1 ml min⁻¹ and carrier gas flow rate was 7 l min⁻¹. This resulted in mercury gas mixtures with concentrations between 0.8 µg m⁻³–14 µg m⁻³, as shown in table 6.
In both cases, the Hg$_0$ channel of the Lumex analyser gave a response close to zero, which is expected as there should be no Hg$_0$ present in the obtained gas mixture. The response of the Hg$_{tot}$ channel is interpolated using the CurveFit programme at VSL according to [2]. The results are shown in figures 11 and 12, respectively.

The results show that both generators have an average output 8% below the expected concentration. Purity analysis preformed on the liquid mixtures shows that the Hg concentration of the solutions are as expected.

### 6. Discussion and conclusions

Based on the tests and measurements performed in this study, the applied evaporation method to dynamically generate reference gases with accurately known concentrations of reactive gaseous compounds is well suited to sticky gases, e.g., mercury, which tend to adsorb to surfaces. Mixing and evaporation are key parameters in this process as well as temperatures and construction materials. These several details were successfully taken into account most essentially during the design of the gas generators’ evaporators. Usage of inert materials only, proper surface quality, a well heated chamber, and the geometry of the chamber together with the selected spraying nozzle types ensured optimized evaporation during the generator operation. This is indicated especially by fast response time and low memory effect for the generators as well as minimal Hg$_0$ content in the generated mercury reference gas.

The reference gas concentrations generated are typically relatively low in normal use. However, over longer periods of use, it is important to observe the generator response time regularly and carefully analyse possible changes in it. The extended response time could be a mark of aging of materials used in the inner parts of the generator, and especially in the evaporator. This may happen over time and specifically in the case where remarkably high concentrations of reactive chemicals are generated. The aging can contribute to the total uncertainty of the generated gas mixture. More information on this effect is not available yet since the design is new. More knowledge may be gathered after longer usage time, and this may lead to further research. In the mean time, the most practical solution is to replace generator parts that have direct contact with vapour, if aging doubts are raised during use.

The evaporation method applied is flexible to use and also easily applicable in field conditions as a transportable calibrator unit. It is capable of generating accurate reference gases with a fast response time. Clean, dry gas is used as carrier gas. In practice, even normal compressed workshop air is suitable as long as the supply line is equipped with pressure regulation and proper filters. The liquid solutions needed can be carefully prepared in laboratory conditions before going on site and there is no need for a stock of heavy and often expensive gas bottles.

Metrological traceability is possible to achieve for the generated gas mixture through traceable system components. The traceability needs to be carefully considered for each system component affecting the final result, i.e., the generated gas mixture. The principle for uncertainty estimation was given in chapter 4, and the whole process chain was calculated through using accurate mercury gas mixture generation as an example. The presented principle is generally applicable, but the numerical values are typical examples for a specified case only. Uncertainties, sensitivity coefficients and contributions may vary by case and by application. Each newly established measurement set-up needs uncertainty estimation of its own.

The results of test, calibration and comparison measurements done at VTT MIKES, Finland, and VSL, the Netherlands, were presented in chapter 5. The results from water evaporation tests show good agreement between the calculated and measured values for gas mixture water content. Based on this, the generator evaporation process for pure water can be considered metrologically ensured. Results from comparison tests for Hg$_0$ and HgCl$_2$ show that both generators have an average output that is approximately 8% below the expected mercury concentration. The exact reason for this large unexpected difference so far remains unclear. Based on the results in chapter 5.1, the reason for this most probably is due to components that are not present in the pure water evaporation process. These are the chemical Hg-solution and evaporator behaviour related to Hg-solution vaporization. It also might be related to the measurement method of mercury, or to the converter efficiency of the Hg$_{tot}$ channel of the analyser, but more tests are still needed before this can be concluded. The further tests are planned within the MercOx project, in which, e.g. sorbent traps will be loaded using the Hg$_2^{2+}$ generator. The results from the analysis of these traps will then be compared with the theoretical output of the generator.

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