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Evaluating the performance of oxidized Hg reference gas generators in the range ng m^{-3} to µg m^{-3} by improved coupling with ICP-MS

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ABSTRACT

We demonstrate a novel way to introduce a so-called Hg reference gas, produced by a gas generator, into an elemental detector, such as ICP-MS, and to directly measure gaseous oxidized mercury (GOM as HgCl$_2$) at a wide range of concentrations, covering 4 orders of magnitude. The approach was tested using two types of generators based on the dilution of a gas saturated with mercury chloride vapours (from dry HgCl$_2$ salt) and on the evaporation of aqueous HgCl$_2$ standards. The former generator provided reference gas at µg m^{-3} concentrations, while the latter was applicable from low ng m^{-3} to µg m^{-3}. The generation and measurement of gaseous Hg was achieved in real time without significant memory effects, and with a response time shorter than 5 min. This unique approach of direct measurement (without thermal conversion) of both gaseous elemental mercury (GEM) and GOM from environmentally relevant to industrial concentrations has been shown to offer the potential to significantly improve the reliability of Hg determination from gas generators. This, in the longer term, will be invaluable to improve accuracy of in-field Hg measurements.

1. Introduction

The purpose of this work was to develop an instrumental design that enables the generation of gaseous oxidized mercury GOM in reference gases with concentrations ranging from ng m^{-3} to µg m^{-3} and their determination with ICP-MS detection in a single step. Such a configuration is of high necessity to allow for future development of a measurement platform for the accurate determination of the GOM in reference gases used in both environmental and industrial measurements and for provision of traceability to national and international standards (ISO 6143:2001). The first step in this process is to assure linearity of the generator with quick response time and minimal memory effects. The investigation of these parameters is presented in this work using HgCl$_2$ as a source of GOM.

The quantitative determination of (GOM) typically relies on a three-step process involving collection of GOM on a selective trap, thermal or wet chemical conversion of different mercury (Hg) species to gaseous elemental Hg (GEM) and their quantitative determination based on optical atomic emission, absorption or fluorescence spectrometry. In addition, building a calibration curve for this purpose is accomplished using elemental Hg dry reference gases (with concentrations from ng m^{-3} to µg m^{-3}) or by absolute mass using a gas tight syringe and bell-jar apparatus containing elemental Hg (Brown et al., 2008). The calibration of such systems by using oxidized Hg generators is not usually performed for atmospheric measurements, because of the lack of commercially available calibration systems for GOM at low concentrations. This effectively means that the measurement of oxidized Hg is accomplished by using a calibration curve based on elemental Hg response, measured directly at the detector, thus bypassing the sampling arrangement and collection media for GOM. There is therefore an increasing need for GOM generators especially at low ng m^{-3} and sub ng m^{-3} concentrations to ensure that accurate measurements are achieved. The drawbacks of the typical indirect three-step measurement methodology combined with current limited concentration range for calibration lead to a relatively large measurement uncertainty for gaseous Hg determination. The major sources of measurement uncertainty are the disproportional loss of GOM on sample pathway and trapping, compared to GEM, and extrapolation of the calibration curve for measurement of lower concentrations of Hg (Cheng and Zhang, 2017; Landis and Ryan, 2014; Lyman et al., 2020).

Metrologically traceable calibration to SI units for gaseous elemental Hg has been recently established for GEM (Ent et al., 2017), but not for

GOM. Different generation approaches exist for µg m^{-3} concentrations for GOM based on permeation devices (Jones et al., 2016), oxidation of elemental Hg (Ohata and Nishiguchi, 2017), and evaporation of liquid phase standards (Wilbring and Röllig, 2000). The calibration accuracy with these generators is difficult to establish (Lyman et al., 2016), and the data agreement with that of elemental Hg generators is poor, especially over concentration ranges exceeding one order of magnitude (Lyman et al., 2016; Saxholm et al., 2020). When applying an indirect measurement approach, which uses a selective trapping media and a conversion from GOM to GEM, the GOM loses and incomplete conversion can affect the calibration accuracy, traceability, and measurement uncertainty (Ebinghaus et al., 2013; EPA, 2017).

Recent laboratory developments for more reliable and precise measurement of Hg typically employ optical spectrometry and techniques based on inductively coupled plasma mass spectrometry (ICP-MS) (Srivastava and Hodges, 2018; Ohata and Nishiguchi, 2018; Maksakova et al., 2019; Bacon et al., 2020). ICP-MS is suitable for Hg determination from low picograms per gram to percent concentrations. It is a high energy ionisation source (temperature of 6000 to 10 000 K, Beauchemin, 2017) that can convert entirely the molecular ions and elements to the same ionic state thus levelling off the mass spectrometer response and providing species independent sensitivity (Moller et al., 2015). However, matching sensitivity can be obtained for the Hg species (GOM and GEM) only if their transfer efficiency from the source to the detector is the same. Instead of using the respective reference gases for GEM and GOM, the calibrations with the above referenced measurements were made either using liquids (Hg standards solutions) or dry GEM gases, which are not matching the chemical behaviour of GOM (Pyhtila et al., 2013). The reason to avoid GOM species for calibration is its reactivity and "stickiness", which result in severe memory and carry-over effects (EPA, 2009). It easily adsorbs onto different materials, causing long response times and sampling losses. This behaviour causes even bigger problems in lower ng m^{-3} concentrations and traditionally prevents construction of systems that would operate over wide concentration range of several orders of magnitude. This is required for Hg environmental and industrial measurements.

A measurement design that enables the direct measurement of the concentration of a GOM reference gas with concentrations ranging from ng m^{-3} to µg m^{-3} has been developed in this study. It is possible to feed the reference gas flow from a generator directly to an elemental detector, such as ICP-MS or ICP-OES, with negligible sampling losses. This setup is useful to directly validate different types of reference gas generators for GOM for example, by providing traceable calibration of these generators through the traceability of a GEM source or by employing primary calibration approaches such as isotope dilution mass spectrometry (IDMS).

2. Materials, methods and instrumentation

2.1. Reagents, standards and other consumables

Unless otherwise stated, all reagents are of analytical grade quality or better and were prepared using 18.2 MΩ cm water (Elga, Veolia, High Wycombe, UK). Concentrated nitric acid, UpA grade (concentration w (HNO$_3$) ≥ 63% w/w, density of ρ(HNO$_3$) = 1.4 g mL^{-1}) and concentrated hydrochloric Acid, UpA grade (concentration w(HNO$_3$) = 32–35%, density of ρ(HNO$_3$) = 1.18 g mL^{-1}) were both purchased from Romil (Cambridge, UK) and were used to prepare mixed 1% v/v HNO$_3$ – 1% v/v HCl solutions in water for generator rinsing. Mercury dichloride (HgCl$_2$, Sigma-Aldrich ACS, purity > 99.5%) with non-altered isotopic composition was used as a source of GOM. The elemental impurities in this salt were determined by ICP-MS and the HgCl$_2$ fractionation in this material was confirmed by analysis of a solution of the salt using HPLC-ICP-MS (column SGE Protecol C18G, 120 Å, 3 µm, 50 mm × 4.6 mm, mobile phase L-Cysteine/mercaptoethanol eluent) with methodology developed at LGC (LGC Ltd, Teddington, UK). A stock solution of 145 µg

g^{-1} Hg(II), prepared from the HgCl$_2$ salt in 40 µg mL^{-1} HCl and 80 µg mL^{-1} HNO$_3$ was used over the course of this work (3 months). Working standard solutions were prepared by gravimetric dilutions of the stock standard in the same acid mixture and used with the liquid evaporative generator (section 2.3). Argon gas (Ar) with a nominal purity of 99.99% was used as a carrier both for GEM and GOM generators. More details of the coupling are present in sections 2.2 and 3.1.

2.2. Element-specific detection of gaseous Hg

An inductively coupled plasma tandem mass spectrometer (Agilent 8800 ICP-MS/MS, Agilent Technologies, Tokyo, Japan) was used for the measurement of total mercury in the gas flow. The commercial peristaltic pump/spray chamber interface was removed and replaced with an *in-house* inert interface, specifically designed to minimize the HgCl$_2$ adsorption. For that purpose, a PTFE tubing (O.D. 1/16", I.D. 1/32"), was inserted inside the ICP-MS torch to approximately 1 cm before the end of the quartz injector. A shielding gas of at least 0.2 L min^{-1} was introduced through the makeup channel to improve the transfer efficiency of HgCl$_2$ through the ICP-MS interface and to prevent the tube from melting. A schematic diagram is presented in Fig. 1. The optimised ICP-MS parameters for Hg determination in gas mixtures generated by PSA (P S Analytical, Orpington, UK) Hg generators and Optoseven (Optoseven Oy, Espoo, Finland) evaporative generator are shown in Table 1. Further details about this interface are presented in the results and discussion section (section 3.).

2.3. Elemental and oxidized Hg generators

Three gas generators were used in this study. A commercially available dynamic calibration gas generator (PSA 10.536) based on the continuous generation and dilution of saturated mercury vapour at known temperature was used as a source of gaseous elemental Hg. The principle of operation and metrological characteristics of the generator were previously described by Brown et al. (Brown et al., 2010). The second generator was a GOM generator, which was made from a PSA 10.536 unit where the elemental Hg reservoir was replaced with a bed of mercury chloride salt (10 g). The principle of their operation is shown in Fig. 2A. A low gas flow (2–20 mL min^{-1} range), controlled by a thermal mass flow-controller (MFC), passes over a mercury reservoir located in a temperature-controlled oven, picking up a known (calculable) mass-flow of mercury. The mercury mass-flow is then diluted by a gas flow from a second thermal MFC operating in the range 2–20 L min^{-1}. The predicted output of the GEM generator was based on the Dumarey equation (Dumarey et al., 2010). For the oxidized Hg generator the HgCl$_2$ saturated vapour pressure expression by Bernard et al. (1997) was used.

The third generator was a liquid evaporative gas generator (Fig. 2B), developed by Optoseven Ltd together with VTT Ltd within the EMPIR Metrology for Oxidized Mercury (MercOx) project (EURAMET, 2017). It is designed for a fast response time through minimization of adsorption to surfaces and stable operation in wide concentration ranges of carrier gas and water content in the generated gas. The evaporator has cylindrical shape and is internally coated with PTFE. An automatic stepper-motor-controlled syringe pump is used for accurate chemical solution dosing. The syringe has capacity for minimum 30 min continuous standard introduction before requiring a few seconds re-filling to resume normal operation. The generator output, which provides the reference gas, is made of 1/4" O.D., 1/8" I.D. PTFE tubing. Details of the configuration are presented on Fig. 2B and in a recent publication (Saxholm et al., 2020). The operating parameters of the liquid evaporative generator are listed in Table 2.

A PSA 10.525 Sir Galahad (P S Analytical, Orpington, UK) coupled to the ICP-MS was used for the validation of the generators output relative to the bell-jar calibration and the estimation of the gas transfer efficiency (section 3.1).
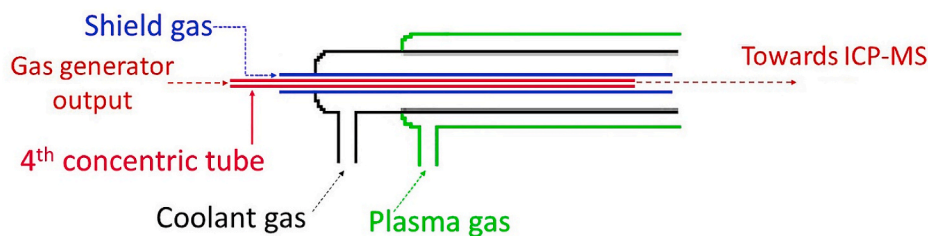
Fig. 1. Schematic diagram of 4-concentric ICP-MS torch. The sum of the gas generator output and makeup gas is 1.1 L min^{-1}. Coolant gas flow rate 0.9 L min^{-1}, Plasma gas 15 L min^{-1}.

Table 1
Optimised ICP-MS parameters for direct measurement of Hg. The remaining parameters were either auto-tuned or fixed to the recommendation by the manufacturer.

Parameter	Value
RF power	1500 W
RF matching	1.68 V (daily optimised)
Sample depth	6.5 mm
Sample (nebuliser) gas	0.0 (split-valve optimised to ~0.9) L min^{-1}
Dilution (shield) gas	0.2 (daily optimised)
Coolant gas	0.9 L min^{-1}
Extract 1	-16 V
Octopole bias	-18 V
Energy discrimination	0 V
Torch X/Y position	1.2/0.3 mm (daily optimised)
Acquisition mode	Single quad, No-gas mode
Monitored Hg isotopes	200, 201, 202 m/z

Fig. 2. A -A dynamic mercury dry vapour generator for GOM and GEM. B – A liquid evaporative generator for GOM.

Table 2
Typical operating conditions of the liquid evaporative generator.

Parameter	Value
Stock HgCl$_2$	145 µg g^{-1} Hg(II)
Liquid standard mass flow rate	0.070 g min^{-1}
Dilution gas flow	7.00 L min^{-1}
Measured pressure	1254 mbar (adjustable)
Total gas flow	7.08 L min^{-1}
Evaporator temperature	120 °C

3. Results and discussion

3.1. Instrument coupling, optimisation and generators performance

3.1.1. Validation of the GEM output against bell-jar standards

Before comparing the GOM and the GEM generators output, the accuracy of the output of the GEM generator was assessed through a comparison with bell-jar GEM gas standards. A PSA 10.525 Sir Galahad trapping and desorption system, coupled to the ICP-MS was used for this purpose. The gas standards from either the GEM generator or the bell-jar were passed over a gold impregnated silica trap (Amasil™ quartz tube trap), followed by thermal desorption and transfer to the ICP-MS *via* 1/8" O.D. PTFE tubing. The traps loading was performed either directly through a 1/8" O.D. port (for the gas generator standards), or by injection through septum (for the bell-jar standards). The flow through the trap in both cases was precisely controlled *via* external MFC set to 250 mL min^{-1}. The trapped Hg was then thermally desorbed and the trap flow was directed to the ICP-MS. By using a gold impregnated silica trap, both oxidized and elemental Hg are trapped and desorbed as Hg^0 and therefore the Hg signal from this system represents the total Hg (Corns et al., 2009, PSA). Seven bell-jar standards and four GEM reference gas concentrations were used to validate the GEM output. The bell-jar standards were in the range 0.33–3.0 ng Hg, which would be equivalent to 1.3–12 µg Hg m^{-3} with 250 mL min^{-1} gas flow rate and 1 min loading time. The GEM generator was set to deliver concentrations between 3.9 and 31 µg m^{-3}. The trapping time was 1 min and the gas flow was 250 mL min^{-1}, which lead to Hg trap loadings between 0.98 and 7.8 ng. The slope of the calibration curve obtained with GEM generator was similar to the slope obtained with the bell-jar standards (the ratio between the two slopes was 0.92), demonstrating the accuracy of the generator with traceability to bell-jar standards (Brown et al., 2008).

3.1.2. GOM accuracy and transfer efficiency using standard ICP-MS interface

The concentration accuracy and transfer efficiency of the GOM dry gas generator (HgCl$_2$ gas mixture) was investigated in the low µg m^{-3} range (2–20 µg m^{-3}). The validated GEM and GOM generators were directly coupled to ICP-MS and the calibration curve slopes were compared, similarly to the experiment performed in section 3.1.1. The standard ICP-MS plasma torch (quartz, three concentric tube design) was used during these initial experiments and three Hg isotopes were continuously monitored - ^{200}Hg, ^{201}Hg and ^{202}Hg. It was found that the sensitivity with the GOM generator was 50% lower than expected from the slope of the GEM generator calibration curve. Since the ICP-MS sensitivities are the same for GEM and GOM if species are equally transported to the plasma, this indicated significant HgCl$_2$ loss. It was suspected that GOM was trapped on the injector of the ICP-MS torch, which is made of quartz. A similar experiment was performed, but with trapping of the GOM generator output on the gold trap of PSA 10.525 Sir Galahad followed by thermal desorption as GEM, which will not be preferentially trapped on the ICP-MS torch like the HgCl$_2$. However, lower sensitivity was obtained again, potentially due to absorption of the HgCl$_2$ on the quartz tube of the trap, before its conversion to GEM.
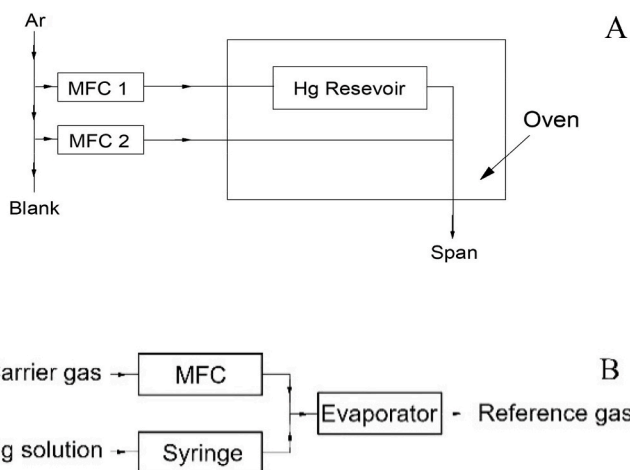
To estimate the $HgCl_2$ loss on the quartz tube of the Au traps more accurately, the output of both the GEM and GOM generators was collected Amasil™ trap for different amount of time (between 30 s and 3 min) and then thermally desorbed as GEM into the ICP-MS. The Hg recovery of the GOM output against GEM generator calibration was estimated to 71%; the remaining 29% were attributed to adsorption on the non-heated entrance part of the quartz tube. This assumption was further investigated and the results are presented in section 3.1.3.

3.1.3. Investigation of adsorption loses. Conversion of GOM to GEM

To investigate whether the monitored differences of the GOM and GEM generator outputs are due to low biased $HgCl_2$ generation from the GOM generator or due to losses on quartz surfaces of the Au trap or plasma torch, a thermal converter (TC) consisting of a quartz tube with quartz wool maintained at 800 °C was installed at the generators' output. The output of the thermal converter was then directed to PSA 10.525 Sir Galahad Au trap, followed by thermal desorption and ICP-MS determination. With this set up the $HgCl_2$ and Hg^0 sensitivities (GOM and GEM generator outputs) matched within 96%–98%. Since the output of the thermal convertor is GEM despite the input species ($HgCl_2$ or Hg^0, respectively), the transfer efficiency all the way to the detector is the same, despite which generator is coupled upfront. The results from this experiment clearly demonstrated accuracy of the GOM generator output and indicate adsorption losses on the quartz surfaces (see 3.1.2). Additionally, identical slopes of the two generators calibration curves were obtained when the PSA 10.525 Sir Galahad Au trapping system was removed, but keeping the thermal converter, which provided GEM species output with both generators. The GOM generator was located on the top of the GEM generator and their ¼" outputs were approximately 25 cm away from each other. Removing the tubing from one generator output and connecting it to the other did not cause the plasma to extinguish, which made these experiments possible.

In summary, from the identical sensitivity obtained at the ICP-MS detector for both GEM and GOM generators (with and without trapping on PSA 10.525 Sir Galahad) it can be concluded that the output of the both Hg generators matches when they are set-up to generate the same Hg concentration. Through the bell-jar validation of the GEM generator output and the matching signals between the GEM and GOM generators, a source of traceability of the generated GOM gas ($HgCl_2$) to bell-jar standard gas is provided. The data from the experiments with PSA 10.525 Sir Galahad trapping are presented on Fig. 3 (two batches, 1 month apart). The reason for the slightly higher concentration of Hg^0

(TC), i.e. the output of the GEM generator with thermal convertor at its output, compared to Hg^0, i.e the GEM without thermal convertor, has not been further investigated since it is within one standard deviation of the two batches. It should be noted that due to the intrinsic ICP-MS sensitivity drift and the long measurement time, the accuracy of the comparison of the generators output is currently limited to approximately 5%. Signal stabilisation time for GEM generator was in the scale of minutes, while for GOM (as $HgCl_2$) a several hours were needed and signal drift as high as five percent cannot be excluded. This is discussed further in Section 3.3.

However, since for GOM calibration purposes the $HgCl_2$ should be supplied in molecular form without prior thermal conversion to GEM, the setup with thermal converter cannot be used and the issue with the $HgCl_2$ adsorption losses, leading to incomplete transfer efficiency, has to be resolved.

3.1.4. Improvement of the GOM transfer efficiency

In an effort to improve the transfer efficiency of the $HgCl_2$ gas from the generator to the ICP-MS plasma, the contact surface was minimized by using the shortest possible length of tubing. Only inert materials like PFA and PTFE were used throughout the sample pathway, including fittings, with narrow diameter tubing with 1/4" O.D. at the generators output step-reduced to 1/16" O.D. at the ICP-MS inlet. To avoid adsorption on the ICP-MS torch a PTFE tubing was insert into the injector to approximately 0.8 cm away from the plasma. Shielding gas was introduced to prevent the PTFE tubing from melting (see section 2.2). However, the flexibility of the inserted tube had a negative effect on stability of the instrument signal. With the conventional ICP-MS interface, a sensitivity drift of less than 10% is to be expected over the course of an one day continuous measurement (data from the instrument manufacturer) while signal drops of more than 50% were monitored with our configuration. The reason for this was identified to be the narrow gas cloud thickness (PTFE tube I.D. only 1/32") and not instrument sensitivity drift. For example, a deviation of 0.1 mm in the torch position has caused signal increase or decrease of up to 30%. When the torch x-y position has just been optimised the signal is stable for at least 30 min. After that re-optimisation of the x-y position was needed in some cases to achieve the same sensitivity. This negative effect was significantly alleviated by pulling the most inner PTFE tube away from the plasma and therefore increasing the make-up gas channel mixing time and Hg cloud thickness. However, pulling out the tube resulted in decreased sensitivity. Furthermore, retracting the 4th concentric tube
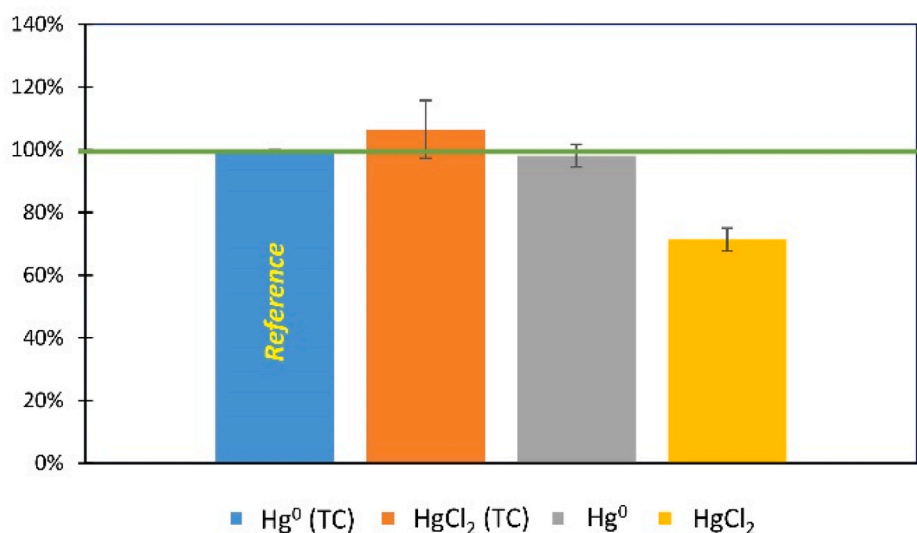

Fig. 3. Comparison between GOM and GEM generators output with ICP-MS detection. The GEM output with thermal convertor Hg0(TC) is used as a reference. The error bars represent two standard deviations of replicated experiments (n = 2).

too much allows contact between the $HgCl_2$ and the quartz surface of the torch injector and, therefore, it is not recommended due to the discussed adsorption loss (section 3.1.3). In this case the optimum distance to the plasma was identified to be at approximately 1.1 cm. The effect of up to 0.2 cm deviation from this value on the sensitivity can be partially compensated by adjusting the flow rate of the makeup channel gas. Although with the optimal setup a good stability was achieved and maintained over the course of one day, further improvement of the positioning and mechanical stability of the most inner tube is needed. Alternatively, replacing the standard torch with a demountable torch with a PTFE injector could provide improved stability and maintain the good transfer efficiency but at the time of the experiment such was not available at our laboratory.

3.2. Interfacing of the evaporative generator to the ICP-MS

The Optoseven liquid evaporative gas generator was connected to 4th concentric tube of the torch *via* 1/8" (O.D.) PTFE tube. The inner PTFE tube (O.D. 1/16") fitted tightly the 1/8" (O.D.) tube and 0.5 cm insertion was sufficient to provide gas-tight connection. The Optoseven generator output flow was set to 7 L min^{-1} and the other generator parameters were fixed at the manufacturer recommended values (see Table 2.). Since the ICP-MS optimal carrier gas flow is between 0.8 and 1.8 L min^{-1}, a flow split was required. Considering the properties of $HgCl_2$ gas, in particular its stickiness to almost any surface, it was decided to avoid flow control of the detector flux and to control the split flow by controlling the exhaust flow. The ICP-MS flow is then equal to the difference between the generator output and exhaust flows. Control was accomplished by using a manual flow meter with a needle valve installed at the exhaust flow line. The split gas flow was optimised for optimum ICP-MS sensitivity. It was observed that with the changing atmospheric pressure during the day, the split ratio slightly changes and therefore the flow of gas directed to the ICP-MS. To compensate for this, a manometer was put immediately after the t-piece used to split the generator output gas and the needle valve was re-adjusted to restore the initial pressure when needed. With this design, the pressure was maintained at a constant value and the detector response was stable, approaching the stability of the standard setup with still relatively inert surfaces (PTFE and PFA only). The optimal split ratio was approximately 1:7. Knowledge of its exact value is not needed since the ICP-MS provides relative response, which requires calibration, but the analyst should assure constant flow delivery, as described above. A schematic diagram is presented on Fig. 4. The interface between the generator and ICP-MS was not subjected to additional heating.

3.3. Response and stabilisation time with liquid evaporative generator

Oxidized mercury, and in particularly mercury chloride dry gas, tends to adsorb on majority of the materials. This includes adsorption on PFA and PTFE surfaces (Feng et al., 2003; Jones et al., 2016), which are sometimes considered as inert. As a result, the stabilisation time for some $HgCl_2$ generators that use dry gas regime can extend to several hours, which prevents the generator to be efficiently used as a calibrator for GOM measurements over any changing concentration range within the course of one working day. In this work a coupling between a liquid evaporative generator and ICP-MS was demonstrated, which provides a minimal GOM surface adsorption and short response times. While most of the other generators rely on change of the reservoir flow to vary the $HgCl_2$ gas concentration, with this generator the concentration of the GOM is varied by changing the feed solution, i.e. the vial containing the dissolved mercury salt (see Fig. 3B). The gas flow, moisture level, temperature and pressure remain unaltered. This flexibility makes it easier to vary the generator output in a broad range with minimal stabilisation time. A graph of the Hg response with time, while changing the source solution concentration is presented on Fig. 5. For this figure, a moving average smoothing was applied for a better representation. As can be
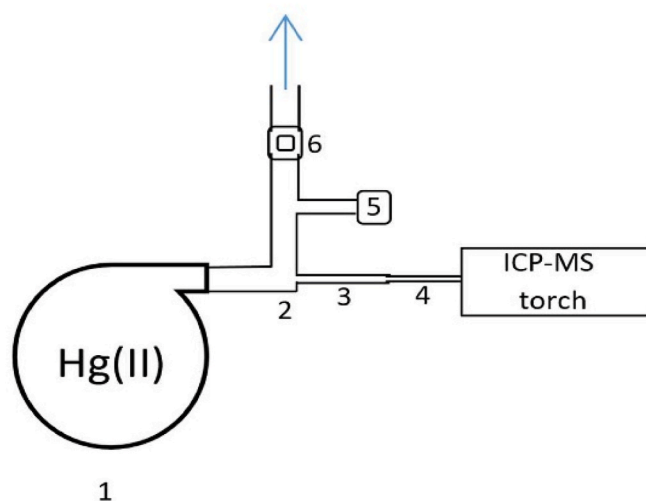
Fig. 4. Schematic diagram of gas generator coupling to ICP-MS. 1 – Optoseven generator; 2 – PFA reducing t-piece from 1/4" to 1/8"; 3 – short 1/8" PTFE adapter tubing; 4 – PTFE torch insert (4th concentric tube 1/16" O.D., ~25 cm); 5 – Barometer; 6 – Flow meter with needle valve for regulating the exhaust flow.

seen from Fig. 5A switching from blank solution to solution that would provide 9.7 ng m^{-3} GOM requires stabilisation time of only 20 min. Although from the figure it looks like the signal is still increasing for the first two concentrations or decreasing for the last two at the time of the data acquisition the signal was stable. Data were collected for 5 min at the end of the measurement periods where the signal varied within 1–2%, calculated with the raw, non-smoothed signal. Fig. 5B presents the signal from the first solution (9.7 ng m^{-3}) after initial 20 min stabilisation (this is zoomed Fig. 5A at 31–36 min). The signal plateaued more quickly when switching back from the 1.0–9.7 ng m^{-3} at the end of this experiment. The required time was 15 min compared to 20 min when switching from blank to 9.7 ng m^{-3}. The signal dips in Fig. 5A correspond to Hg feed solution replacement and syringe flushing and not to loss of gas supply. The short response times (under 0.5 h) even at low ng m^{-3} concentrations demonstrated that the adsorption losses to system surfaces and memory effect of GOM are minimal. Since the only difference between the $HgCl_2$ generators that use dry gas regime (e.g. the PSA GOM, see 3.1.2 and 3.1.3) and the liquid evaporative generator presented in this section is the presence of approximately 1% moisture in the gas mixture for the later, the authors presume that the moisture is the reason for its better performance. The effect of the moisture presence on the stability of the gas has been demonstrated in an EPA study (EPA, 2009). For reference, the output of the liquid evaporative generator used in this study includes 1–2% of GEM, as previously demonstrated by Saxholm et al. (2020).

3.4. Linearity and applicable range

The lower limit of the working range of the generator was determined by the system blank. For the response time experiments (section *3.3*), the background equivalent concentration (BEC) was approximately 1.5 ng m^{-3}. The upper limit of the working range was not determined in this work, but the system was tested up to 10 000 ng m^{-3} GOM concentrations. Three different ranges were then tested for linearity - from 0 to 10 ng m^{-3}, from 10 to 100 ng m^{-3} and a broader range from 10 to 10 000 ng m^{-3}. A good linearity was observed over the investigated ranges with all the monitored isotopes. The coefficient of determination exceeded 0.999 in all cases, except for the lowest range 0–10 ng m^{-3} where values of 0.99 only was observed. Considering that the BEC was 1.5 ng m^{-3}, the impaired linearity was expected due to the closeness of the Hg gas standard concentrations to the Hg background. Graphical
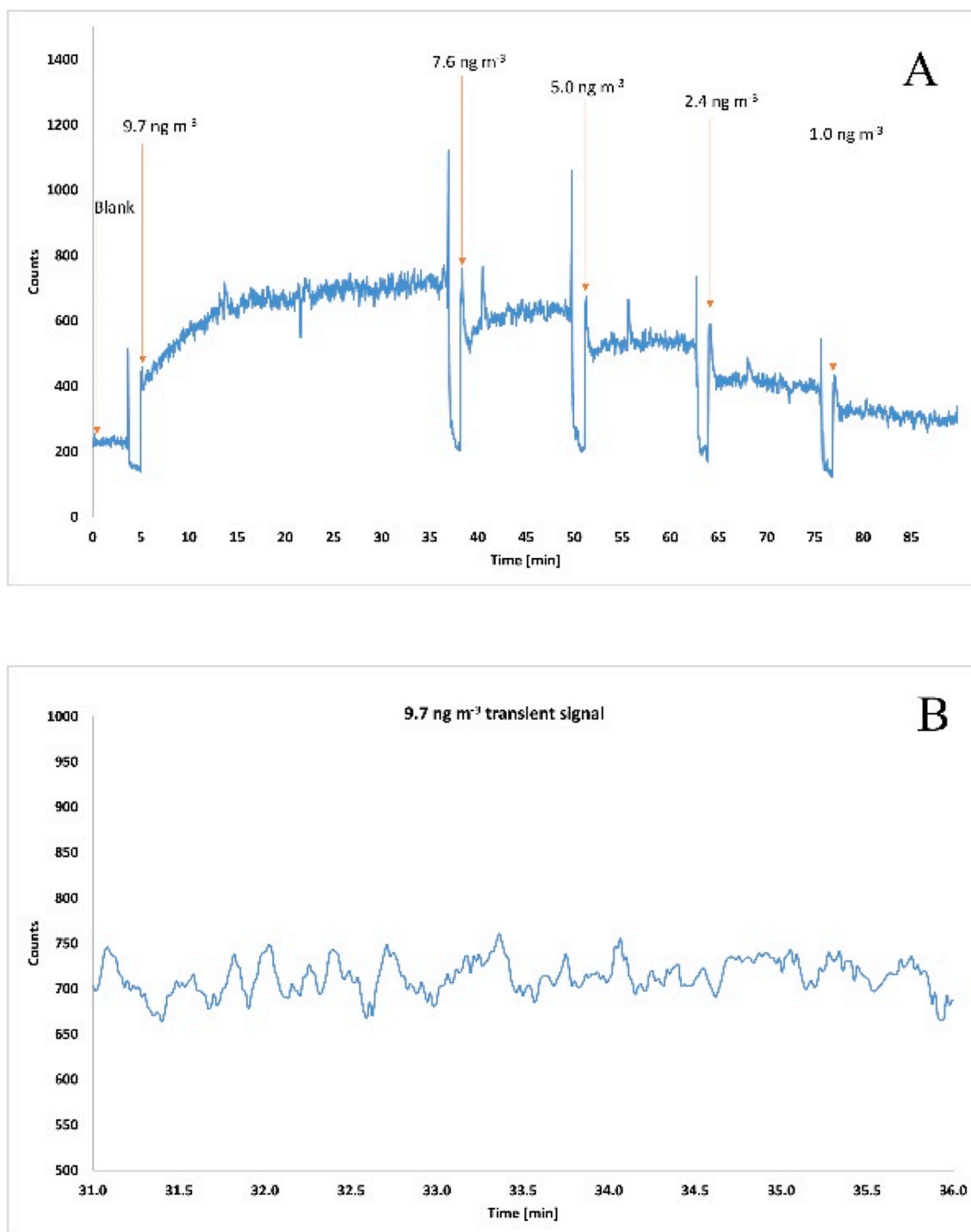
Fig. 5. Response time of the generator including tubing saturation with sequentially introduced Hg solutions of variable concentrations. A – transient signal demonstrating the short stabilisation times. B – Signal stability after 20 min from switching between blank and 9.7 ng m^{-3} GOM. The arrows with values correspond to the start of the solution introduction to the evaporator.

representation of the three experiments can be seen if Fig. 6 A, B and C. For better visual representation the data for Fig. 6C were log-transformed before plotting but the coefficients of determination from the linear plotting were kept. The signal variation, expressed as relative standard deviation of continuously acquired 200 data points was calculated. For the standard solutions, used to build these calibration curves, it was below five percent. Based on these experiments (linear calibration curves 1–10 ng m^{-3}, 10–100 ng m^{-3} and 10–10000 ng m^{-3}) the working range for the Optoseven generator coupled to ICP-MS

detector was determined as 1–10 000 ng m^{-3}. However, reagent and gas contamination should be considered as a substantial factor at the lower end of this range and therefore only high purity acids and carrier gasses must be used.

The experiments for the low (0–10 ng m^{-3}) and the expanded (10–10 000 ng m^{-3}) ranges were performed during the course of one day. In this particular case the slopes matched well, e.g. being 146 and 144 cps ng^{-1}, respectively, when monitoring ^{201}Hg isotope. The matching slopes within the different ranges is another demonstration of
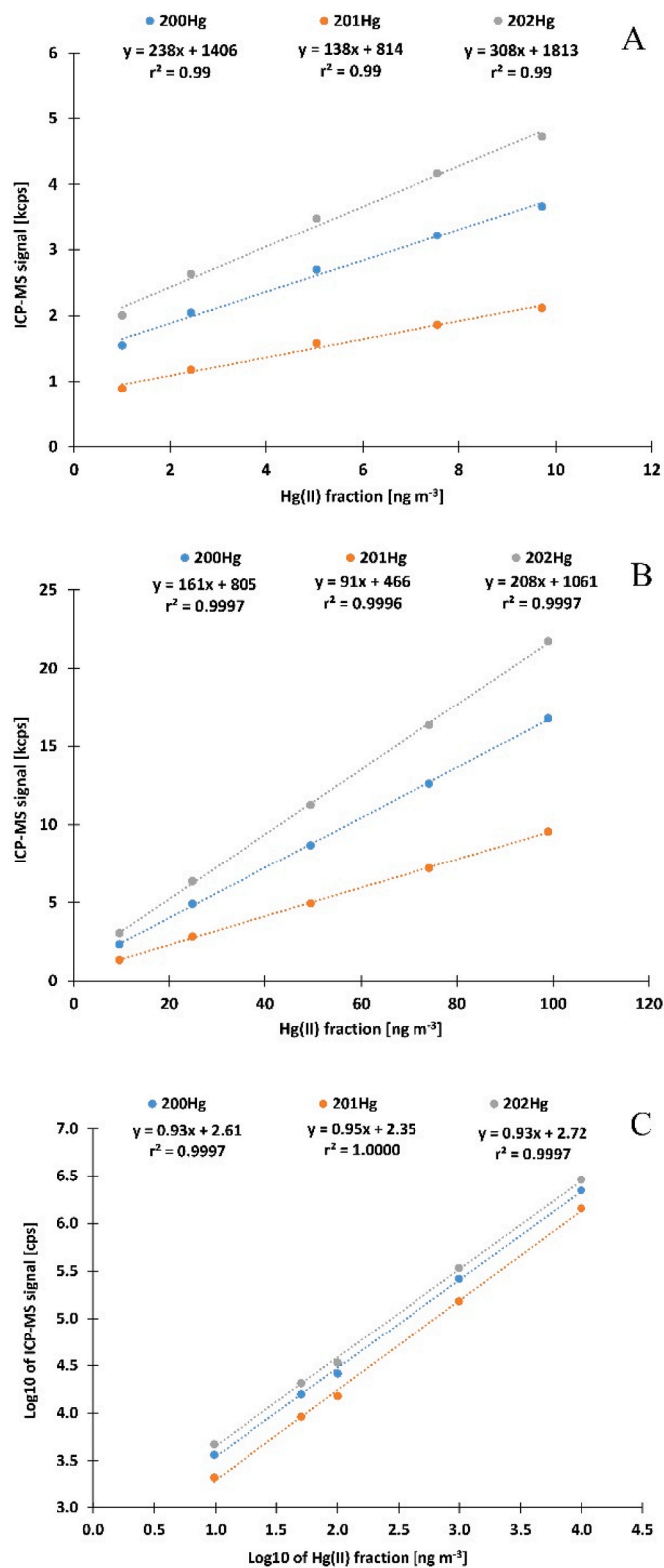
Fig. 6. Demonstration of $HgCl_2$ linearity and working range over four orders of magnitude. A - 0–10 ng m^{-3}, B - 10–100 ng m^{-3} and C - log-transformed data for expanded range between 10 and 10 000 ng m^{-3}. Error bars representing the signal variation, expressed as relative standard deviation, are presented on the figures but may be too small to see.

the linearity of the GOM generator. It should be noted that the data presented in Fig. 6B were generated on a different day. Considering that ICP-MS sensitivity can vary significantly between days (with each plasma ignition) slope comparison cannot be made between days, especially when the 4th concentric setup is used which further sensitise the instrument response depending on the precise torch x-y position within less the 0.1 mm. Since this is the smallest positioning increment for the torch position, more precise adjustment is not possible.

4. Conclusions

A novel approach for the generation and the direct measurement of the concentration of $HgCl_2$ (GOM) in reference gases with concentrations ranging from ng m^{-3} to μg m^{-3} has been developed. The centrepiece of the approach is an improved interfacing that allowed for the direct measurement of $HgCl_2$ and GEM with minimal losses. Two methods of generating $HgCl_2$ reference gas have been tested – based on a dynamic dry gas generator and on a liquid evaporative generator. The output concentration of Hg from the dry gas GOM generator, which employs mercury chloride salt, was in good agreement with the expected concentration when estimated against calibrations from a commercially available elemental generator and bell-jar standards. However long equilibration times were experienced with this setup. Furthermore, the approach is currently only suitable for $HgCl_2$ calibrations in the μg m^{-3} concentration range.

The performance of an evaporative $HgCl_2$ generator was tested by measuring the Hg concentration by ICP-MS through a newly developed 4-concetric tube interface. A good linearity, response time and stability of the signal from the generated Hg gas were achieved. The developed approach was found applicable from low ng m^{-3} to μg m^{-3} GOM concentrations with excellent response times over the whole range. Additionally, an equilibration time of between five and 30 min was required. More work is ongoing to demonstrate accuracy and traceability to SI units (kg) of the Hg concentration in reference gases through the use of the gravimetric gas standard developed at VSL and isotopically enriched Hg standards. The approach will be used to standardise commercially available GOM generators and validate their output within a European EMPIR normative project (19NRM03 SI–Hg).

Author contributions

Panayot Petrov designed the 4-concentric plasma interface and planned and performed the majority of the practical experiments. Timo Rajamäki participated in the coupling of the evaporative generator with the ICP-MS and initial linearity studies. Warren T Corns participated in the coupling of the dry gas generators, ICP-MS coupling and performing the Hg^0/$HgCl_2$ measurements with traceability to bell-jar standard. Heidi Goenaga Infante contributed with project winning and planning and with scientific guidance. All authors have contributed to writing and editing the paper and they have read and agreed to the published version.

CRediT authorship contribution statement

Panayot Petrov: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Timo Rajamäki:** Conceptualization, Methodology, Investigation, Resources, Writing - original draft, Writing - review & editing, Funding acquisition. **Warren T. Corns:** Conceptualization, Methodology, Investigation, Resources, Writing - original draft, Writing - review & editing, Funding acquisition. **Heidi Goenaga-Infante:** Resources, Writing - original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

Acknowledgments

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