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## An isotope dilution approach for validating the output of mercury gas generators for mercury pollution monitoring†

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Mercury (Hg) gas generators produce a continuous flow of Hg vapour and are used to calibrate detectors used in the field for Hg pollution monitoring. Typically, Hg gas generators are certified using empirical equations such as Dumarey or Huber which lead to results that can differ considerably and lack traceability. This work presents, for the first time, a novel online gas phase isotope dilution (IDMS) method for the accurate quantification of the output of Hg gas generators achieving SI traceability via NIST SRM 3133 certified reference material. To achieve this, a <sup>199</sup>Hg isotopically enriched standard was vapourised using a cold vapour generator and mixed with the gaseous output of a Hg gas generator. The <sup>202</sup>Hg/<sup>199</sup>Hg ratio of the gaseous blend was then measured by ICP-MS, and the generator output calculated using a single IDMS equation adapted for gas mixtures. The efficiency of the <sup>199</sup>Hg vapour generation is a key contributing parameter to the measurement uncertainty and was therefore quantified using a <sup>197</sup>Hg radiotracer and found to be greater than 99.5%. The feasibility of this method for validating the output of Hg gas generators was demonstrated by quantifying the output of one elemental Hg at an Hg flow of approximately 32 ng L<sup>-1</sup> and one oxidised Hg gas generator at an Hg flow of approximately 4 ng L<sup>-1</sup>. In both cases, a relative expanded uncertainty ( $k = 2$ ) of less than 9% was obtained. This method represents an important step towards improving the traceability, and therefore comparability of measurements for gaseous Hg which are essential for global environmental monitoring and reduction of atmospheric Hg pollution.

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### 1. Introduction

Mercury (Hg) is a pollutant that is highly toxic to human, animal, and environmental health. It has been shown to damage the nervous, digestive, and immune systems, and cause developmental issues in foetuses and young children.<sup>1–3</sup> Atmospheric Hg is of specific interest because airborne elemental Hg is readily carried around the globe by air currents and can be deposited into soils, waters, and plants where it can enter the food chain or be re-volatilised back into the atmosphere. Whilst

Hg can enter the environment naturally from volcanic activity, geothermal springs, and cinnabar ore deposits, anthropogenic Hg sources are of particular concern because they contribute over 50% of current atmospheric Hg emissions.<sup>4</sup> Anthropogenic sources include coal combustion, waste incineration, mining, and industrial uses such as cement production and smelting. Coal combustion and artisanal gold mining are the largest contributors, making up 60% of anthropogenic emissions.<sup>4</sup> When coal is burned, Hg is released as gaseous elemental Hg (Hg<sup>0</sup>). In the flue, Hg<sup>0</sup> can react with chlorine to form mercuric chloride (HgCl<sub>2</sub>) and other oxidised Hg species which are more soluble than Hg<sup>0</sup> and highly toxic. Mercury can also attach to particulate matter in the flue gas producing particulate-bound Hg (PBM), however this represents less than 5% of total atmospheric Hg emissions and over 99% of it is removed from flue gases using electrostatic precipitators and fabric filters.<sup>5</sup> Therefore, the two most prominent species of Hg in coal power plant stack gases are Hg<sup>0</sup> and volatile Hg<sup>II</sup> compounds.

Due to the known link between Hg exposure and toxicity in humans,<sup>1–3</sup> and notable case studies such as Minamata Bay, European legislation such as the Industrial Emissions Directive (IED) 2010/75/EU,<sup>6</sup> the Air Quality Directive (AQD) 2004/107/EC,<sup>7</sup>

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and the Waste Incineration Directive (WID) 2000/76/EC,<sup>8</sup> set maximum limits for gaseous Hg emissions and require combustion and waste incineration plants to monitor their total gaseous Hg emissions. Accurate and traceable determinations of both elemental and oxidised gaseous Hg are therefore vital in both understanding and monitoring the concentration of Hg in the environment and the contributions from emission sources. This knowledge is essential to protecting human health, enforcing regulatory limits, and ensuring legislation remains sufficient to control and reduce atmospheric Hg levels.

Gaseous Hg monitoring typically utilises atomic detectors such as atomic absorption spectroscopy (AAS), atomic fluorescence spectrometry (AFS), and atomic emissions spectrometry (AES). There are several manual and automatic calibration approaches for Hg detectors where set points are created by introducing gases of known Hg concentration. The most common calibration techniques use either a bell jar or a Hg gas generator. The bell jar method utilises a glass vessel containing a small droplet of Hg<sup>0</sup>. The contents are exposed to the atmosphere *via* a tube to allow a Hg-saturated atmosphere to form inside the vessel.<sup>9,10</sup> For calibration purposes, a known volume of Hg vapour can be extracted with a syringe *via* a septum. The concentration of the Hg vapour is calculated by theoretical calculations such as the Dumarey<sup>11</sup> or Huber<sup>12</sup> equations that are based on temperature, pressure, and gas flow rates. However, results from these equations have been shown to disagree by more than 7% at 20 °C.<sup>13</sup>

Mercury gas generators produce a continuous stream of Hg vapour that can be used to calibrate Hg measurement systems. Depending on the type of generator, the concentration of Hg in gas is either constant or dynamic and can contain Hg<sup>0</sup> and/or Hg<sup>II</sup>. Typically, the output of Hg<sup>0</sup> generators is calculated by empirical equations such as the Dumarey or Huber equation, which lack traceability; however comparable measurements for gaseous Hg are required globally to understand, monitor, and reduce atmospheric Hg levels.

Isotope dilution mass spectrometry (IDMS) is a high accuracy and low uncertainty quantification method that can provide SI-traceability by using an isotopically enriched standard. It therefore offers a potential tool for traceable quantification and validation of Hg gas generators. Quétel *et al.* (2014) developed a low uncertainty IDMS method traceable to ERM-AE640 – a certified <sup>202</sup>Hg isotopically enriched standard – for quantifying Hg mass concentrations in air.<sup>13</sup> Mercury vapour samples were trapped in the liquid phase and mixed with the liquid <sup>202</sup>Hg isotopically enriched standard. However, this method is based on collecting only millilitre samples of air for which Hg concentrations are orders of magnitude lower than the  $\mu\text{g m}^{-3}$  Hg mass flows of many Hg gas generators, thus making it difficult to use to validate output of higher mass flows from Hg gas generators.

A high accuracy and low uncertainty method able to quantify and validate the output of Hg gas generators that negates the need for Hg trapping, is SI-traceable, and has an expanded uncertainty of less than 10% is therefore, increasingly needed. It is also desirable that the method uses a species-independent detector to avoid the need for separate thermal converters or

pyrolysis for which the efficiency and uncertainty are not always known.

This work describes, for the first time, methodology based on the use of IDMS with ICP-MS for the traceable and direct quantification of gaseous Hg from Hg<sup>0</sup> and Hg<sup>II</sup> gas generators. This is achieved by mixing the output of a Hg gas generator with a cold vapour from an <sup>199</sup>Hg-enriched standard. The <sup>202</sup>Hg/<sup>199</sup>Hg ratio of the gaseous blend was measured by ICP-MS, and the generator output calculated using a single IDMS equation adapted for gas mixtures. The efficiency of <sup>199</sup>Hg vapour generation was determined using a <sup>197</sup>Hg radiotracer. The method was applied to quantification of the output of one elemental Hg and one oxidised Hg gas generator. A full uncertainty budget and key contributing factors to the overall measurement uncertainty are described.

## 2. Experimental

### 2.1. Materials

All reagents were prepared in 10% v/v hydrochloric acid prepared with concentrated 32–35% assay UpA grade hydrochloric acid (Romil Ltd, Waterbeach, Cambridge, UK) and 18.2 MΩ cm ultra-high purity water (Elga, Veolia, High Wycombe). All liquid standards used in this work were introduced to the instrumental set-up as vapours obtained by reduction. This was performed using 4% (w/v) tin chloride dihydrate (low in Hg, suitable for AAS, Thermo Scientific Chemicals, Belgium) in 10% v/v HCl in a continuous cold vapour generation system (CV, Cetac HGX-200). A working solution of <sup>199</sup>Hg standard ORNL SAMD/116 (Oak Ridge National Laboratory, Oak Ridge, Tennessee) was prepared in 10% v/v HCl and used as the IDMS isotopically enriched standard. The Hg mass fraction of the isotopically enriched standard was determined by reverse IDMS measurements using NIST SRM 3133 (National Institute of Standards and Technology, Gaithersburg, Maryland) as the natural Hg. Enriched <sup>199</sup>Hg solutions of variable concentration between 0.1 and 10 ng g<sup>-1</sup> were used. NIST SRM 3133 was also used for mass bias correction in the gas phase IDMS method.

### 2.2. Instrumental set-up

Two different Hg gas generators were used. Firstly, a 10.534 dynamic Hg<sup>0</sup> generator (P S Analytical, Orpington, Kent, UK), utilising a temperature-controlled Hg<sup>0</sup> reservoir across which a low flow of gas is passed. The flow of gas takes up an amount of Hg<sup>0</sup> that can be estimated empirically using, for example, the Dumarey equation.<sup>11</sup> The gas is then further dynamically diluted by merging it with an additional gas with controlled flow. In this way, the Hg<sup>0</sup> gas generator follows the saturation method as described by ISO 6145-9:2009.<sup>14</sup> The second Hg generator was a 10.532 critical orifice Hg<sup>II</sup> generator with a fixed output (P S Analytical, Orpington, Kent, UK). This generator uses a similar principle and passes a controlled low of gas across a saturated HgCl<sub>2</sub> reservoir that is again diluted; however, the flow rates are fixed using critical orifices, rather than being mass flow controlled. Simple schematics of both Hg gas generators can be found in Fig. 1.



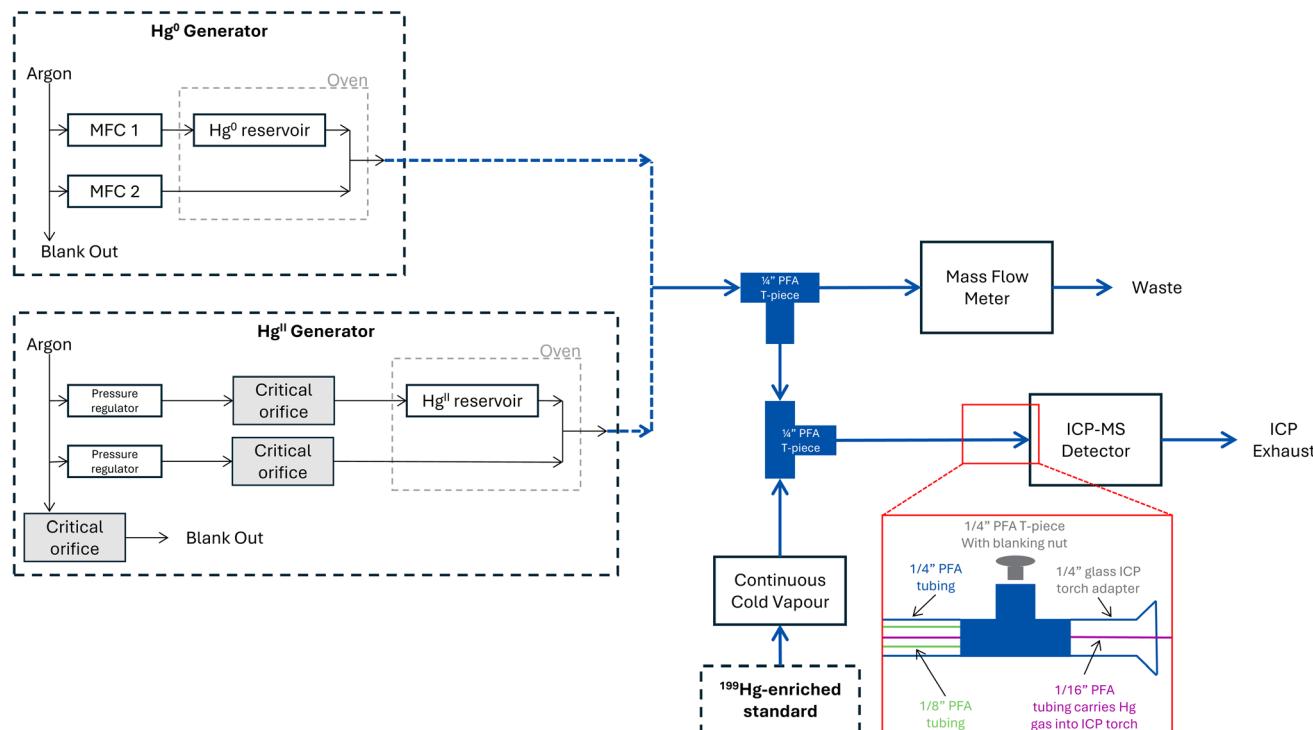


Fig. 1 Schematic of the set-up used to determine the mass flow of Hg from a gas generator using gas phase IDMS ICP-MS (only one out of the two generators was used at a time). All blue arrows represent  $\frac{1}{4}$  inch PFA tubing. The green tubing is  $\frac{1}{8}$  inch PFA and the purple is  $\frac{1}{16}$  inch. All tubing lengths were chosen to achieve the desired generator split flow ratio between the vent and the ICP-MS.

Fig. 1 also shows the set-up used for the gas phase IDMS method to determine the Hg output of a Hg gas generator using an Agilent 8800 ICP-MS (Agilent Technologies, Tokyo, Japan) operated by Agilent MassHunter software (Version C.01.06). A Cetac HGX-200 CV system was used to vaporise the liquid  $^{199}\text{Hg}$  isotopically enriched standard using the ICP-MS peristaltic pump to control the uptake rate of the liquid standard. An Ohaus GA200D balance (Parsippany, New Jersey, USA) was used to record the uptake rate of the pump as a weight loss function. The balance was calibrated with a weight set traceable to the kilogram (National Physical Laboratory, Teddington, UK), thus providing SI-traceability. The gaseous output of the generator was mixed with a vapourised  $^{199}\text{Hg}$  isotopically enriched standard in PFA tubing. Typical operating flow rates for many Hg gas generators exceed  $10 \text{ L min}^{-1}$ . However, to maintain the ICP-MS plasma, flow rates entering the torch cannot exceed  $1.2 \text{ L min}^{-1}$ . Therefore, a portion of the generator output was vented to achieve a combined generator and CV flow rate between  $1.0$  and  $1.2 \text{ L min}^{-1}$ . For each tested generator and generator flow setting, the tubing lengths were adjusted until the desired flows were achieved.

Before measurement, the Hg gas generator was connected to a nitrogen gas supply and set to the operating conditions to be tested and left to stabilise for three to seven days. This allowed the tubing to be saturated with Hg and thereby minimise drift. Once stabilised, the generator gas supply was switched to argon for compatibility with the ICP-MS. All samples were measured ten times, and the data averaged. All sequences contained at

least three blanks, the generator alone, the generator/isotopically enriched standard blend, and NIST SRM 3133 *via* the CV generator for mass bias correction. The blend raw  $^{202}\text{Hg}$  and  $^{202}\text{Hg}$  counts were corrected for blank and mass bias, then ratioed and averaged to give the  $^{202}\text{Hg}/^{199}\text{Hg}$  blend ratio for use in eqn (1). The uncertainty of the  $^{202}\text{Hg}/^{199}\text{Hg}$  blend was calculated as the standard deviation of the ten  $^{202}\text{Hg}/^{199}\text{Hg}$  ratios of the gas blend (corrected for mass bias and blank) as measured by the ICP-MS. The ICP-MS parameters used for this work are outlined in Table 1.

### 2.3. Calculation of generator mass flow

To calculate the mass flow of natural isotopic composition Hg from a Hg gas generator,  $q_m(\text{Hg}_n)$ , in  $\mu\text{g m}^{-3}$  (this is the average

Table 1 ICP-MS settings for the determination of the Hg mass flow from Hg gas generators by gas phase IDMS

Parameter	Setting
RF power	1450
Make-up gas (for CV generator)	$0.95 \text{ L min}^{-1}$
Sample/skimmer cone	Ni/Ni
Reaction gas	No gas
Monitored mass shift	No mass shift
Monitored masses	199, 201, 202
Data acquisition mode	Time resolved analysis
Sampling period	0.3 s
Acquisition time	60 s
Integration time	0.1 s

Hg concentration in the gaseous output of the generator over time of analysis), eqn (1) was used, where  $q_m(\text{Hg}_e)$  is the mass flow in  $\text{g min}^{-1}$  of the  $^{199}\text{Hg}$  isotopically enriched standard;  $q_v(\text{Hg}_n)$  is the volumetric flow of natural Hg from the generator in  $\text{sL min}^{-1}$  (standard  $\text{L min}^{-1}$ , *i.e.* corrected to  $20\text{ }^\circ\text{C}$  and  $100\text{ kPa}$ ) entering the ICP-MS;  $A_r(\text{Hg}_n)$  and  $A_r(\text{Hg}_e)$  are the atomic weights of the generator Hg ( $\text{Hg}_n$ ) and the  $^{199}\text{Hg}$  enriched standard ( $\text{Hg}_e$ ), respectively;  $x(^{199}\text{Hg}_e)$  and  $x(^{202}\text{Hg}_n)$  are the isotope amount fractions of  $^{199}\text{Hg}$  in the enriched Hg standard and of  $^{202}\text{Hg}$  in the generator output, respectively;  $R_b(^{202}\text{Hg}/^{199}\text{Hg})$  is the measured isotope ratio in the generator/enriched standard blend;  $R_e(^{202}\text{Hg}/^{199}\text{Hg})$  is the measured isotope ratio in the enriched  $^{199}\text{Hg}$  standard; and  $R_n(^{199}\text{Hg}/^{202}\text{Hg})$  is the measured isotope ratio in the natural Hg output from the generator. All measured isotope ratios were corrected for mass bias at the beginning of each measurement session by introducing NIST SRM 3133 *via* the CV generator and using argon gas as a blank in place of the generator.

$$q_m(\text{Hg}_e) = \frac{q_m(\text{Hg}_e)}{q_v(\text{Hg}_n)} \times \frac{A_r(\text{Hg}_n)}{A_r(\text{Hg}_e)} \times \frac{x(^{199}\text{Hg}_e)}{x(^{202}\text{Hg}_n)} \times \left( \frac{R_b(^{202}\text{Hg}/^{199}\text{Hg}) - R_e(^{202}\text{Hg}/^{199}\text{Hg})}{1 - R_b(^{202}\text{Hg}/^{199}\text{Hg}) - R_n(^{199}\text{Hg}/^{202}\text{Hg})} \right) \quad (1)$$

The atomic weight and isotope amount fraction of the  $^{199}\text{Hg}$ -enriched standard were taken from the supplier certificate. The isotope amount fractions and atomic weight of Hg in the generator output were assumed to be those for natural Hg according to IUPAC (International Union of Pure and Applied Chemistry).<sup>15</sup> The Hg isotopic ratios for the enriched ( $R_e$ ) and natural ( $R_n$ ) sources were calculated from the isotope amount fractions, and all other parameters in eqn (1) were measured.

The mass flow of the  $^{199}\text{Hg}$  isotopically enriched standard,  $q_m(\text{Hg}_e)$ , in  $\text{pg min}^{-1}$  was calculated from eqn (2) where  $w(\text{Hg}_e)$  is the mass fraction of total Hg in the working  $^{199}\text{Hg}$ -enriched standard solution in  $\text{pg g}^{-1}$ ,  $q_m(\text{pump})$  is the uptake rate of the peristaltic pump in  $\text{g min}^{-1}$ , and  $E(\text{CV})$  is the CV generator efficiency which was determined by the Jožef Stefan Institute using a  $^{197}\text{Hg}$  radiotracer (described below). The uptake rate of the peristaltic pump was determined by measuring the weight lost from the  $^{199}\text{Hg}$ -enriched standard solution vial during the method at 10 seconds intervals and averaging over 10 minutes.

$$q_m(\text{Hg}_e) = q_m(\text{pump}) \times w(\text{Hg}_e) \times E(\text{CV}) \quad (2)$$

The volumetric flow from the generator that entered the ICP-MS,  $q_v(\text{Hg}_n)$ , was determined either directly or indirectly. The direct method used an ADM G6691E mass flow meter to measure the flow rate of the generator flow after splitting and before it merged with the gaseous  $^{199}\text{Hg}$ -enriched standard. However, this measurement could not occur while the ICP-MS torch was lit as it required disconnecting tubing after the first T-piece in Fig. 1. The indirect method involved measurement of the flow rate at the output of the generator prior to the IDMS method using the Mesalabs Flex Cal-H flow meter, and then subtracting the flow rate of the waste generator gas measured during the ICP-MS acquisition. This provided real time data on

the volumetric flow but was subject to higher uncertainties that increased considerably with the generator flow rate.

## 2.4. Cold vapour efficiency

Efficiency of the CV generator used to introduce the  $^{199}\text{Hg}$ -enriched standard during gas-phase IDMS,  $E(\text{CV})$ , was determined using a  $^{197}\text{Hg}$  radiotracer of known activity to allow detection of Hg within the CV waste. The  $^{197}\text{Hg}$  radiotracer was produced *via* a neutron capture reaction by irradiating the ampoule containing enriched  $^{196}\text{Hg}$  in 2% v/v  $\text{HNO}_3$  with a high neutron flux ( $10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ ) for 12 h in the central channel of the TRIGA Mark II research reactor (Jožef Stefan Institute, Ljubljana, Slovenia). Working standards were prepared by dilution of an irradiated  $^{197}\text{Hg}^{\text{II}}$  stock solution to an approximate concentration of  $5\text{ ng mL}^{-1}$  in 5% v/v  $\text{HNO}_3$  to ensure the activity in the collected waste would be detected. Precise concentrations of the  $^{197}\text{Hg}$  in the working standards were then determined by CV-atomic absorption spectroscopy (CV-AAS) using NIST SRM 3133 as a calibrant. The same CV conditions were applied as for gas-phase IDMS as noted above, except for the use of nitrogen gas instead of argon. Once the  $^{197}\text{Hg}^{\text{II}}$  working standard solutions had passed through the CV generator, aliquots of the waste as well as the remaining working standard were transferred to glass vials and the activity of the waste measured relative to the working standards using a CANBERRA high-purity germanium (HPGe) well detector (Mirion Technologies (Canberra) Inc., Atlanta, Georgia, USA). All activity peak areas were corrected for radioactive decay since the irradiation and were used to calculate the percentage losses of  $^{197}\text{Hg}$  as described in Gačnik *et al.* (2022).<sup>16</sup>

## 2.5. Uncertainty estimation

Measurement uncertainty associated with each determination of Hg generator output was estimated for each run using the Kragten method,<sup>17</sup> and an uncertainty budget was created. The contribution of each parameter in eqn (1) to the overall uncertainty was calculated using either uncertainties from certificates or measured uncertainties.

# 3. Results & discussion

## 3.1. Measured IDMS parameters

The method was applied to two different Hg gas generators from PS Analytical (Orpington, Kent, UK): a  $\text{Hg}^0$  generator of variable output (PSA 10.534) and a fixed output  $\text{Hg}^{\text{II}}$  generator (PSA 10.532). During testing the mean measured  $^{202}\text{Hg}/^{199}\text{Hg}$  ratio in the gaseous blend was 0.97 with a typical relative expanded uncertainty ( $k = 2$ ) of 0.4%. The uptake rate of the  $^{199}\text{Hg}$ -enriched standard varied between 0.25 and  $0.28\text{ g min}^{-1}$  an overall expanded uncertainty ( $k = 2$ ) of  $0.03\text{ g min}^{-1}$ . The mass fraction of total Hg in the working  $^{199}\text{Hg}$ -enriched standard varied between 0.51 and  $4.2\text{ ng g}^{-1}$  with a mean relative expanded uncertainty ( $k = 2$ ) of 2%.

## 3.2. Cold vapour efficiency

The CV efficiency was determined as a ratio of  $^{197}\text{Hg}$  losses after vapour generation at the flow rates used in the IDMS method.



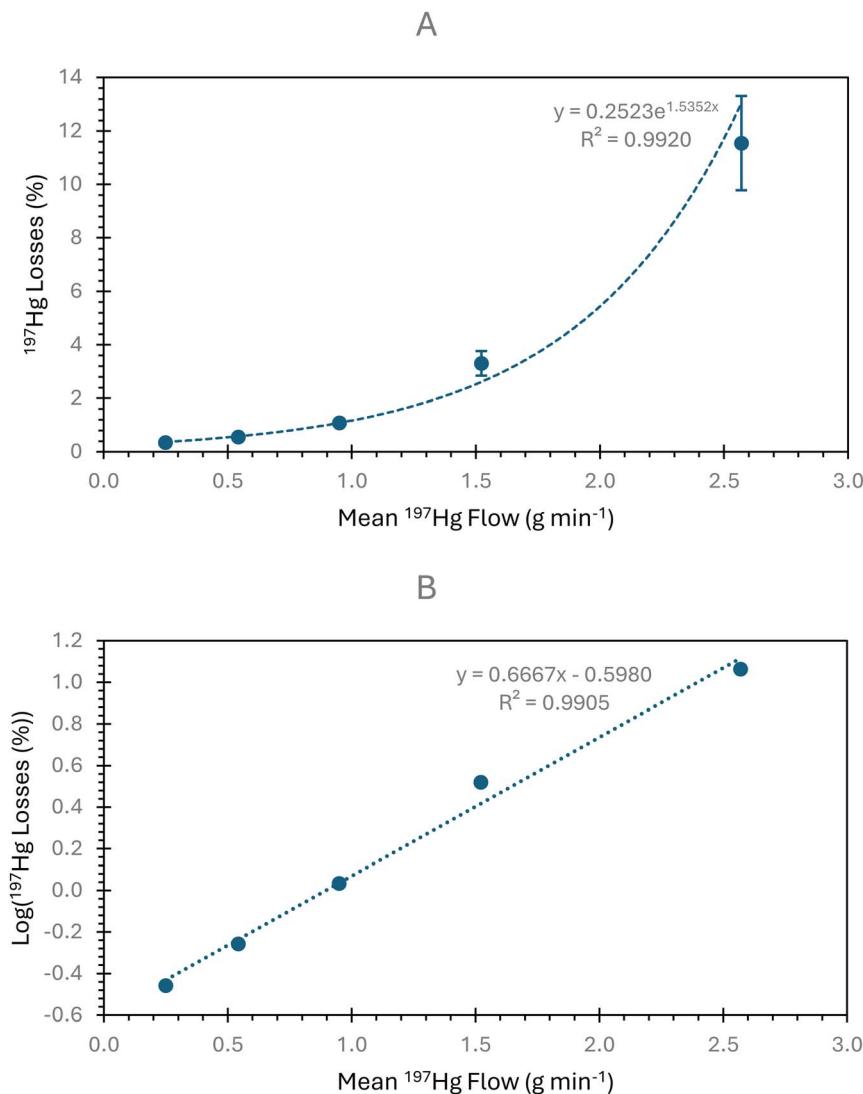


Fig. 2 Panel A: Graph of the  $^{197}\text{Hg}$  losses in waste collected from the CV generator at different sample flow rates. Error bars represent the standard deviation of the  $^{197}\text{Hg}$  loss across the replicate measurements using the same nominal Hg flow. Panel B: Log  $^{197}\text{Hg}$  losses again against the sample flow rate.

Higher flow rates were also tested to examine how the CV generator efficiency changes and determine the optimal flow rates for maximum efficiency. The results from the CV generator efficiency experiments are outlined in Fig. 2. The percentage losses of  $^{197}\text{Hg}$  increased exponentially with the flow of the Hg sample and reductant with the  $R^2$  value for the loglinear plot being close to unity (Fig. 2B). Therefore, low sample and reductant flow rates achieve high CV generation efficiency. The mean  $^{197}\text{Hg}$  loss at the  $0.245 \text{ g min}^{-1}$  flow rates used in the IDMS method were 0.35%, giving a mean efficiency of 99.65% with an expanded uncertainty ( $k = 2$ ) of 0.05%.

### 3.3. Mass flow of the $^{199}\text{Hg}$ -enriched standard, $q_m(\text{Hg}_e)$

The CV generator efficiency and associated uncertainty were taken from the efficiency measurements most closely matching the use of the instrument system for online IDMS. Therefore, the mean and standard deviation at the  $0.245 \text{ g min}^{-1}$  flow rates

were used. The uncertainty of the peristaltic pump uptake rate was the standard deviation of the weight loss measurements in  $\text{g min}^{-1}$  over a 10 minutes period (Fig. 3) and was on average  $1.4\%$  ( $k = 1$ ). The uncertainty of the mass fraction of the  $^{199}\text{Hg}$ -enriched standard was determined by combining the uncertainty of the reverse IDMS result used to calculate the concentration of the  $^{199}\text{Hg}$ -enriched standard stock solution and the uncertainty from serial dilutions calculated using replicate weighing and balance uncertainty. The mean relative uncertainty of  $^{199}\text{Hg}$ -enriched standard mass fraction was  $1.0\%$  ( $k = 1$ ). The uncertainty in the mass flow of the  $^{199}\text{Hg}$ -enriched standard was consistently one of the two highest uncertainty contributors in the IDMS method (Fig. 5). Given eqn (2), the contribution of uncertainty in  $q_m(\text{Hg}_e)$  to the uncertainty in the IDMS result might be further reduced through the use of a pump capable of a more stable delivery of the  $^{199}\text{Hg}$ -enriched standard solution to the CV system.



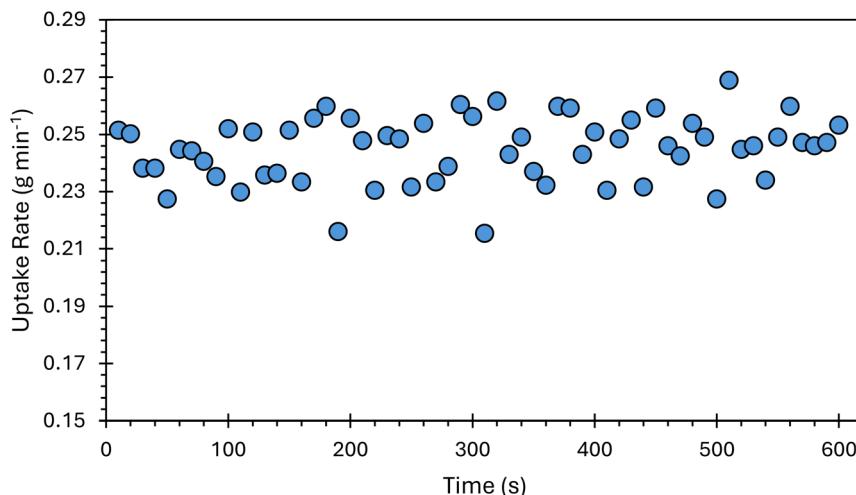


Fig. 3 Variation in the uptake rate of the  $^{199}\text{Hg}$ -enriched standard over a 10 minutes period to the CV generator via the ICP-MS peristaltic pump. The uptake rate was determined by measuring the weight lost from the vial.

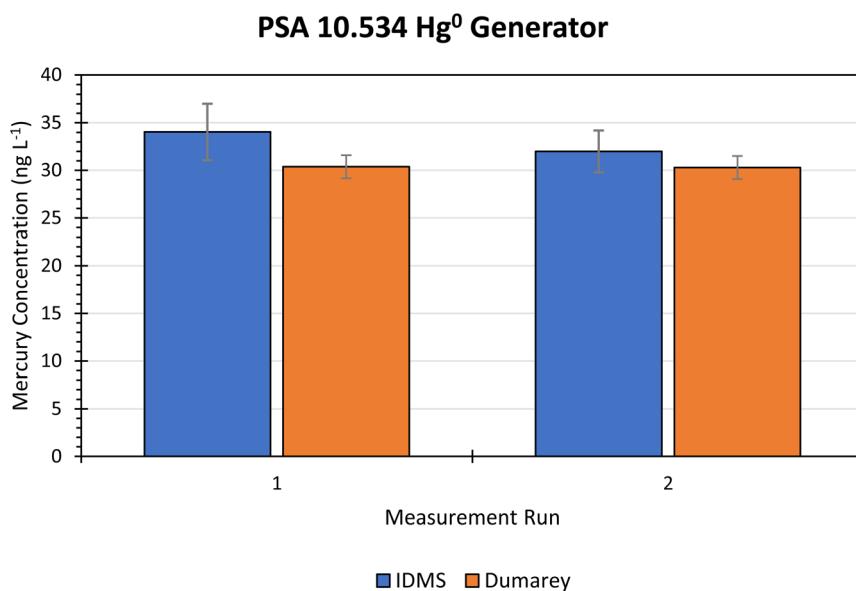


Fig. 4 Bar chart comparing the measured mass flow of Hg from the PSA 10.534 generator determined using the new gas phase IDMS method, and the theoretical Hg mass flow based on the Dumarey equation using the generator temperature, pressure, and flow settings. The vertical error bars for the IDMS bars are the expanded measurement uncertainties ( $k = 2$ ). The vertical error bars for the Dumarey bars are the indicative expanded uncertainty ( $k = 2$ ) from Dumarey *et al.* (2010).<sup>11</sup>

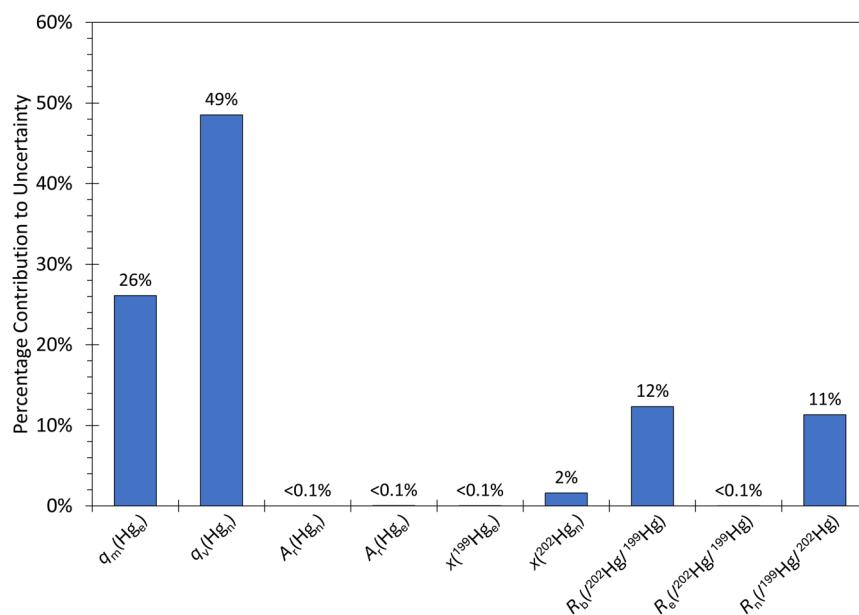
### 3.4. Gas-phase IDMS method performance

**PSA 10.534  $\text{Hg}^0$  generator.** The PSA 10.534  $\text{Hg}^0$  generator is a dynamic Hg vapour generator that can produce a continuous stream of Hg vapour at concentrations between  $100 \text{ ng m}^{-3}$  and  $3000 \mu\text{g m}^{-3}$ . Since the temperature, reservoir flow rate, and dilution flow rate each affect the Hg mass flow, it is hard to replicate conditions exactly across different runs. Therefore, each measurement run for this generator was treated independently, and the results were not averaged. The mass flow of the PSA 10.534 generator was determined on two different days using the IDMS method at a reservoir flow setting of  $1 \text{ mL min}^{-1}$ , a dilution flow setting of  $1.5 \text{ L min}^{-1}$ , and

a temperature of  $35^\circ\text{C}$ . Fig. 4 and Table 2 show that the results were  $34.03$  and  $31.99 \mu\text{g m}^{-3}$  with expanded uncertainties ( $k = 2$ ) of 8.7% and 6.9% respectively. The theoretical Hg mass flow for this generator can also be calculated using the Dumarey equation (Table 2). The IDMS results are 112% and 106% of that theoretical mass flow, respectively.

In the field, this generator is typically used at diluent flow rates of between  $10$  and  $20 \text{ L min}^{-1}$ . However, this generator was tested using the indirect volumetric flow measurement technique with the Mesalabs Flex Cal-H flow meter which has a high uncertainty at high flow rates. The uncertainty of the volumetric flow,  $u(q_v(\text{Hg}_n))$ , was calculated as the sum of the





**Fig. 5** Uncertainty budget for the PSA 10.534 IDMS run two calculated using the standard uncertainties of each parameter in the gas phase IDMS equation. The abbreviations on the x-axis correspond with those used in eqn (1). The major contributions are  $q_m(\text{Hg}_e)$  – the mass flow of the  $^{199}\text{Hg}$  isotopically enriched standard – and  $q_v(\text{Hg}_n)$  – the volumetric flow of natural Hg from the generator. This uncertainty budget is also typical of the PSA 10.532 generator.

**Table 2** Results of the gas phase IDMS quantification of the PSA 10.534  $\text{Hg}^0$  generator Hg output. The mass flow was determined on two different days, and the generator settings were replicated as closely as possible, however there were small differences in temperature and pressure. The theoretical Hg output was calculated by the Dumarey equation. The uncertainties are the relative expanded ( $k = 2$ ) measurement uncertainties for each run

Generator	Reservoir flow ( $\text{mL min}^{-1}$ )	Dilution flow ( $\text{L min}^{-1}$ )	Temperature ( $^{\circ}\text{C}$ )	Pressure (hPa)	Theoretical Hg output ( $\mu\text{g m}^{-3}$ )	Run	Measured Hg mass flow ( $\mu\text{g m}^{-3}$ )	$U_c$ ( $k = 2$ ) (%)
PSA 10.534 $\text{Hg}^0$	1	1.5	35.2	1027.1	30.38	1	34.03	8.7
			35.1	1021.6	30.30		31.99	

squares of the standard deviations of the total and vent generator flows. The volumetric flow was consistently the highest contributor to uncertainty in the IDMS result for the PSA 10.534 generator (Fig. 5) and the magnitude of the uncertainty increased with the generator flow rate. Increasing the generator flow rate increased the overall expanded IDMS measurement uncertainty from 6.9% to 8.7% ( $k = 2$ ) at  $1.5 \text{ L min}^{-1}$  (Table 2 and Fig. 5), to 17.8% ( $k = 2$ ) at  $10 \text{ L min}^{-1}$ . At the higher flow rate, 94% of overall uncertainty in the IDMS result was from the determination of the flow rate itself. The relative uncertainty ( $k = 2$ ) of the volumetric flow at  $10 \text{ L min}^{-1}$  was 20%, but only 5% at  $1.5 \text{ L min}^{-1}$ .

For this method to be applicable to Hg gas generators with the higher flow rates of  $10$  to  $20 \text{ L min}^{-1}$  with reasonable uncertainties, there are two options. Firstly, the direct volumetric flow measurement method could be applied such that the measurement of lower flow rates is required leading to reduced measurement uncertainties. Alternatively, to continue applying the direct method, a flow meter capable of measuring the necessary flow rates with low uncertainty is required. To bring the overall IDMS uncertainty down to the level achieved

with the direct flow measurement technique, any lower uncertainty flow meter would need to achieve a volumetric flow uncertainty ( $k = 1$ ) of at most 3% in the  $10$  to  $20 \text{ L min}^{-1}$  range.

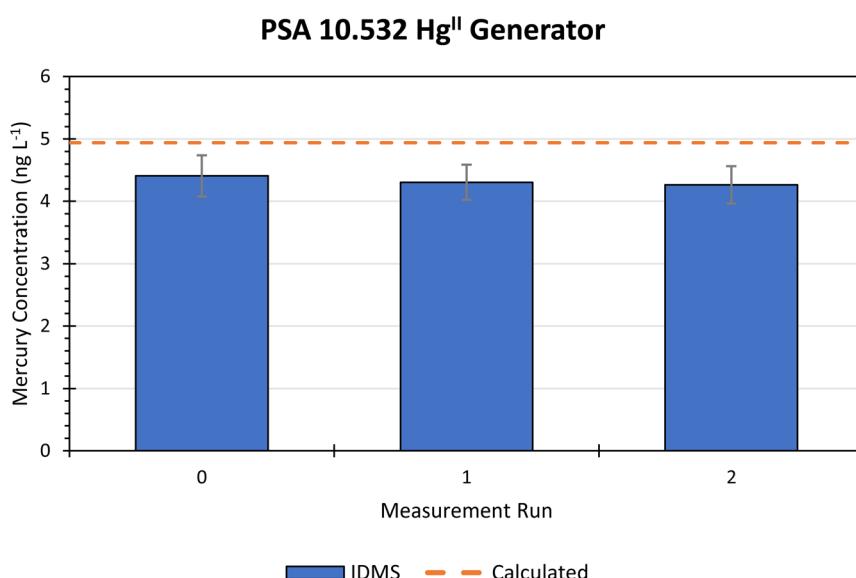
**PSA 10.532 critical orifice  $\text{Hg}^{\text{II}}$  generator.** The PSA 10.532 critical orifice  $\text{Hg}^{\text{II}}$  generator produces a continuous stream of Hg saturated vapour of predominantly  $\text{Hg}^{\text{II}}$  at a fixed mass flow. The Hg mass flow was determined in  $\mu\text{g m}^{-3}$  at the fixed reservoir and dilution gas flow rates of  $9 \text{ mL min}^{-1}$  and  $14.8 \text{ L min}^{-1}$  respectively, and  $40 \text{ }^{\circ}\text{C}$ . The generator was tested on three different days. Given the high dilution flow rate, the volumetric flow was measured using the direct method where the ADM flow meter was used to directly measure the generator split flow just before merging with the  $^{199}\text{Hg}$ -enriched standard at the second T-piece in Fig. 1. The mean Hg mass flow determined by the IDMS method was  $4.32 \mu\text{g m}^{-3}$  with an overall relative expanded uncertainty ( $k = 2$ ) of 7.9% (Table 3 and Fig. 6). This result shows that the IDMS method can produce high precision, repeatable results, with reasonable uncertainties at high flow rates.

The expected mass flow from the generator can be calculated using the saturated vapour pressure of  $\text{HgCl}_2$  at the oven



**Table 3** Results of the gas phase IDMS quantification of the PSA 10.532 critical orifice  $\text{Hg}^{\text{II}}$  generator. The generator flow conditions are fixed at approximately  $9 \text{ mL min}^{-1}$  and  $14.8 \text{ sL min}^{-1}$  for the reservoir flow and diluent flow, respectively. The generator mass flow was quantified on three different days, and the overall relative expanded uncertainty ( $k = 2$ ) accounts for the mean measurement uncertainty from the three days and the standard deviation of the results

Generator	Run	Measured Hg mass flow ( $\mu\text{g m}^{-3}$ )	$U_c$ ( $k = 2$ ) (%)	Mean Hg mass flow ( $\mu\text{g m}^{-3}$ )	Standard deviation	Overall $U_c$ ( $k = 2$ ) (%)
PSA 10.532 critical orifice $\text{Hg}^{\text{II}}$	1	4.41	7.5	4.32	0.08	7.9
	2	4.29	6.5			
	3	4.26	7.0			



**Fig. 6** Bar chart comparing the measured mass flow of Hg from the PSA 10.532 generator determined using the new gas phase IDMS method, and the expected Hg mass flow based on the generator temperature, pressure, and critical orifice. The vertical error bars are the expanded measurement uncertainties ( $k = 2$ ). The orange dashed line is the quoted output as measured by the manufacturer.

temperature setpoint, and the reservoir and dilution flowrates.<sup>18</sup> The expected Hg mass flow was estimated by calculation as  $5.12 \mu\text{g m}^{-3}$ . The manufacturer has also directly measured the mass flow of the generator as  $4.94 \pm 0.2 \mu\text{g m}^{-3}$  using thermal conversion of  $\text{Hg}^{\text{II}}$  to  $\text{Hg}^0$  followed by cold vapour-AFS using the Dumarey equation calibration from a bell jar. This measurement did not account for the efficiency of thermal conversion. The IDMS result of  $4.32 \mu\text{g m}^{-3}$  was 84.5% of the calculated estimate and 87.6% of the manufacturer's measured output. A re-evaluation of the theoretical output by accounting for flow suppression imparted on the  $\text{Hg}^{\text{II}}$  reservoir may reduce the expected output. If the reservoir flow is suppressed by around 10% the IDMS and expected values should be similar.

The critical orifice  $\text{Hg}^{\text{II}}$  generator required substantial stabilisation time (Section 2.2) prior to measurement to minimise drift in Hg mass flow resulting from adsorption to tubing and fittings between the generator reservoir and ICP-MS torch.<sup>19</sup> In this way, it was expected that saturation of adsorption sites could be achieved. Nevertheless, the possibility of a minimal loss in Hg within the gas stream remained and could also account for some of the difference between theoretical estimated generator output and the IDMS results.

The direct flow measurement technique significantly reduced the expanded uncertainty of the IDMS result for the PSA 10.532 generator. However, the direct measurement is not possible while the ICP-MS plasma is ignited, and therefore the measured flow rate may not reflect the true flow rate during the IDMS measurement. In addition, the ADM flow meter is not operational at flow rates more than  $1 \text{ L min}^{-1}$  and cannot therefore be used to measure the generator output or waste flows. For future applications of this method to Hg gas generators at higher flow rates within their suggested operating parameters of  $10$  to  $20 \text{ L min}^{-1}$  and achieving a reasonable uncertainty, either assumptions are needed that the ADM flow meter reading is comparable to the flow rate during measurement when the ICP-MS torch is lit, or a high level flow meter with a lower uncertainty is required.

### 3.5. Wider applications of the developed methodology

The method outlined here could easily be applied to the IDMS quantification of the output of other Hg generators where the isotopically enriched standard cannot be added directly to the sample. Examples include oxidative Hg gas generators, liquid



evaporative generators and reduction generators that reduce Hg salts to Hg<sup>0</sup>. In addition, this method could be used with other isotopically enriched standard introduction systems that vaporise a liquid standard instead of a cold vapour generator and could therefore be used in laboratories where a cold vapour generator is not available.

## 4. Conclusions

A gas-phase IDMS method has been implemented for dry-based Hg gas generators that produced results within 12% of the theoretical Hg<sup>0</sup> generator output predicted by the Dumarey equation but crucially provided results that were fully traceable to the SI. The method also produced repeatable results with a low combined expanded uncertainty of 7.9% ( $k = 2$ ) for the fixed flow critical orifice Hg<sup>II</sup> generator at a mercury mass flow of between 4 and 5  $\mu\text{g m}^{-3}$ . The IDMS results did not agree with the estimated theoretical output provided by the manufacturer within expanded uncertainty; however this is likely be due to an underestimation of the generator mass flow, or losses of oxidised Hg in the IDMS set-up. To the best of our knowledge, this is the first method that can provide traceability to the SI for Hg<sup>II</sup> generators used during *in situ* measurements of Hg concentrations.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

SP: conceptualisation, methodology, analysis, data processing, first draft; PJHD: methodology, supervision, writing-/review and editing; PP: conceptualisation, methodology, analysis, supervision, writing-/review and editing, funding acquisition; SVN: methodology, analysis, writing-/review and editing; IZ: methodology, analysis, supervision, writing-/review and editing; MH: methodology, resources, supervision, writing/review and editing, funding acquisition; WC: methodology, resources, writing/review and editing, funding acquisition; HGI: conceptualisation, methodology, resources, supervision, writing/review and editing, funding acquisition.

## Conflicts of interest

There are no conflicts to declare.

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