Supporting information

Calibration Approach for Gaseous Oxidized Mercury Based on Nonthermal Plasma Oxidation of Elemental Mercury

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Table of Contents

S1 - Standard operating procedure (SOP) for gaseous oxidized mercury species calibration by non-thermal plasma (NTP) oxidation of elemental mercury .............................................. S-1

S2 - Chemicals and instruments used in the validation work ................................................................. S-6

Table S1. Chemicals used in the validation work .................................................................................. S-6
Table S2. Instruments used in the validation work .................................................................................. S-6

S3 - Calculation of the decay time-corrected peak areas for samples and standards and the calculation of oxidation or thermal reduction efficiency ................................................. S-7

Equations (1) to (3) .................................................................................................................................. S-7

S4 - Electrolytic production of reaction gases Cl₂ and Br₂ ................................................................... S-8

Figure 1. Experimental setup for electrolytic production of reaction gases Cl₂ and Br₂ ...................... S-8

S5 - All replicates for the thermal reduction efficiency and NTP oxidation efficiency calculation ................................................................................................................................. S-9

Table S3. Hg²⁺ to Hg⁰ thermal conversion, Hg²⁺ loaded by spike, all replicates ........................................ S-9
Table S4. Production of Hg²⁺ species by NTP, all replicates ................................................................. S-9

S6 - Calculation of the combined standard uncertainty for the proposed Hg²⁺ species calibration ................................................................................................................................. S-10

Equations (4) to (18) ............................................................................................................................... S-10, S-11
Table S5. Example: calculation of the combined standard uncertainty of HgCl₂ species calibration .... S-12

References ............................................................................................................................................... S-13
S1 - Standard operating procedure (SOP) for gaseous oxidized mercury species calibration by non-thermal plasma (NTP) oxidation of elemental mercury

1. Foreword and scope of the method

The calibration method is based on generation of a known amount of gaseous elemental mercury (Hg₀), its quantitative oxidation to gaseous oxidized mercury species (HgⅡ) by NTP in the presence of reaction gas, HgⅡ thermal reduction back to Hg₀, and its determination by cold vapor atomic fluorescence spectrometry (CV-AFS). The method is designed to be suitable for calibration of any commercially available atmospheric mercury speciation unit. In the presented SOP, the medium used for HgⅡ collection is a sorbent trap (in the following sections named “plasma trap”; see Figure 1 of the article’s main body for more information). Instead of a sorbent trap, commonly used atmospheric Hg speciation methods often utilize denuders or sorbent membranes. Although these HgⅡ collection methods can be used for calibration instead of sorbent traps, their compatibility with our calibration was not validated in our work. The instructions provided in this SOP are fit-for-purpose regardless of the method used for HgⅡ collection and regardless of the method used for mercury detection.

The intended amounts of HgⅡ species produced using this method for calibration of ambient concentration levels of HgⅡ are in the order of 50-100 pg. Therefore, ultra-trace analysis protocols have to be applied to prevent contaminations: keeping the laboratory clean, providing appropriate ventilation, and adequately washing glassware, tools, and containers.

2. Safety precautions

Follow universal precautions. Wear gloves, a lab coat, and safety glasses whilst handling chemicals. For handling the non-thermal plasma and its power supply unit, the safety rules for working with electrical equipment should be followed: turn off the power supply of the equipment before inspecting it; use only tools/equipment with non-conducting handles; avoid contacting the setup with wet hands and wet materials; do not store highly flammable chemicals near the electrical equipment; call expert electrician if the power supply or instrument keeps causing burn-out of fuses.

3. Chemicals, materials, and equipment

3.1 Chemicals and materials

- 65% nitric acid (HNO₃, Suprapur, Merck, Germany)
- 30% hydrochloric acid (HCl, Suprapur, Merck, Germany)
- Potassium permanganate (KMnO₄, analytical grade, Merck, Germany)
- Potassium chloride (KCl, Suprapur, Merck, Germany)
- Potassium hydroxide (KOH, analytical grade, Merck, Germany)
- Sodium thiosulfate (Na₂S₂O₃, analytical grade, Merck, Germany)
- Potassium bromate (KBrO₃, Suprapur, Merck)
- Potassium bromide (KBr, Suprapur, Merck)
- Tin(II) chloride dihydrate (SnCl₂ · 2H₂O, analytical grade, Merck, Germany)
- Hydroxylammonium chloride (NH₂OH · HCl, analytical grade, Merck, Germany)
- Gold(III) chloride hydrate (HAuCl₄·xH₂O, 99.995% trace metal basis, Merck, Germany)
- NIST SRM 3133: Mercury (Hg) Standard Solution (NIST, USA)
- Aluminum oxide, corundum (Al₂O₃, 0.60–0.85 mm grain size)
- Type I purified water (resistivity 18.2 MΩ cm)
- Quartz wool (Supelco, USA)

3.2 Equipment

- High-voltage high-frequency power generator (Information Unlimited, model Amazing PMV500, or similar)
- Cold vapor atomic fluorescence spectrometer (CV-AFS)

3.3 Preparation of reagents and materials

10% w/v SnCl₂ in 10% v/v HCl:

- Weigh accurately 10 g of SnCl₂ into a clean glass beaker using a plastic spatula (beaker and spatula are used only for SnCl₂).
- Add 10 mL of concentrated HCl directly to the SnCl₂ and transfer to a 100-mL volumetric flask. Mix and wait for complete dissolution of SnCl₂.
- Add Milli-Q water to the mark (100 mL).
- Purge the SnCl₂ solution with Hg-free nitrogen gas for two hours in order to obtain a mercury-free solution.

16% w/v NH₂OH · HCl solution:

- Weight 16 g of NH₂OH · HCl in a suitable glass bottle, add Milli-Q water to a 100-mL mark, and mix well.
- Add 20 μL of SnCl₂ solution and purge for 2 hours with Hg-free nitrogen gas.

10% w/v KOH:

- Dissolve 10 g of KOH in Milli-Q water to the final volume of 100 mL.
- Purge the KOH solution with nitrogen for two hours in order to obtain a mercury-free solution.

10% w/v Na₂S₂O₃:

- Dissolve 10 g of Na₂S₂O₃ in Milli-Q water to the final volume of 100 mL.
- Purge the Na₂S₂O₃ solution with nitrogen for two hours in order to obtain a mercury-free solution.
0.5% w/v KMnO₄ solution:
- Dissolve 0.5 g of KMnO₄ in Milli-Q water to the final volume of 100 mL.

Bromine monochloride (BrCl) oxidizing solution:
- Weigh 15 g of KBrO₃ and 11 g of KBr into a clean 1-liter glass bottle.
- Add 200 mL of Milli-Q water.
- Add 800 mL of concentrated HCl. The dilution has to be carried out in a well-ventilated fume hood to prevent exposure to toxic fumes released during dissolution of KBrO₃.
- Keep the bottle wrapped with aluminum foil.
- The prepared solution can be kept for an unlimited time if stored in darkness at 5 °C in a tightly closed Teflon or glass bottle.

Gold-coated corundum and gold trap preparation:
- Gold-coated corundum: Dissolve 1 g of HAuCl₄·xH₂O in 10 mL of Milli-Q water and add 10 g of Al₂O₃. Evaporate the solution in an automatic rotary evaporator under reduced atmospheric pressure and then heat the remaining material at 500 °C for 4 h in an argon atmosphere.
- Gold trap preparation: Insert a small piece of quartz wool at the end of the longer part of the column. Then insert about 2 cm of gold-coated corundum. It is recommended to weigh the gold-coated corundum in order to obtain a better reproducibility between the traps. Insert a larger piece of quartz wool. Precondition the new trap by heating it at least 4 times before use.

Plasma trap preparation: shown in the main body of the article, in Figure 1.

Drying columns preparation: similar as for gold trap preparation, except that the gold-coated corundum is replaced with soda lime.

3.4 Mercury standard solutions (SRM NIST 3133)

Standard stock solution, 99.54 µg g⁻¹ of Hg in 5% HNO₃: Important note: record the mass after each volume addition or subtraction step, otherwise the Hg mass concentration cannot be evaluated correctly. Fill a weighed 100-mL glass flask with 5% HNO₃ solution exactly to mark of 100 mL and remove 1 mL of the solution. Gently shake an ampoule of Standard Reference Material 3133, Mercury (Hg) Standard Solution for 2 minutes and open it according to the certificate. Take 1 mL of SRM solution with a pipette directly from the ampoule to the prepared glass flask containing acid solution. By doing so, a solution with an approximate Hg concentration of 99.54 µg g⁻¹ is obtained (the exact value depends on the mass weighing). Cap the flask, shake it well and leave it on room temperature for 1 hour before further dilutions.

Intermediate and working standard solutions, 0.9954 µg g⁻¹ of Hg in 5% HNO₃ and 0.9954 ng g⁻¹ of Hg in 5% HCl: Prepare an intermediate Hg standard solution with the concentration of 0.9954 µg g⁻¹ by 100-fold dilution of standard stock solution in the same manner as for standard stock solution. At the end, prepare a working Hg standard solution with the concentration of 0.9954 ng g⁻¹ by 1000-fold dilution of the intermediate standard. The last dilution is made with 5% HCl solution instead of a 5% HNO₃ solution. Calculate the exact concentrations of the Hg standard solutions by taking into account the exact mass of pipetted aliquots.

3.5 Cleaning glassware
Prior to use, thoroughly wash all laboratory glassware following the procedure:

- Allow the glass vessels to soak overnight in 2% Micro-90 detergent solution.
- Rinse the vessels thoroughly, first with tap water, and then with Milli-Q water.
- Rinse with 0.5% KMnO$_4$ solution.
- Rinse with water until the color of the KMnO$_4$ solution is no longer visible.
- Rinse with 2 mL of 16% NH$_2$OH · HCl solution.
- Rinse three times with Milli-Q water.
- Fill the vessels with 1% HCl solution and store in mercury-free storage facilities.
- Vessels should be emptied just before use for sample processing and allowed to dry at 60 °C.

4. **NTP calibration protocol**

As previously stated, the calibration method is comprised of three main steps: i) Hg$^0$ generation, ii) NTP oxidation of Hg$^0$ to Hg$^{II}$ species in the presence of a reaction gas, and iii) thermal reduction of Hg$^{II}$ species to Hg$^0$ with subsequent CV-AFS analysis. The second step has three different setup variations depending on the used reaction gas (O$_2$, Cl$_2$, or Br$_2$).

4.1 **Hg$^0$ generation**

Similar setup is used as in Figure 2a of the manuscript’s main body.

- Provide a clean 250-mL glass impinger (“bubbler”) and add 100 mL of Milli-Q water and 3 mL of 10% w/v SnCl$_2$ in 10% v/v HCl.
- Connect a drying column (soda lime trap) to the impinger gas exit and a gold trap downstream of the drying column.
- Add 100 pg of Hg from the working Hg standard solution. In the case of concentrations listed in the section 3.4, this means that 100.5 µL of working standard solution (Hg concentration of 0.9954 ng g$^{-1}$) needs to be pipetted directly to the impinger.
- As soon as the Hg standard is added, quickly close the impinger and connect it to a N$_2$ flow of 1 L min$^{-1}$ for 10 minutes to purge the Hg$^0$ to the gold trap. Note: lower total volume of the solution in the impinger can be used together with a lower N$_2$ flow and shorter purging time since these parameters mostly depend on the shape, size, and design of the impinger.
- After 10 minutes, remove the Hg-loaded gold trap from the impinger and use it for the second step.

4.2 **NTP oxidation of Hg$^0$ to Hg$^{II}$ species**

Similar setup is used as in Figure 2a of the manuscript’s main body. Three different Hg$^{II}$ species can be produced via NTP oxidation: HgO with O$_2$ reaction gas, HgCl$_2$ with Cl$_2$ reaction gas, and HgBr$_2$ with Br$_2$ reaction gas. Therefore, we can have three setups that marginally differ from each other.
- Assemble the following parts of the setup (similar as in Figure 2a in the manuscript’s main body, going downstream in consecutive order): Hg-loaded gold trap, T-split for the introduction of reaction gas, plasma trap, and impinger with solution for reaction gas reduction. The reaction gas is obtained from i) O₂ gas cylinder for O₂ reaction gas and ii) electrolytic reaction for Cl₂ and Br₂ reaction gases (electrolysis described in section S4 of the Supplementary Information). The solution for reaction gas reduction is 50 mL of 10% w/v KOH for Cl₂ reaction gas and 50 mL of 10% w/v Na₂S₂O₃ for Br₂ reaction gas. In the case of O₂ reaction gas, the reduction of the reaction gas is not needed. The final flow of the gas mixture (He + reaction gas) should be 370 mL min⁻¹, where He represents >99% of the gas mixture and reaction gas represents <1% of the gas mixture.

- IMPORTANT NOTE: Cl₂ and Br₂ reaction gases are strong oxidants on their own (even without NTP). Therefore, it is important to release them into the system only when every part of the setup is gas-tight. Always connect the reaction gas the last (to avoid unnecessary reactions), after the whole setup is already on the flow of He gas.

- When the setup is assembled and under gas-tight He flow, connect the copper electrodes as shown on Figure 2a in the main text of the article, turn on the plasma driver and set it to these parameters: power applied to the electrodes of 180 µW, radiofrequency of 20 kHz, effective voltage of 345 V.

- After plasma is homogeneous, release the reaction gas flow and after approximately 10 seconds start heating the gold trap (e.g., using a heating coil) to 400 °C to release the Hg⁰ from the trap.

- After heating is finished, wait for 60 s to ensure complete release of Hg⁰ and then close the reaction gas flow and turn off plasma by turning off the plasma driver.

- After the reaction gas flow is closed and plasma driver is turned off, the setup can be safely disassembled. The produced Hg²⁺ that is needed for further calibration is trapped on the plasma trap.

4.3 Thermal reduction of Hg²⁺ species to Hg⁰ and subsequent CV-AFS analysis

Similar setup is used as in Figure 2b of the manuscript’s main body.

- Connect the plasma trap that is loaded with Hg²⁺ species to a gold trap downstream.

- Connect both traps to the He flow of 370 mL min⁻¹.

- Heat the whole plasma trap (both KCl crystal part and Al₂O₃ catalyst) to >600 °C. The temperature should be achieved as fast as possible to avoid desorption of Hg²⁺ and its re-deposition on cold spots of the system. For complete thermal reduction of Hg²⁺ to Hg⁰ (without Hg²⁺ desorption), the plasma trap should be heated to >600 °C in under 20 s.

- After the heating is completed, wait for 60 seconds to ensure complete downstream transport of Hg⁰ to the gold trap.

- The gold trap is now ready for the determination of mercury by double amalgamation CV-AFS measurement."
### S2 - Chemicals and instruments used in the validation work

#### Table S1. Chemicals used in the validation work.

| Description of chemicals | Purity / type                              | Producer                                              |
|--------------------------|--------------------------------------------|-------------------------------------------------------|
| 65% nitric acid (HNO₃)   | For analysis                               | Supelco, Darmstadt, Germany                           |
| 30% hydrochloric acid (HCl) | Suprapur                                | Merck, Darmstadt, Germany                             |
| Tin(II) chloride dihydrate (SnCl₂·2H₂O) | For analysis, max. 0.000001% Hg | Merck, Darmstadt, Germany                             |
| Gold(III) chloride hydrate (HAuCl₄·xH₂O) | 99.995% trace metal basis | Merck, Darmstadt, Germany                             |
| Potassium chloride (KCl) salt | Suprapur                                | Merck, Darmstadt, Germany                             |
| Mercury(II) oxide-yellow (HgO)   | 99.5%                                     | May & Baker, Essex, United Kingdom                    |
| Mercury(II) chloride (HgCl₂)      | 99.998%                                   | Merck, Darmstadt, Germany                             |
| Mercury(II) bromide (HgBr₂)      | 99.0%                                     | Merck, Darmstadt, Germany                             |
| NIST SRM 3133: Mercury (Hg) Standard Solution | 9.954 mg g⁻¹ ± 0.053 mg g⁻¹ | NIST, Gaithersburg, MD, USA                          |
| ¹⁹⁶Hg enriched elemental Hg | 51.58% ¹⁹⁶Hg                              | Isoflex, San Francisco, CA, USA                       |
| Type I purified water | Electrical resistivity 18.2 MΩ cm | Merck, Darmstadt, Germany                             |

#### Table S2. Instruments used in the validation work.

| Description of instruments | Model                  | Producer                                           |
|----------------------------|------------------------|----------------------------------------------------|
| High-voltage high-frequency power generator | Amazing PMV500 | Information Unlimited, Amherst, NH, USA            |
| High-voltage probe        | Tektronix P6105A       | Tektronix Inc., Beaverton, OR, USA                 |
| Electrical current monitor | Pearson 2877           | Pearson Electronics Inc., Palo Alto, CA, USA       |
| Oscilloscope              | Picoscope 3204d        | Pico Technology Ltd., Cambridgeshire, UK           |
| High-purity germanium (HPGe) coaxial-type detector | Model 7229P        | Canberra Industries Inc., Meriden, CT, USA         |
| High-purity germanium (HPGe) well-type detector | Model GCW6023/S     | Canberra Industries Inc., Meriden, CT, USA         |
| Cold vapor atomic absorption spectrometer | Model Hg-20 Semi-Automated Mercury Analyzer | Sanso Seisakusho Co., Ltd., Tokyo, Japan           |
| Quadrupole mass spectrometer (QMS) | Model QMS 700 | Pfeiffer Vacuum Ltd., Asslar, Germany              |
Calculation of the decay time-corrected peak areas for samples and standards and the calculation of oxidation or thermal reduction efficiency

The peak area of the sample and standard activity had to be corrected for the decay since the start of irradiation. From the corrected peak areas for samples and standards, the oxidation or thermal reduction efficiencies were calculated as shown in the following paragraphs.

Eq. (1) was applied for calculation of both $A_{0,i}$ (sample peak area at reference time) and $A_{0,\text{std}}$ (standard peak area at reference time). If we insert the $A_{0,i}$ and $A_{0,\text{std}}$ values from Eq. (1) into the Eq. (2) (used for oxidation or thermal reduction efficiency calculation), we obtain Eq. (3).

\[
A_{0,i} = \frac{A_i \cdot \ln 2}{e^{\frac{t_{\text{passed},i} \ln 2}{t_{1/2}}}} \left[ 1 - e^{\frac{t_{\text{measurement},i} \ln 2}{t_{1/2}}} \right]
\]  

where $i$ is either sample (s) or standard (std).

\[
\eta = \frac{A_{0,s}}{A_{0,\text{std}}} \cdot 100 \cdot F_d \cdot F_r
\]

\[
\eta = \frac{A_s \cdot e^{\frac{t_{\text{passed},s} \ln 2}{t_{1/2}}} \left[ 1 - e^{\frac{t_{\text{measurement},s} \ln 2}{t_{1/2}}} \right]}{A_{\text{std}} \cdot e^{\frac{t_{\text{passed},s} \ln 2}{t_{1/2}}} \left[ 1 - e^{\frac{t_{\text{measurement},s} \ln 2}{t_{1/2}}} \right]} \cdot 100 \cdot F_d \cdot F_r
\]

Where:

- $A_{0,s}$ is the sample peak area at reference time $t=0$,
- $A_{0,\text{std}}$ is the standard peak area at reference time $t=0$,
- $A_i$ is the sample peak area at the time of measurement,
- $A_{\text{std}}$ is the standard peak area at the time of measurement,
- $t_{1/2}$ is the half-life of $^{197}\text{Hg}$ [s],
- $t_{\text{passed},s}$ is the time passed since reference time $t=0$ till the start of the sample measurement [s],
- $t_{\text{measurement},s}$ is the time passed during the sample measurement [s],
- $\eta$ is the oxidation or thermal reduction efficiency [%],
- $F_d$ is the dilution factor,
- $F_r$ is the repeatability factor (value of i).
S₄ - Electrolytic production of reaction gases Cl₂ and Br₂

Since Cl₂ and Br₂ are notoriously difficult to handle, they were produced in the laboratory just for the needs of our experiments. We used electrolysis of 1 M NaCl solution to produce Cl₂ and electrolysis of 1 M KBr solution to produce Br₂. 4.5 V battery was used as a power source for electrolysis. NaCl infused agar gel was used as a salt bridge to provide a closed electric circuit. The experimental setup for electrolytic production of Cl₂ and Br₂ is shown in Figure S1.

Figure S1. Experimental setup for electrolytic production of reaction gases Cl₂ and Br₂.

As Cl₂ and Br₂ are both water-soluble, the impinger solution containing the anode was always purged with He. This increased the amount of Cl₂ and Br₂ in the gas stream. As Br₂ immediately dissolves in the solution, it is not released into the gas stream until enough Br₂ is produced and its vapor pressure is sufficiently high.
**S5 - All replicates for the Hg$^{II}$ thermal reduction and production of Hg$^{II}$ species by NTP.**

Table S3. Hg$^{II}$ to Hg$^{0}$ thermal conversion, Hg$^{II}$ loaded by spike, all replicates.

| Catalyst used        | Hg$^{0}$, thermal reduction efficiency [%] | Unconverted Hg$^{II}$ [%] | Mass balance [%] |
|----------------------|------------------------------------------|---------------------------|------------------|
| No catalyst          | 106                                      | 22.5                      | 129              |
|                      | 69.1                                     | 28.6                      | 97.7             |
| Au-coated silica     | 34.5                                     | 65.5                      | 100              |
|                      | 40.2                                     | 56.5                      | 96.7             |
|                      | 39.0                                     | 61.0                      | 100              |
| Pt wire              | 80.2                                     | 1.92                      | 82.1             |
|                      | 28.9                                     | 59.4                      | 88.3             |
|                      | 26.5                                     | 64.8                      | 91.3             |
|                      | 20.6                                     | 71.5                      | 92.1             |
| Quartz wool          | 98.0                                     | 5.33                      | 103              |
|                      | 96.2                                     | 11.6                      | 108              |
|                      | 64.7                                     | 27.8                      | 92.5             |
|                      | 106                                      | <0.1                      | 106              |
|                      | 102                                      | <0.1                      | 102              |
|                      | 97.4                                     | <0.1                      | 97.4             |
|                      | 98.6                                     | <0.1                      | 98.6             |
|                      | 99.1                                     | <0.1                      | 99.1             |

Table S4. Production of Hg$^{II}$ species by NTP, all replicates.

| Species used | Mass used [pg] | Unconverted Hg$^{0}$ [%] | Hg$^{II}$ on plasma trap, oxidation efficiency [%] |
|--------------|----------------|--------------------------|-------------------------------------------------|
| HgO          | 100            | 1.19                     | 97.6                                            |
|              |                | 2.22                     | 101                                             |
|              |                | 0.47                     | 100                                             |
|              |                | 2.26                     | 102                                             |
|              |                | 2.17                     | 102                                             |
| HgCl$_2$     | 250            | 2.30                     | 93.2                                            |
|              |                | 1.57                     | 93.2                                            |
|              |                | 1.60                     | 99.7                                            |
|              |                | 1.87                     | 98.4                                            |
|              |                | 3.71                     | 99.3                                            |
| HgBr$_3$     | 250            | <0.1                     | 79.3                                            |
|              |                | 3.03                     | 79.0                                            |
|              |                | 1.91                     | 68.8                                            |
|              |                | 2.96                     | 82.2                                            |
S6 - Calculation of the combined standard uncertainty for the proposed Hg^{II} species calibration

The uncertainty of the developed calibration was estimated according to the GUM and Eurachem guidelines.\textsuperscript{3,4} The model used for uncertainty evaluation was shown in Eq. (3). To make the model clearer, we substituted the exponential terms:

\[
\begin{align*}
EF_{p,\text{std}} &= e^{\left(\frac{t_{\text{passed, std}} \ln 2}{t_{1/2}}\right)} \quad (4) \\
EF_{p,s} &= e^{\left(\frac{t_{\text{passed, s}} \ln 2}{t_{1/2}}\right)} \quad (5) \\
EF_{m,\text{std}} &= e^{\left(\frac{t_{\text{measurement, std}} \ln 2}{t_{1/2}}\right)} \quad (6) \\
EF_{m,s} &= e^{\left(\frac{t_{\text{measurement, s}} \ln 2}{t_{1/2}}\right)} \quad (7)
\end{align*}
\]

This way, the model can be re-written as:

\[
\eta = \frac{A_s \cdot EF_{p,\text{std}} \cdot \left[1 - EF_{m,\text{std}}\right]}{A_{\text{std}} \cdot EF_{p,s} \cdot \left[1 - EF_{m,s}\right]} \cdot 100 \cdot F_{\text{dil}} \cdot F_{\text{rep}} \quad (8)
\]

The equations for the standard uncertainty of the exponential terms (e.g. $EF_{p,\text{std}}$) are as follows:

\[
\begin{align*}
u(EF_{p,\text{std}}) &= \frac{\partial EF_{p,\text{std}}}{\partial t_{1/2}} \cdot u(t_{1/2}) = EF_{p,\text{std}} \cdot \frac{\ln 2 \cdot t_{\text{passed, std}}}{t_{1/2}^2} \cdot u(t_{1/2}) \quad (9) \\
u(EF_{p,s}) &= EF_{p,s} \cdot \frac{\ln 2 \cdot t_{\text{passed, s}}}{t_{1/2}^2} \cdot u(t_{1/2}) \quad (10) \\
u(EF_{m,\text{std}}) &= EF_{m,\text{std}} \cdot \frac{\ln 2}{t_{1/2}} \cdot u(t_{\text{measurement, std}}) \quad (11) \\
u(EF_{m,s}) &= EF_{m,s} \cdot \frac{\ln 2}{t_{1/2}} \cdot u(t_{\text{measurement, s}}) \quad (12)
\end{align*}
\]

Note that we assumed constant $t_{\text{passed, std}}$ and $t_{\text{passed, s}}$ to obtain Eq. (9) and Eq. (10) and constant $t_{1/2}$ to obtain Eq. (11) and Eq. (12). This assumption was made because in Eq. (9) and Eq. (10), the relative standard uncertainties of $t_{\text{passed, std}}$ and $t_{\text{passed, s}}$ were negligible in comparison to the relative standard uncertainty of $t_{1/2}$ (three orders of magnitude smaller relative standard uncertainties for $t_{\text{passed, std}}$ and $t_{\text{passed, s}}$ than for $t_{1/2}$). Similar assumption was made for Eq. (11) and Eq. (12); in this case, the relative standard uncertainty of $t_{1/2}$ was negligible in comparison to the relative standard uncertainty of $t_{\text{measurement, std}}$ and $t_{\text{measurement, s}}$.

The equation for obtaining standard uncertainties for $A_s$ and $A_{\text{std}}$ is calculated according to Poisson distribution with some adjustments due to background correction for the peak areas. The exact equation used for calculation is provided by the Genie 2000 gamma analysis software tool and is calculated automatically by the software, using Eq. (13).\textsuperscript{5} Since $^{201}\text{Hg}$ has two doublet peaks in the activity measurement spectrum, the equation can be applied for both peaks, giving us two uncertainties $u(A_s)$ and $u(A_{\text{std}})$. The standard uncertainty of the combined peaks (no overlapping of the peaks for our case) is calculated using Eq. (14).
\[ u(A_i) = \sqrt{A_i + B_i \left( \frac{W_{p,i}}{W_{b,i}} \right)^2} \quad ; i = 1, 2 \] (13)

\[ u(A) = \frac{1}{\sqrt{u(A_1)^2 + u(A_2)^2}} \quad ; A = A_s \text{ or } A_{std} \] (14)

Where:
- \( A_i \) is the sample peak area for the observed peak,
- \( B_i \) is the background peak area for the observed peak,
- \( W_{p,i} \) is the spectral width of the sample peak region for the observed peak,
- \( W_{b,i} \) is the spectral width of the background peak region for the observed peak.

The last uncertainty components are present in \( F_{diil} \) and \( F_{rep} \). \( u(F_{diil}) \) originates from two pipetting steps, one for the standard (5 mL pipette, \( u(V_{std}) \)) and one for the sample (1 mL pipette, \( u(V_i) \)). Both \( u(V_{std}) \) and \( u(V_s) \) are calculated from uncertainty due to temperature influences \( (V_T) \) and uncertainty due to repeatability \( (V_{rep}) \); 10 replicate measurements) with Eq. (15). By combining both pipetting uncertainties, \( u(F_{diil}) \) is calculated with Eq. (16). \( F_{rep} \) value equals 1, but has to be included due to the components of the measurement procedure that influence the repeatability.

\[ \frac{u(V_i)}{V_i} = \sqrt{\left( \frac{u(V_T)}{V_T} \right)^2 + \left( \frac{u(V_{i,rep})}{V_{i,rep}} \right)^2} \] (15)

\[ \frac{u(F_{diil})}{F_{diil}} = \sqrt{\sum_i \left( \frac{u(V_i)}{V_i} \right)^2} \] (16)

where \( i \) is either sample (s) or standard (std).

\( u(F_{rep}) \) is the repeatability standard uncertainty and is calculated from the standard deviation of replicate oxidation efficiency measurements.

All listed uncertainty components are then used in calculation of combined standard measurement uncertainty by the law of uncertainty propagation. Combined standard measurement uncertainty is calculated as follows:

\[ u_c(\eta) = \eta \cdot \sqrt{\left( \frac{u(A_s)}{A_s} \right)^2 + \left( \frac{u(A_{std})}{A_{std}} \right)^2 + \left( \frac{u(EF_{p,s})}{EF_{p,s}} \right)^2 + \left( \frac{u(EF_{p,std})}{EF_{p, std}} \right)^2 + \left( \frac{u(EF_{m,s})}{EF_{m,s}} \right)^2 + \left( \frac{u(EF_{m, std})}{EF_{m, std}} \right)^2 + \left( \frac{u(F_{diil})}{F_{diil}} \right)^2 + \left( \frac{u(F_{rep})}{F_{rep}} \right)^2} \] (17)

The expanded standard uncertainty is obtained by multiplication of the combined standard measurement uncertainty with a coverage factor, \( k \) (\( k=2 \)) with Eq. (18).

\[ U = u_c(\eta) \cdot k \] (18)
Table S5. Example: calculation of the combined standard measurement uncertainty for HgCl₂ species calibration

| Parameter, c, c | Value       | Assumed distribution | Standard uncertainty, \(u(c)\) | Comment                                      |
|----------------|-------------|----------------------|---------------------------------|-----------------------------------------------|
| \(t_{\text{passed, s}}\) | 741 s       | rectangular          | /                               | Assumed negligible                           |
| \(t_{\text{passed, std}}\) | 700 s       | rectangular          | /                               |                                               |
| \(t_{\text{measurement, s}}\) | 150 s       | rectangular          | 0.029 s                         | Standard uncertainty value used only for the calculation of \(u(\text{EF})\) |
| \(t_{\text{measurement, std}}\) | 150 s       | rectangular          | 0.029 s                         |                                               |
| \(t_{\text{c/2}}\) | 230904 s    | rectangular          | 404 s                           |                                               |
| \(A_s\)     | 2020        | Poisson              | 23.8                            | Parameters and their standard uncertainties that were used in calculation of combined standard uncertainty using the simplified model in Eq. (8) |
| \(\Delta_{\text{std}}\) | 2144        | Poisson              | 20.1                            |                                               |
| \(\text{EF}_{\text{p, std}}\) | 0.122       | rectangular          | 4.49E-04                        |                                               |
| \(\text{EF}_{\text{p, s}}\) | 0.117       | rectangular          | 4.40E-04                        |                                               |
| \(\text{EF}_{\text{m, std}}\) | 0.9995      | rectangular          | 6.04E-06                        |                                               |
| \(\text{EF}_{\text{m, s}}\) | 0.9995      | rectangular          | 4.95E-05                        |                                               |
| \(F_{\text{dil}}\) | 1           | Gaussian             | 0.004                           |                                               |
| \(F_{\text{rep}}\) | 1           | Gaussian             | 0.034                           |                                               |

| Parameter, c | Value       | Assumed distribution | Relative standard uncertainty \(u(c, r)\) | Relative contribution | Combined standard uncertainty | Expanded standard uncertainty, \(k=2\) |
|--------------|-------------|----------------------|---------------------------------------------|-----------------------|-------------------------------|------------------------------------------|
| \(A_s\)     | 1.18E-02    | 1.39E-04             | 9.78%                                       |                       |                               |                                         |
| \(\Delta_{\text{std}}\) | 9.36E-03    | 8.76E-05             | 6.18%                                       |                       |                               |                                         |
| \(\text{EF}_{\text{p, std}}\) | 3.68E-03    | 1.36E-05             | 0.96%                                       |                       |                               |                                         |
| \(\text{EF}_{\text{p, s}}\) | 3.75E-03    | 1.41E-05             | 0.99%                                       |                       |                               |                                         |
| \(\text{EF}_{\text{m, std}}\) | 6.04E-06    | 3.65E-11             | 0.00%                                       |                       |                               |                                         |
| \(\text{EF}_{\text{m, s}}\) | 4.95E-05    | 2.45E-09             | 0.00%                                       |                       |                               |                                         |
| \(F_{\text{dil}}\) | 4.48E-03    | 2.01E-05             | 1.42%                                       |                       |                               |                                         |
| \(F_{\text{rep}}\) | 3.38E-02    | 1.14E-03             | 80.68%                                      |                       |                               |                                         |

\(\eta = 0.97 \pm 0.07 \text{ (k=2)}\)

Expanded standard uncertainty for the calibration of gaseous HgCl₂ by NTP oxidation is therefore 0.07 (k=2). Similar as for gaseous HgCl₂, we applied the above calculation for the uncertainty evaluation for gaseous HgO and gaseous HgBr₂. The expanded standard uncertainties amounted to 0.05 (k=2) for HgO and 0.09 (k=2) for HgBr₂.
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