

Good practice guide for Hg sample preparation and interspecies conversion correction

MercOx Deliverable D5

Igor Živković¹, Panayot Petrov², Jože Kotnik¹, Jan Gačnik¹, David Amouroux³, Maria del Rocio Arvizu⁴, Francisco Javier Martínez Ríos⁴, Edith Valle Moya⁴, Timo Rajamäki⁵, Jarkko Makkonen⁶, Reinhold Moeseler⁷, Sergey Sholupov⁷, Suleyman Can⁸, Warren Corns⁹, Milena Horvat¹

¹ *Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia*

² *LGC Limited, Teddington, Middlesex, TW11 0LY, UK*

³ *UPPA, Avenue de l'Université, 64000 Pau, France*

⁴ *CENAM, Carretera a Los Cués, Municipio El Marqués, Qro. C.P. 76246 México*

⁵ *National Metrology Institute VTT MIKES, Tekniikantie 1, 02150 Espoo, Finland*

⁶ *Optoseven Oy, Tekniikantie 2, 02150 Espoo, Finland*

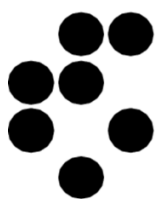
⁷ *LUMEX Analytics GmbH, Naher Str. 8, 24558, Wakendorf II, Germany*

⁸ *TUBITAK, Gebze Yerleşkesi P.K. 54, 41470 Gebze/Kocaeli, Turkey*

⁹ *P S Analytical, Arthur House, Orpington, Kent, BR5 3HP, UK*

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Hg-ox



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Executive summary

This deliverable was initially designed to present a good practice guide only for Hg sample preparation and interspecies conversion corrections within two specific tasks. The first task was to develop and compare methods for determining selectively trapped gaseous Hg(II) at environmentally relevant concentrations, i.e., in the atmosphere and in the stack emissions. The second task was to develop methods for measuring Hg(II) on particulate matter via the determination of total Hg and by species-specific analysis. Initially, it was planned that the good practice guide would have referred only to these two tasks performed within the activities A2.1. and A2.2. However, due to the overall complexity and size of the MercOx project and the closely related interconnections between its' all components, it was realized that it would be more appropriate to present a good practice guide for the overall project. It was difficult to prepare a good practice guide to only specific tasks and activities without necessarily referring to other important findings that were previously reported. Therefore, we have reviewed our Deliverables to identify the most important findings and summarized them in here, as good practice guide. These important findings were collected into guidelines how to perform a specific task/measurement/operation and the appropriate application of instrumentation/analysis to specific measurand. In addition, these guidelines include important negative findings that recommend how certain procedures should not be performed. Furthermore, the detailed results relevant for tasks initially planned for this deliverable are extensively described in Appendix A1.

From the Deliverable 1, we have summarized the most important recommendations about traceable calibration methods for elemental and oxidized Hg in the atmosphere and stack emissions. We assessed the benefits and shortcomings of investigated instrumentations (VSL primary Hg⁰ generator, Lumex two-channel analytical system, liquid evaporative HgCl₂ generators, Hg⁰ and HgCl₂ generators from PSA, and non-thermal plasma system from JSI). Recommendations from Deliverable 2 included the proper development of a certification protocol for the traceable generation of HgCl₂ at $\mu\text{g m}^{-3}$ levels for stack gas emission measurements. We discussed steps (traceability, analyser, baseline, calibration...) required for the development of such a protocol according to the ISO standard 6143. Guidelines for measurements of selectively trapped gaseous Hg(II) at environmental concentrations are obtained from Deliverable 3. These guidelines refer to strategies for measurement of Hg⁰ and Hg(II) in reference gasses and carbon materials, species conversion during trapping on activated carbon, effectiveness of Hg(II) to Hg⁰ conversion, and solubility studies of Hg⁰ in Hg(II) impinger trapping solutions. Biomonitoring guidelines for using in situ and transplanted lichens, determination of Hg isotopic composition in lichens and mosses, long-term biomonitoring of Hg isotopic composition in the atmosphere, and the determination of Hg content and isotopic composition in particulate atmospheric and industrial emission materials are also given (Deliverable 4). Feasibility of novel pre-concentration and digestion methods used for the determination of Hg isotopic ratios in different matrices, and laser ablation coupled with ICP-MS and temperature desorption for the characterization of Hg species in solid samples are also discussed. Appendix A1 of this Deliverable 5 provides detailed recommendations for strategies for total Hg and Hg species determination in activated carbon/carbon rich materials, and corresponding species conversion during Hg trapping and thermal desorption. We also address the stability and conversion of Hg(II) on various KCl sorbent traps during exposure in ambient airflow, stability of Hg(II) loaded using non-thermal plasma, and stability of Hg(II) solution used for evaporative calibrator. Guidelines for application of gas evaporative generator for low atmospheric concentrations are based on work described in Deliverable 6 (time response tests of gas evaporative calibrator, comparison of behavior of HgCl₂ and HgBr₂ reference gasses, use of quartz wool impregnated with KCl as a trap for capturing HgCl₂, estimation of the HgCl₂ and HgBr₂ adsorption inside a gas evaporative calibrator, and the use of Hg speciation traps for capturing low levels of HgCl₂

reference gas). Suggestions are also provided for stack gas emission measurements based on work performed at the Marl coal-fired power plant and Salanit cement production plant (Deliverable 7). Suggestions are based on method validation for sorbent traps (CEN TS 17286 guidance and examples), calibration studies, optimization of method for the determination of total mercury in cement samples, mercury speciation using sorbent traps, and the comparison between continuous emission monitoring systems and sorbent traps. Finally, based on Deliverable 8, we have created a good practice guide for Hg speciation in atmospheric samples. The guide is based on active and sorbent-based Hg measurements (including lichens), the comparison of active measurements, active – passive measurements, and the comparison of active air measurements with biomonitoring approach. Listed together, these good practice guides provide a detailed overview of the tremendous and valuable work that has been performed within the MercOx project.

1. Introduction

1.1. Task 2.1: Measurement of selectively trapped gaseous Hg(II) at environmental concentrations

The aim of this task is to develop and compare methods for determining selectively trapped gaseous Hg(II) at environmentally relevant concentrations i.e. in the atmosphere ($\mu\text{g}/\text{m}^3$ levels) and in stack gas emissions ($\mu\text{g}/\text{m}^3$). This will be undertaken by determining Hg^{tot} with bulk (i.e. elution, digestion, or LA) and species-specific analysis (i.e. GC) using conventional element specific detection techniques such as CV AAS, CV AFS, and ICP-MS; and novel techniques such as APCI-MS. The calibration methods and the reference gas standards from Tasks 1.1 – 1.3 will be used to evaluate the performance and to compare the methods developed in this task.

1.2. Task 2.2: Measurement of Hg(II) on particulate matter (PM)

The aim of this task is to develop methods for measuring Hg(II) on PM via the determination of the Hg^{tot} and by species-specific analysis. PM is an integral part of an air sample from the atmosphere or from stack gas emissions and is usually removed prior to the separation of Hg(0) and Hg(II) in the gaseous phase. However, due to the reactivity of Hg(II) in the gaseous phase a substantial proportion of Hg(II) is absorbed/bound on PM and thus species specific measurements for evaluating origin discrimination and Hg species interconversion are needed.

Activity number	Activity description	Partners (Lead in bold)
A2.1.2	LGC, UPPA, and CENAM will investigate the mercury species interconversion that occurs during the measurement steps in the methods from A2.1.1 using Hg isotopically enriched compounds (e.g. Hg(0), Hg-halides). JSI will also do this, but using a radioactively labelled Hg tracer (i.e. ^{197}Hg prepared from enriched ^{196}Hg). Methods to minimise species interconversion will be investigated by LGC, JSI, UPPA and CENAM and where significant species conversion does occur, correction methods will be developed. The results of this activity will be used in A2.2.5 to produce D5.	LGC , UPPA, CENAM, JSI
A2.1.3	LGC, with support from JSI, VSL, VTT, PSA, UPPA and CENAM, will evaluate the performance of the methods from A2.1.1 and A2.1.2 for determining selectively trapped gaseous Hg(II) at environmentally relevant concentrations using the calibration methods and reference gas standards from A1.1.4 and A1.3.3, and the artefact free sampling methods from A3.2.3.	LGC , JSI, VSL, VTT, PSA, UPPA, CENAM
A2.2.1	LGC and TUBITAK will evaluate the suitability of the novel digestion and subsequent ICP-MS methods developed in A2.1.2 for determining the Hg^{tot} content within filter-captured particles i.e. PM. The methods will be adapted as necessary. UPPA will evaluate combustion and acid digestion followed by conventional CV AAS/AFS for determining the Hg^{tot} content within PM. The samples, to be used with the methods, will be denuders, sorbent traps and particles on filters and they will be provided by UPPA and JSI.	LGC , TUBITAK, UPPA, CENAM, JSI

	<p>CENAM will investigate the stability of Hg^{tot} and $\text{Hg}(\text{II})$ in PM using samples of PM emitted from coal-fired power plants. The subsequent validation (i.e. proficiency testing) will be undertaken only for Hg^{tot} in particle matter. CENAM will subcontract this work as it does not have the necessary skills/expertise for the validation. Furthermore, as the validation has to be undertaken in Mexico, the other partners cannot undertake the work.</p>	
A2.2.2	<p>Building on work in EMRP JRP ENV51 MeTra, LGC will further develop novel LA-ICP-MS for the direct sampling and quantification of Hg^{tot} in filter-captured particles i.e. PM in order to reduce the uncertainty of the measurement from 50 % to 15 %.</p> <p>The samples, to be used with the methods, will be denuders, sorbent traps and particles on filters and they will be provided by UPPA and JSI.</p>	LGC, UPPA, JSI
A2.2.3	<p>JSI will investigate methods for $\text{Hg}(\text{II})$ species specific determination at environmentally relevant concentrations (i.e. typically a few tens of $\text{pg}\cdot\text{m}^{-3}$) for PM bound $\text{Hg}(\text{II})$ using the novel APCI-MS methodology.</p> <p>In parallel, LGC and UPPA will evaluate methods for derivatisation, pre-concentration by cryotrapping and subsequent GC-ICP-MS or LC-ICP-MS for $\text{Hg}(\text{II})$ species specific determination at environmentally relevant concentrations for PM bound $\text{Hg}(\text{II})$.</p> <p>The samples, to be used with the methods, will be denuders, sorbent traps and particles on filters and they will be provided by UPPA and JSI.</p>	JSI, LGC, UPPA
A2.2.4	<p>JSI will investigate methods for selectively determining $\text{Hg}(0)$ and $\text{Hg}(\text{II})$ absorbed to PM using temperature desorption and subsequent MS detection.</p> <p>The samples, to be used with the methods, will be denuders, sorbent traps and particles on filters and they will be provided by UPPA and JSI.</p>	JSI, UPPA
A2.2.5	<p>LGC, TUBITAK, UPPA and CENAM will investigate species interconversion during sample preparation and extraction for GC-ICP-MS analysis of particle bound (PM) $\text{Hg}(\text{II})$ using Hg isotopically enriched compounds. Methods to minimise conversion will be investigated and where significant conversion does occur, correction methods will be developed.</p> <p>The samples, to be used with the methods, will be denuders, sorbent traps and particles on filters and they will be provided by UPPA and JSI.</p>	LGC, TUBITAK, UPPA, CENAM, JSI
A2.2.6	<p>LGC, TUBITAK, UPPA, CENAM and JSI will use the results from A2.1.3, A2.2.1-A2.2.5, and A3.2.5 to produce a good practice guide for Hg sample preparation and interspecies conversion.</p>	LGC, TUBITAK, UPPA, CENAM, JSI
A2.2.7	<p>LGC, with support from TUBITAK, UPPA, CENAM and JSI, will review the good practice guide from A2.2.6, and the coordinator will then submit it to EURAMET as D5 'Good practice guide for Hg sample preparation and interspecies conversion correction'.</p>	LGC, TUBITAK, UPPA, CENAM, JSI

2. Good practice guides

2.1. Good practice guide for Hg(II) and Hg⁰ generation, optimized and traceable calibration, and analytical determination

When studying analytical parameters of oxidized mercury (Hg(II)) the concentrations of elemental mercury (Hg⁰) and total mercury (Hg^{tot}) are typically measured since there are no sufficiently sensitive detector systems available which are selective to Hg(II). The concentration of Hg(II) is therefore calculated by difference. In the stream of an ideal Hg(II) generator, the fraction of oxidized Hg should be 100% and elemental Hg should be absent. To reliably measure the Hg(II) concentration by difference, a two channel detector is required. Sequential measurements of Hg⁰ and Hg^{tot} are not favourable since the short term variability of candidate Hg generators could be masked which could result in incorrect Hg(II) estimation. A good example of such system is the two-channel analytical system developed by Lumex (Figure 1; Deliverable 1, MercOx project).



Figure 1. The dual analytical system by Lumex Analytics GmbH in operation with gas generators.

This system consists of an input unit and two gas channels, for determination of Hg⁰ and Hg^{tot} concentration, respectively. To avoid water vapour condensation in the entrance, the input unit of the analyser should be heated (optimum 130°C for this analyser). Its Hg⁰ channel consists of a heated cell, an atomic absorption spectrometer utilizing the Zeeman effect (RA-915F) and a pump. Temperature of the cell is kept about 130°C. To avoid catalytic reduction of Hg²⁺ in the channel of Hg⁰ all wetted parts are made of quartz, PTFE or other inert plastics with no metal components. The Hg^{tot} channel consists of an atomizer, a heated cell, the same spectrometer of the same type (RA-915F) and a pump. The optimum temperature of the atomizer which provides quantitative reduction is 700°C. Two manually operated valves are used on the input unit to direct ambient air in the channel via a Hg scrubber before entering the measurement cell for zeroing the equipment or analyte gas in the measurement cells for analysis. Such a system can be operated with gas flow rate of 1 L min⁻¹. With these conditions, complete reduction of all mercury compounds to the elemental form occurs provided that the HCl content is no higher than 20 – 30 ppm (v/v). For optimal performance of the two channel analytical system presence of traces of nitric acid vapours proved beneficial to prevent reduction of Hg(II). The concentrations of HCl/HNO₃ have to be optimized, depending on the instrumental setup. For the investigated LUMEX system, the liquid standard used to quantitatively generate Hg(II) by the means of liquid evaporative generator contained approximately 40 mg L⁻¹ HCl and 80 mg L⁻¹ HNO₃. The equivalent mercury concentration if produced in dry gas by such generator is defined in the following Equation:

$$c(\text{Hg(g)}) = c(\text{Hg(aq)}) \times Q_{\text{liquid}} / Q_{\text{gas}}$$

where:

$c(\text{Hg(g)})$ - mercury concentration in the output of the generator [$\mu\text{g m}^{-3}$]

$c(\text{Hg(aq)})$ - mercury concentration in solution [$\mu\text{g L}^{-1}$]

Q_{liquid} - flow rate of the solution [ml min^{-1}]

Q_{gas} - dry gas flow, moisture equivalent volume considered [L min^{-1}].

Since the basis of the MercOx project is the development of calibration methods to establish and implement a traceable calibration methodology for the most important oxidized mercury species, particularly for mercury chloride (HgCl_2), the appropriate calibration of generators and analysers is crucial to establish metrological traceability to the international system of units (SI). This approach is also recommended to be followed where possible. A traceable Hg^0 source for the preparation of dynamic gas mixtures containing Hg^0 in air, in the range from $0.1 - 100 \mu\text{g m}^{-3}$, according to ISO 6145-8, was developed by VSL (the Dutch Metrology Institute). This primary Hg^0 generator enables traceable mercury gas phase calibrations based upon gravimetry, i.e. traceable to the kilogram. This Hg^0 source was used to calibrate both channels of the two-channel analytical system in the range $0.8 - 14 \mu\text{g m}^{-3}$ for stack gas emission measurements (see Deliverable 1, MercOx project). The conversion steps in the traceability chain from the Hg^0 sources via HgCl_2 or Hg^{tot} are described as follows:

Hg^0 (traceable source) \rightarrow Hg^0 (measurement)

Hg^0 (traceable source) $\rightarrow \text{HgCl}_2 + \text{Hg}^0 \rightarrow \text{Hg}^{\text{tot}}$ (measurement)

The next step in the traceability chain is certification of HgCl_2 generators. As part of the project various types of generators were certified, among them two liquid evaporative generators: one commercially available system, provided by The Finnish National Metrology Institute VTT MIKES, with peristaltic pumps and a newly developed system by Optoseven Oy using syringe injection. In both generators, the reference gas is generated by mixing a liquid solution with a known concentration of HgCl_2 into a carrier gas. The mixture is evaporated to yield the reference gas. The certification showed an average recovery of 92 % for both the Optoseven and the HovaCal generator. The third system, from P S Analytical, is based on the continuous generation and dilution of saturated HgCl_2 vapour (dry-salt generator) for the automated calibration of online mercury analysers. A low gas flow (mL min^{-1} range) passes over a mercury reservoir located in a temperature-controlled oven. The mercury mass-flow is then diluted by a gas flow in the range of L min^{-1} to obtain a dynamic calibration gas mixture. For very low flows over the reservoir very high recoveries are obtained. When applying higher flows an average recovery of 103 % is observed. Although the generators are only certified at levels relevant for measurements in emission sources, the generators can be used over a much wider range and good practice will be testing the evaporators at lower mercury concentrations.

HgCl_2 dynamic generators also offer a viable approach and the theoretical output based on the HgCl_2 saturation vapour pressure concentration is actually in good agreement with the measured. There are

some practical issues with stability that still need to be resolved and also the unanswered question of the high bias at lower concentrations. In-house verifications were performed around $10 \mu\text{g m}^{-3}$ and at that concentration very good agreement was found with the primary traceable Hg^0 generator with better measurement uncertainty than available using the empirical equations. Currently dynamic gas mixtures containing $0.1 \mu\text{g m}^{-3} - 100 \mu\text{g m}^{-3} \text{Hg}^0$ can be obtained using the primary generator. These reference gas mixtures can be used to directly, and more important traceably, calibrate an analyser or load sorbent materials (e.g. gold or carbon) which can be used as transfer standards. Comparison to directly to primary generator or a calibrated generator against the primary one is recommended in each case. However, as demonstrated above, the typical oxidized mercury gas generators (e.g. the evaporative HgCl_2 generators by Optoseven and Hovacal, or the dry-salt based generator by PSA, Deliverable 1) are applicable to relatively high concentrations of oxidised mercury (process levels). At low Hg(II) levels (such as in non-contaminated air samples at sub $\text{ng m}^{-3} \text{Hg(II)}$ concentrations) cold-plasma Hg(II) generator, developed by JSI for the MercOx project, should be applied.

2.2. Good practice guide for the certification of liquid evaporative generators

In the framework of the MercOx project, a protocol for the traceable generation of HgCl_2 at $\mu\text{g m}^{-3}$ levels for stack gas emission measurements was developed. An essential part of this protocol was the validation of the output of liquid evaporative generators. A step by step procedure to confirm the output of liquid evaporative HgCl_2 generators is explained below. The process consists of two main parts:

- a) Calibration of a two-channel analyser using a primary elemental mercury (Hg^0) gas standard.
- b) Measurement of the output of the generator using the calibrated two-channel analyser.

To select a suitable analyser for the certification of a gas generator, the operational principle and measurement range needs to be considered: these must cover the range which is going to be certified and the analyser must be capable to measure either selectively HgCl_2 , i.e. one channel system, or the total mercury concentration (Hg^{tot}) and elemental mercury concentration (Hg^0), i.e. two channels system. The HgCl_2 output concentration of the latter type is then calculated by the difference ($(\text{Hg}^{\text{tot}}) - (\text{Hg}^0)$). Presented below is an example of certification process of a liquid evaporative generator by the use of two-channel analytical system, designed by Lumex, as introduced in Deliverable 1 of the MercOx. The two-channel analytical system (analyser) consists of an input unit and two gas channels, for determination of Hg^0 and Hg^{tot} concentration. To avoid water vapour condensation in the entrance the input unit must be heated to 130°C . The channel of Hg^0 consists of a heated cell, an atomic absorption spectrometer (AAS) utilizing the Zeeman effect background correction (Lumex RA-915F) and a carrier gas pump. To decrease catalytic reduction of Hg^{2+} in the channel of Hg^0 , metallic surfaces should be avoided at all wetted components but the use of quartz, PTFE or other plastic is recommended. The Hg^{tot} channel consists of an atomizer (thermal converter), a heated cell, and the same AAS spectrometer as at the Hg^0 channel (Lumex RA-915F) and a pump. The temperature of the atomizer must be optimized but should not be lower than 700°C to avoid incomplete HgCl_2 thermal conversion. Two manually operated valves on the input unit can direct ambient air in the channels via a Hg scrubber before entering the measurement cells for measuring the background and zeroing the equipment or alternatively the valves are directing the analyte gas in the measurement cells for analysis. In the Hg^{tot} channel, HgCl_2 is thermally converted to Hg^0 and measured along with the already present Hg^0 ; detector response represents Hg^{tot} . The analyser must be calibrated, preferably by using the primary Hg^0 gas standard or other SI traceable gas standard. The traceability chain for its calibration is the same as the presented in section 2.1. The next step is planning the calibration points, covering

the concentration range which is going to be certified, measurement sequences needed to investigate the repeatability and reproducibility, linearity, and hysteresis. The calibration points must include at least points close to the both minimum and maximum values of the analyser's measurement range, and at least one mid-range point. If there is an evidence of impaired linearity ($r^2 \leq 0.999$), at least five evenly distributed over the operational range test points are needed for acceptable calibration measurement uncertainty. Additionally, it is recommended to include typical measurement points used during actual measurements. Alternatively, higher order calibration (e.g. polynomial) can be used. Large calibration data interpolations or extrapolations should be avoided. Another parameter that need evaluation is the hysteresis from the calibrations results. A simple way to check for hysteresis it to measure the selected calibration points in order from minimum towards maximum value and same in the opposite direction; the hysteresis then is calculated as the difference of the ascending and descending responses at each level. Before starting the actual calibration measurements, the analyser needs to be warm-up according to the manufacturer's recommendation or for 2 hours, whichever is longer. The zero (baseline) level of the analyser is checked after the warm-up time is completed and if there is evidence for significant baseline drift, zeroing of the detectors is recommended after every measurement. The uncertainty of the concentration of the calibration points needs to be considered at this stage. For example, for the VSL primary gas standard with Hg in the range $0.8\text{--}10\text{ }\mu\text{g m}^{-3}$, this parameter was below 3%. The ambient temperature and pressure need to be considered and concentrations adjusted to normal cubic meter (at 20°C , 1 atm). The generated gas mixture must be fed from the (primary) Hg^0 gas standard to the analyser through an inert material pipeline (e.g. Teflon tubing). After a stabilization period where constant signal attained, the analyser reading is recorded for a period of time to provide enough data for uncertainty evaluation (e.g. for five minutes Lumex analyser can provide 300 readings). The hysteresis has to be estimated at this stage (see instructions in section 2.2 above). To assess the reproducibility of the calibration, the calibration procedure, including the hysteresis estimation, must be repeated at least three times during different days. The calibration data is analysed according to EN ISO 6143:2006, which is an international standard providing methods to determine the analysis function, and to calculate the concentration and corresponding uncertainty of calibration gas mixtures. A software (e.g. CurveFit 2.15, designed by VSL) can be used to perform these calculations. With this step the calibration of a two-channel analyser using a primary/traceable elemental mercury (Hg^0) gas standard is complete validation of the generators output can proceed.

To confirm the output of liquid evaporative HgCl_2 generator the output is measured using the calibrated analyser. Furthermore, the appropriate preparation of the evaporated liquid mixtures (Hg standards), their concentration and purity (both elemental and compound based) are essential to obtain SI traceability. If these data are not available from the standards manufacturer, alternative measurement techniques (e.g. ICP-MS/MS and LC-ICP-MS) should be used to estimate the purity parameter. A measurement plan for the generator output calibration should be then made. The calibration points levels, measurement sequences needed to investigate the repeatability and reproducibility, linearity, and hysteresis, are planned. The calibration points should include at least points close to the both minimum and maximum values of the generator's operational range, and sufficient amount of points between those (e.g. 7 calibration point). It is highly recommended to include those concentration points, where the generator is most typically going to be used. This ensures to get enough information for linearity analysis and optimises the corrections and fitting curves used during the actual field usage of the analyser by avoiding large interpolations or extrapolations of the calibration data. Similar to the analyser calibration, to observe the possible hysteresis from the calibrations results, the selected calibration points need to be generated in order from minimum towards maximum value, and the same in the opposite direction. Before starting the

actual certification measurements, the generator must be allowed to warm-up according to the manufacturer's recommendation. A typical value cannot be given, since depending on the particular design this parameter can vary from a few minutes to several hours. The baseline and its stability must be checked after the warm-up time is completed. This should be made using humid gas with water content set to value typical to measurement conditions since the actual calibration gas made through evaporation was humid gas as well. The humid gas is able to detach mercury, which is adsorbed on the system surfaces (including Teflon!) in contact with the generated gas. Dry gases do not have the adsorption properties and can cause incorrect zero reading and drifts due to adsorption. To check the zero level, ultrapure water is fed to the evaporator. Additionally, checking the zero level during the calibration measurements, between the calibration points, is recommended to detect any baseline offsets. The generated gas mixture must be supplied from the generator to the analyser using inert tubing (see above). The analyser reading has to be observed and waited to be stabilized. After the stabilization period the analyser reading must be recorded for a period of time to obtain enough data for statistical evaluation. Additional considerations are the response time and measurement time, which should not be too long considering the analyser drift. The liquid flows have to be the optimum for the generator and within the manufacturer recommendation. For example (see Deliverable 1, MercOx project) Hg standards flow rates between 0.1 g/min and 0.03 g/min can be used. Dilution gas flow between 5 and 20 L min⁻¹ (N₂, Ar or clean air) is typically applied. With these parameters 8 different Hg concentrations between 14 µg m⁻³ and 0.8 µg m⁻³ were generated by liquid evaporative generator and their output validated.

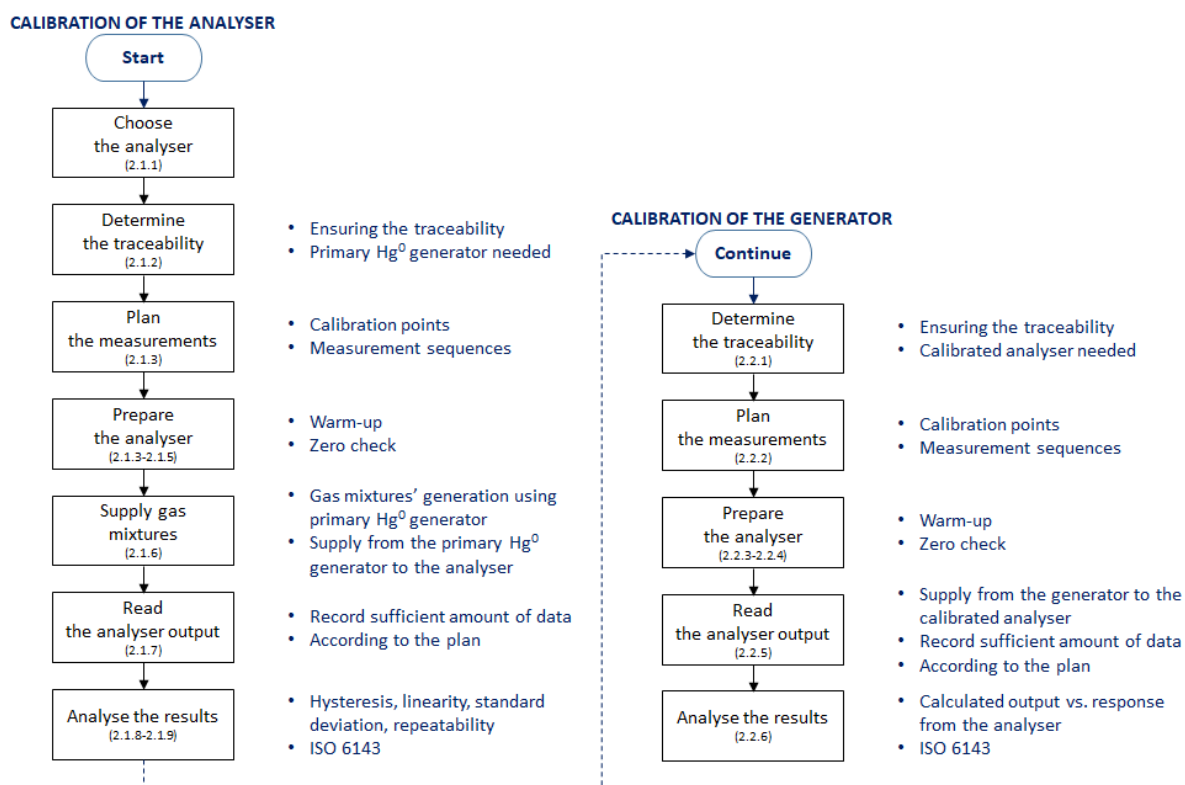


Figure 2. Protocol for the validation of the output of liquid evaporative HgCl₂ generators.

The outputs from the generator were analysed using the calibrated two-channel Lumex analyser. The calibration data was then analysed according to EN ISO 6143:2006. Finally, the generator theoretical output concentration value was compared to the response from the analyser. It should be noted that the uncertainties of both the generator output and the analyser measurement have to be considered when comparing these results. From these results, a calibration curve and uncertainty budget must be calculated. It should be highlighted that the certified values are specific for the certified generator only; other devices of the same brand have to pass through all the certification stages. A schematic diagram of the validation process is presented in Figure 2. Such certification protocols are fit for purpose and can be used even daily to certify liquid evaporative generators for oxidised mercury. Future parameters for consideration include thermal converter efficiency, confirmation of efficiency of sample gas transportation inside the gas generator and the measurement system, as well as mercury species conversion in different steps of the process. This would eventually enable obtaining SI traceable results for the output of the generator via application of a refined certification protocol.

2.3. Good practice guide for the comparison of methods for measuring oxidized Hg and methods for determination of Hg^{tot} in generated standard gases

The determination of $\text{Hg}(\text{II})$ and Hg^0 concentrations in gaseous samples is often performed after their selective trapping using appropriate traps. KCl and high-carbon content materials are frequently used as a trapping media for $\text{Hg}(\text{II})$ and $\text{Hg}(\text{II})+\text{Hg}^0$ in environmental and industrial applications. To assure accuracy and comparability of the Hg determinations, the project partners participated in the interlaboratory comparison for the Hg^{tot} determination in high-carbon content solid sample (Figure 3). It is mandatory that sample is well prepared to assure homogeneity and consequently identical results between bottles. Prior to determinations, moisture should be determined so that all results refer to dry mass. Following the analyses, a proper statistical analysis of the data should be performed; outliers, dispersion, and the symmetry of the distribution should be determined. Data obtained near the quantification limit should be evaluated with care. Several statistical methods should be used to calculate a consensus estimate.

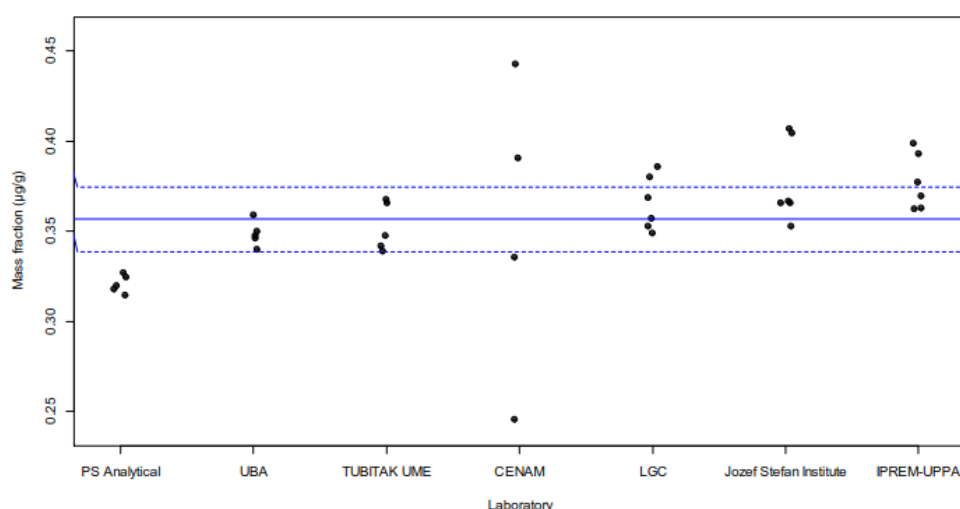


Figure 3. Individual measured values shown by laboratory. The blue lines represent the arithmetic mean of the individual estimates and its 95 % confidence interval.

Calibration of methods for Hg determination in activated carbon using thermal decomposition/AAS can be performed either by spiking Hg(II) solution or by purging Hg⁰ traceable to the same standard solution (SRM NIST 3133). Whenever a new carbon material is prepared, we recommend verification that the detector's response is the same for both loading methods to assure the absence of differences in Hg release from the material. Comparison of in-house and commercially available activated carbon showed that the latter usually performs better regarding repeatability and breakthrough. To assess how many Hg compounds are present on the material, we suggest using deconvolution of fractionation thermogram peaks.

To demonstrate the accuracy and comparability of transfer standards obtained with the primary mercury gas standard, a comparison study against typical calibration methods using the SRM NIST 3133 was performed. For that purpose, we loaded sorbent traps with variable mercury mass (10 – 1000 ng) to obtain transfer standards. We recommend loading lower Hg amount on gold traps and higher amount on carbon traps. To assure comparability on the results between gold and carbon traps, we suggest using only one method; thermal desorption/AAS seems to be the most appropriate. All analytical parameters, including proper preparation of the Hg standard solutions, should be well controlled to assure good repeatability, reproducibility, and uncertainty of Hg determinations.

The species conversion effect during the trapping and desorption of Hg from activated carbon can be investigated using a thermal decomposition coupled to ICP-MS/MS and the forth-concentric tube torch interface. To differentiate between Hg⁰ and Hg(II) in the thermogram, we suggest using a spike of an enriched isotopic Hg(II) solution in methanol on Hg⁰-loaded activated carbon. Following the thermal decomposition, Hg⁰ and Hg(II) can be well distinguished to confirm possible transformations (e.g., Hg(II) reduction to Hg⁰, but not the oxidation of Hg⁰ to Hg(II)). For this coupled system, linearity should be checked, but more important, the quantitative recovery should be proved due to sticky nature of Hg(II).

For the Hg^{tot} determination in Hg⁰ reference gas, direct or indirect coupling to ICP-MS are both possible. A commercially available Hg⁰ generator, applicable in the $\mu\text{g m}^{-3}$ fraction range, can be directly coupled to ICP-MS using a flow split just before the ICP-MS interface to provide appropriate reference gas flow. However, if the achieved sensitivity is incompatibly high for continuous operation, the lens should be detuned to decrease the sensitivity. The traceability of the Hg determination by ICP-MS in reference gas to a bell-jar standard can be also achieved through the use of gold-trap amalgamation system, followed by thermal desorption ICP-MS.

Reference gas generators for Hg(II) can be directly coupled to ICP-MS using the standard plasma torch. Initial experiments using the Hg(II) generator showed that the transport efficiency of oxidized mercury is far below quantitative and a fraction of the gas is lost either on the ICP-MS torch (50 %) or on the quartz surface of the gold traps (30 %). An in-house inert interface, similar to the one developed by LGC for the MercOx project, should be used (in absence of commercially available) to couple ICP-MS to liquid evaporative generator to shorten the memory effect and stabilization time. Data should be collected only at the end of the measurement periods where the signal varied within 1–2 % within 5 min window. Very good linearity can be achieved using this approach for all isotopes. As the sensitivity of the instrument changes even within 0.1 mm of the torch position, the torch should be carefully positioned. Furthermore, the quantitative recovery should be also proved due to sticky nature of Hg(II).

To address the potential biases or losses in the conversion of Hg(II) to Hg⁰ during Hg speciation measurements in the atmosphere and stack gas emissions, we tested the efficiency of thermal conversion of Hg(II) to Hg⁰ on KCl crystal sorbent traps that were spiked with Hg(II). For these kind of

measurements, we suggest spiking a solution of Hg(II) on various types of KCl traps to assess which ones are the best for quantitative catalyst-assisted thermal conversion to Hg⁰. We recommend using a heated Al₂O₃ trap as a catalyst for complete conversion, over e.g., heated quartz wool or platinum wire. We suggest using a rapid heating gradient (20 – 600 °C in 20 s in nitrogen carrier gas) to avoid sublimation of Hg(II) instead of conversion to Hg⁰; Hg(II) should be retained on the alumina (or some other material) until a high temperature is achieved. In the case of Hg(II) loaded using non-thermal plasma, the conversion of Hg(II) to Hg⁰ was also not satisfactory without the use of proper catalyst. The experiments that utilized Al₂O₃ as a catalyst also resulted in quantitative transformation of the plasma-loaded Hg(II) to Hg⁰.

The selectivity of KCl trapping solutions was studied using elemental and oxidized Hg in the presence of flue gas components. We have also developed a method based on propylation GC-AFS to enable a measurement of oxidized Hg in the KCl trapping solutions. To assess a bias in the oxidized Hg measurement special attention has to be paid to the solubility of Hg⁰ in the trapping solution and the oxidation/reduction effects from acid gas components and impurities in the KCl solution, converting it to Hg(II). The method developed using the extractor stripping vessel to establish the Henry's law constant offers significant advantages over other methods especially when higher temperatures are being tested. The oxidation of Hg⁰ in solution can be excluded by applying a short residence time and by using SnCl₂ as a reductant to prevent oxidation. We recommend conducting an experimental mercury mass balance to identify if oxidation has occurred.

The Hg⁰ solubility in Hg(II) trapping media was demonstrated and the uncertainty budget for the determination of the Hg species by this method calculated. The species conversion induced by the matrix components have highlighted the importance of further analytical developments to achieve sufficient accuracy and low measurement uncertainty determinations of Hg(II) in presence of much higher concentrations of Hg⁰. Impurities present in the KCl trapping solution could oxidize a small percentage of Hg⁰ vapour which is continuously being introduced. In this respect, all tested gases are showing a lower concentration relative to the baseline test indicating a possible oxidation of Hg⁰ by flue gas components. The results show that the KCl solution will collect a small quantity of elemental Hg and this elemental Hg could be determined as oxidized Hg by using GC-AFS.

2.4. Good practice guide for isotope ratio measurements for the determination of Hg origin, migration pathways, and species interconversion

Epiphytic lichens can be used as air-quality bioindicators as they accumulate atmospheric contaminants. For transplanted lichens, *Hypogymnia physodes* lichen should be used (if possible), because it is considered as the most studied lichen in relation to biomonitoring. Large amounts of lichen thalli should be collected from a remote site far from any influence of anthropogenic activities. After cleaning the lichens from excess wood material, lichens should be packed in several nylon net bags. We recommend the exposure of the transplanted lichens on selected locations on tree branches at the height of 1.5 – 2 m above the ground for a certain duration of time (e.g., 3, 6, 9, and 12 months). After the exposure time, transplanted lichen bags should be cleaned from the dead parts and wood. We recommend lyophilisation of cleaned lichens and homogenization following immersion in liquid nitrogen. For the in-situ lichens, locally present species should be collected from the same locations where the exposed lichen bags were placed. The preparation of in-situ lichens for analysis is the same as for the transplanted lichens. Due to possibility that lichens might have adsorbed inorganic material,

we recommend applying a method for the determination of Hg in inorganic matrices. Certified reference materials analysed alongside the samples should be of similar composition and Hg concentration as samples (e.g., IAEA-336, BCR 482). Analysis should be performed using an appropriate detector (e.g., CV AAS, CV AFS, ICP-MS).

For stable Hg isotopic determinations, mineralization of lichens and mosses can be achieved by digesting 0.5 – 1 g of sample in a high-pressure Asher with sub-boiled nitric acid for 3 hours at 300 °C and 130 bar. We recommend that mercury isotopes analyses are performed according to previous works, by using a cold vapour generation (CVG) with SnCl₂ reduction, coupled to a Multicollector (MC) ICP-MS. For the correction of the instrumental mass-bias, internal thallium standard (NIST 997) and sample standard bracketing with NIST 3133 standard solution should be used. To avoid any bias caused by differences in concentration, all the samples and standards should be measured at the same Hg concentration (e.g., 1 ng g⁻¹). Mass-dependent fractionation (MDF) should be reported using $\delta^{202/198}\text{Hg}$ notation relative to the NIST 3133 Hg solution. Mass-independent fractionation (MIF) of Hg should be reported as the difference between the theoretical value predicted by MDF of $\delta^{\text{xxx}}\text{Hg}$ and the measured values, as $\Delta^{\text{xxx}}\text{Hg}$. Analytical reproducibility for CVG/MC-ICP-MS should be evaluated by multiple measurements of the secondary standard NIST 8610, and the certified reference material for lichens (e.g., BCR 482). For the interpretation of the Hg isotopic results, we suggest using a classical tri-isotopic graph, i.e., $\Delta^{199}\text{Hg}$ vs. $\delta^{202/198}\text{Hg}$ (e.g., Figure 4), which provides an overview of possible Hg fractionation processes.

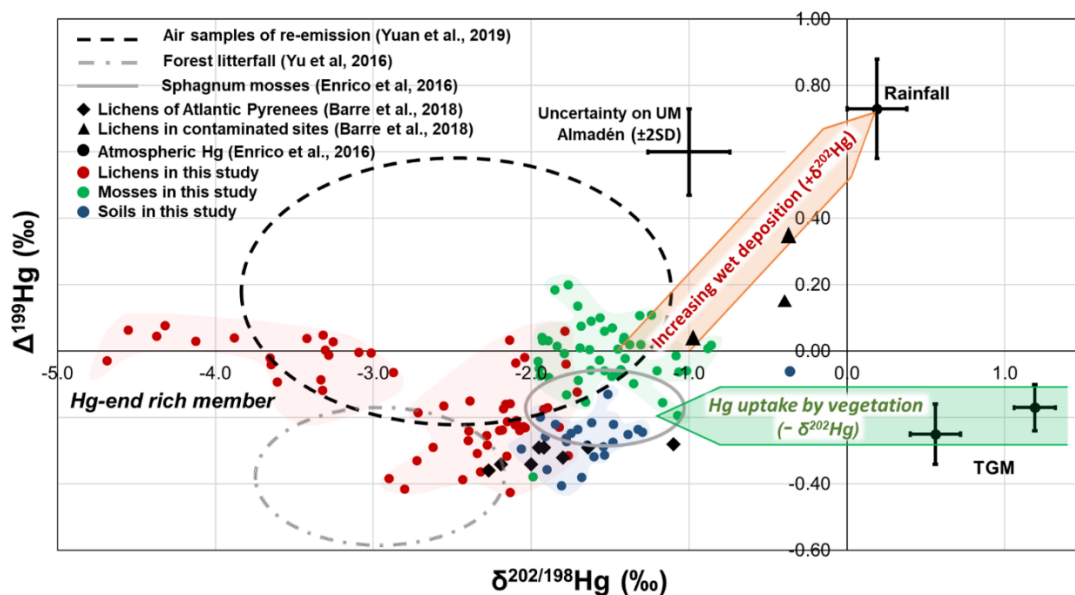


Figure 4. Tri-isotopic plot of $\delta^{202}\text{Hg}$ vs. $\Delta^{199}\text{Hg}$ (‰) for lichens, mosses and soils from Iraty forest.

A similar approach can be made to evaluate Hg isotopic composition in the atmosphere using specimen bank spruce needles. However, for this application, the long-term storage should be carried out under conditions which exclude a change in state or a loss of chemical characteristics over a period of several decades. The one-year shoots should be cut off with stainless steel scissors, collected in a stainless-steel trough, and immediately rapid-frozen on-site using liquid nitrogen. We recommend that samples are cryo-milled and stored in 10 g aliquots under liquid nitrogen until further analysis. For isotopic

determination, samples can be mineralized using HNO_3 in a microwave at 230 °C for 25 min. To manage the analytical accuracy of the method, Hg isotopic measurement of the secondary references (e.g., BCR-482 and NIST 1575a) must be also performed using the same method. Determined Hg isotopic composition should be reported as described for lichens.

Mercury content in some solid samples can be very low ($< 10 \text{ ng/g}$), which complicates the determination of Hg stable isotope ratios. Large amount of sample needs to be concentrated in a small amount of acid, which can introduce a considerable matrix effect. Therefore, for samples like coal, activated carbon, soils, sediments, or particulate matter, we suggest applying an optimized method based on Hg pre-concentration in on quartz wool impregnated with KMnO_4 after sample combustion in air at 700°C. Hg captured on the KMnO_4 trap needs to be leached using HNO_3/HCl acid mixture so it can be suitable for isotope determinations. Another method that can be applied to samples with low Hg content and high content of inorganic particles is digestion using $\text{HNO}_3/\text{HF}/\text{HCl}$ mixture. In this case, digested samples should be subjected to slow sub-boiling evaporation at 100°C for about 5 – 6 hours to remove HF and reduce the volume. To test whether this evaporation procedure cause Hg artefact, several blanks and standard solutions should be prepared in the same manner as samples, and the amount of Hg compared with the respective Hg content in blanks and standard solutions that were not evaporated. The procedure must ensure that solutions do not lose Hg during evaporation and that Hg isotopic signature is preserved.

Project partners have also characterized reference material NIES CRM No. 28 (urban aerosol). The Hg isotopic composition of the CRM was determined following digestion by mixture of $\text{HNO}_3/\text{HCl}/\text{H}_2\text{O}_2$ in Hotblock, or by mixture of HNO_3/HCl with in a microwave and a digestion bomb. Although Hg was not completely dissolved in the sample solutions obtained by bomb and microwave digestions, all analysis results were consistent with each other, and variations were found to be smaller than the repeated measurements of the secondary standard. Therefore, all three methods can be used for isotope determinations; slight preference is given to $\text{HNO}_3/\text{HCl}/\text{H}_2\text{O}_2$ digestion due to quantitative recovery. The determination of total mercury in NIES CRM No. 28 was performed using three methods: extraction using $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{KBr}/\text{Br}_2$ mixture or pre-mixed aqua regia, or by k_0 -instrumental neutron activation analysis. All three methods gave similar results and within acceptable agreement with the mean value obtained by interlaboratory study. Therefore, all three methods could be used for the determination of THg in particulate matter. Our results indicate that this CRM is appropriate for use in environmental and geochemical studies for the quality control of particulate matter analyses.

We have also evaluated methods for the characterization of particle bound Hg. First results indicate that laser ablation coupled with inductively coupled plasma mass spectrometry might be used for the quantification of THg in air-filter collected particulate matter. If the sampling area for the analysed real sample is smaller than that of the standard, correction for radial distance and homogeneity should be undertaken. We also recommend the use of a post laser mix bulb to reduce variation between lines.

Temperature desorption method can be used for the characterization of Hg species in solid samples from the cement production by employing quadrupole MS. The sample should be heated to 800 °C at a rate of 10 °C/min under high vacuum ($< 10^{-5} \text{ mbar}$). Multiple ion detection mode can observe and detect Hg and other volatile species in samples (e.g., chlorine). Commonly, two different isotopes, ^{200}Hg and ^{202}Hg should be measured simultaneously. The obtained spectra in different parts of the process could contribute to a better understanding of Hg mobility and fractionation in solid samples in the production process.

2.5. Good practice guide for appropriate Hg sample preparation and interspecies conversion corrections

This chapter summarizes the work presented in Appendix A1. KCl (as denuders), carbon (as traps) and acids/oxidizing reagents (as impinger solutions) are among the most frequently used media for trapping and preconcentration of Hg and Hg species prior to their quantitative determination. Therefore, good practice guide will focus on the above listed sampling media and the methods that employ their use since appropriate usage of sampling methods is the first and crucial step in sample analysis as it is known to introduce the largest share of uncertainty into the overall uncertainty budget. Species trapping efficiency and interconversion is discussed as well.

LGC employed a microwave digestion procedure with HNO_3 acid and H_2O_2 which did not result in complete digestion for most of the real trap samples from Marl power plant (see Deliverable 7) even with sample weights as low as 50 mg. Therefore, the method was further adapted. We suggest the use of the new digestion method that includes the sulphuric acid pre-mixed with nitric acid to facilitate higher temperature digestion and lower the vapour pressure in the MW digestion vessel. With ratio of 7:3 v/v ($\text{HNO}_3:\text{H}_2\text{SO}_4$) approximately 0.2 g of activated carbon (iodinated AC) and SRM materials (NIST SRM 2445, and 2448) were completely digested without the loss of Hg species. This suggests that the method is suitable for the intended use. The method applicability was further confirmed with the analysis of samples from cement clinker production facility (in Anhovo, Slovenia, see Deliverable 7) and the same SRM (e.g. NIST 2445). Quantitative recoveries were obtained for both the SRM samples and for the NIST 3133 SRM laboratory spiked real samples.

The results have also shown that the application of thermal desorption for speciation analysis of mercury, trapped on activated carbon is not always possible and not applicable with the typically used atomic absorption and atomic fluorescence detectors. We propose that the species should be selectively trapped and therefore temporary resolved otherwise we do not recommend the above-mentioned application of activated carbon use.

Speciation traps for atmospheric mercury consist of glass wool sections, acid gas scrubber (AGS) section, KCl section and finally AC sections which were shown to have potential for Hg(II) absorption. If the results from the speciation trap tests confirm those from the model experiments presented in Appendix A1, we suggest that the structure of the so-called speciation traps is reconsidered as the intention of the trap is to selectively bind Hg(II) on the KCl section of the trap.

In the framework of MercOx project, good laboratory practice for measuring mercury in coal using microwave-assisted acid digestion in combination with standard addition and cold vapour generation system coupled to inductively coupled plasma atomic emission spectrometry (EC-SA-CV-ICP-AES) was also proposed. Good practice guide for EC-SA-CV-ICP-AES consists of:

- Laboratory and work requirements such as temperature, relative humidity, pressure, air quality, security parameters and proper staff training and working environment;
- Use of appropriate material and reagents, such as: borosilicate bottles (for light protection), closed system temperature control for microwave oven, polyethylene bottles for preparation of SnCl_2 solution, high purity chemicals and double-sub-boiling distillate quality acids;
- Sample preparation good practice: weighing appropriate amount of sample directly into reaction vessels, applying ultrasonic bath prior to acid digestion (to break coal agglomeration), keeping controlled conditions of microwave digestion (to prevent ruptures of protective membranes of the reaction vessels) and inclusion of blank digestion samples and reagent blank samples;

- Instrumental measurement good practice: ensuring leak-free sample introduction system, precise control of flow to improve measurement repeatability, minimizing memory effects via 2 % nitric acid rinsing, CRM sample measurements for control and controlling interferences / matrix effects.

One of the crucial factors that considerably influence sampling methods for atmospheric Hg speciation is the specificity of sorbent traps. The Hg^{2+} -specific sorbent traps should therefore have high level of specificity towards Hg^{2+} and low affinity for other Hg species (mainly Hg^0). The KCl sorbent traps studied by JSI retained much more Hg^0 when they were re-used (Hg^0 retention is undesirable). From these findings we suggest that fresh KCl traps are to be used instead of re-used KCl traps. Prolonged sampling and preconcentration time might result in losses of Hg^{2+} or reduction to Hg^0 . Results of Hg^{2+} stability under different sampling conditions showed that highest relative losses were always present in the low-concentration experiments in the first 30 min of exposure to airflow (Figure 19 – Figure 22), while other variations (calibrator loading/spiking, high/low flow, $\text{HgCl}_2/\text{HgBr}_2$ species) did not result in statistically significant differences in Hg^{2+} losses. Therefore, we recommend that Hg^{2+} losses should be considered when evaluating atmospheric Hg speciation measurement results especially when low Hg^{2+} concentrations are measured with long preconcentration times. .

Oxidation of Hg^0 to Hg^{2+} can be effectively achieved using a non-thermal plasma as shown in the previous deliverables of the MercOx project (Deliverable 1). To accompany these developments, we conducted stability tests of non-thermal plasma loaded Hg^{2+} on KCl + Al_2O_3 traps. The difference between daylight and dark conditions was small (5.2% difference in stability) and within the standard deviation of replicate measurements (10.9% standard deviation of replicates for fresh traps in darkness). The difference between the re-used and fresh KCl + Al_2O_3 traps was considerable and large (24.6 % difference in stability); re-used traps had much lower losses than the fresh traps. In contrast, results for KCl + Al_2O_3 traps showed that re-used traps retain relatively high amounts of Hg^0 (15% on average) in comparison to fresh traps which did not retain Hg^0 . This is not desirable as Hg^0 retention on Hg(II)-specific trap results in biased Hg speciation. Indications are therefore conflicting and we suggest that if fresh KCl + Al_2O_3 traps are used for Hg(II) loading, they should not be stored for longer time periods. If the longer storage time period is inevitable, it is best to pre-condition it by heating it to 600°C since the Hg(II) loading is much more stable.

2.6. Good practice guide for sampling methods for gaseous Hg species

Different sampling methods are used in atmospheric Hg speciation ranging from sorbent trap designs, denuders and impinging solutions. To ensure that all sampling methods and the data obtained by them are directly comparable, it is crucial to have a reliable calibration system. Therefore, attention was given to optimization and validation of an evaporative generator for oxidized mercury developed within the framework of the MercOx project. Highly sensitive ^{197}Hg radiotracer was used as it was found to be the most suitable for validation due to the low detection limits and elimination of problematic blanks.

As found in our validation efforts, the generator should be used at high carrier gas flows ($> 5 \text{ L min}^{-1}$) and evaporation chamber temperatures of $> 120 \text{ }^\circ\text{C}$. Tubing and in general the setup surfaces for capturing the calibrator output should be minimized as adsorption of Hg^{2+} was found to be increasing as we increase the surface area that is available for Hg^{2+} adsorption. Adsorption was also dependent on Hg^{2+} gas concentration, lower Hg^{2+} gas concentration resulting in higher adsorption levels and lower calibrator recoveries. Therefore, we recommend that the calibrator is used mostly for high Hg^{2+} concentrations ($> 1 \mu\text{g m}^{-3}$). Lower concentrations can be used if the calibrator is operating for long

periods before the calibration itself, since the stabilization of the calibrator output takes longer as the gas concentrations are low. If the Hg^{2+} gas concentrations are much lower than the recommended $> 1 \mu\text{g m}^{-3}$, the time needed for the stabilization of the calibrator output might be in the range of a few days. For the lowest concentration level that was tested (5.90 ng m^{-3}), the output was not stable even after 4-days of constant operation. During the course of 4-day operation for the lowest concentration level, the calibrator recovery was constantly rising, however it never reached a plateau value. In general, the calibrator performed better the longer it was operating for all concentration levels as the recoveries were rising with time. Hg^0 fraction of the calibrator output will increase as the gas concentrations decrease, which is an additional reason why we recommend high Hg^{2+} gas concentrations for the optimal performance of the newly developed evaporative calibrator. Hg^{2+} solution that is used for Hg^{2+} gas production was tested for stability during 5 days of constant calibrator operation and was found to be very stable with negligible losses. This suggests that the calibrator can be used for longer periods of constant operation without experiencing significant Hg^{2+} losses in the calibrator solution.

While minimizing the tubing length and setup surfaces decreased the adsorption, it was never eliminated. The future users of the unit should expect that some Hg^{2+} is adsorbed also on the tubing and parts inside the calibration unit. This is most evident shortly after the start of calibrator operation ($< 2 \text{ h}$ since calibrator start-up) and cannot be avoided unless changes are made to the calibration units manufactured in the future.

Regarding Hg^{2+} species that can be produced with the evaporative calibrator, we investigated HgCl_2 and HgBr_2 species. The calibrator output was found to be more stable and the recoveries higher when using HgCl_2 gas than when using HgBr_2 gas. HgBr_2 gas had more adsorption due to its lower water solubility as suggested by the Lundelius' rule (Lyubchik et al., 2011). Consequently, we recommend that the calibrator is used for HgCl_2 gas rather than for HgBr_2 gas. HgBr_2 gas calibration will have to be addressed in the future as HgBr_2 is a proxy for all atmospheric Hg-Br species.

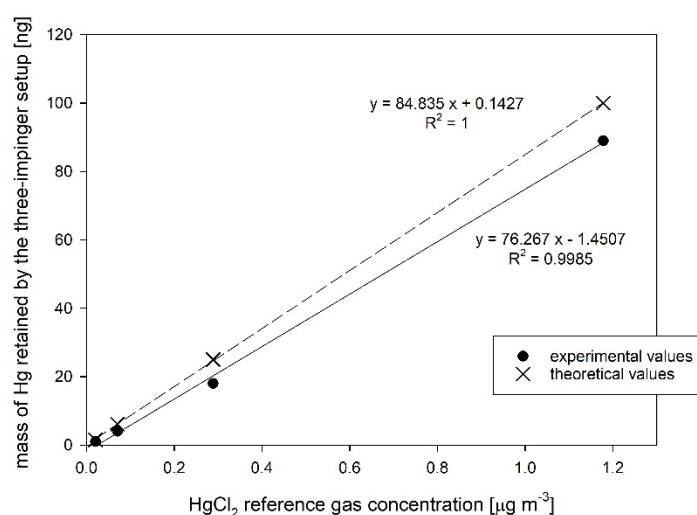


Figure 5. The relation between the mass of Hg retained by the three-impinger setup (ng) and the corresponding HgCl_2 gas concentrations (from 5.90 to 1178 ng m^{-3}). Comparison is shown for theoretical and experimentally determined values.

The linearity of the calibrator was also studied. Results showed that even when the recoveries of the calibrator were very low, the output of the calibrator remained linear (Figure 5). From this observation we strongly advise that in the future, linearity should not be used as the lone indicator of calibrator output validity since the slopes obtained from the experimental points were lower than expected slopes calculated from equations provided by the instrument manufacturer (Figure 5).

The calibrator was tested for two different sampling methods: impinging solutions and sorbent traps. The use of impinging solutions resulted in higher recoveries than the use of sorbent traps which was contributed to the fact that gas flow had to be greatly reduced for sorbent trap usage. This was the case both for experimental sorbent traps (mimicking commercially available sorbent traps) and the Lumex speciation traps. In addition to the low recoveries obtained by the sorbent traps, there was very little robustness as changing from one type of a sorbent trap to the other vastly changed the outcome of the Hg^{2+} calibrator loading. As already stated above, low flows lead to low calibrator recoveries. Low recoveries were also the reason why the slope of a linearity experiment (similar as in Figure 5) was lower for sorbent traps than for impinging solutions. Again, this indicates that linearity needs accompanying validation to ensure reliable calibration and is not a good standalone indicator for good calibration. We suggest that the calibrator is used in combination with sampling methods that allow $>5 \text{ L min}^{-1}$ flows, otherwise adsorption will be increased greatly, resulting in low recoveries of the calibrator output.

Adsorption enthalpy for HgCl_2 adsorption of Teflon tubing was calculated from results obtained in our work. Langmuir isotherm was found to be the best fit and the obtained adsorption enthalpy value was $-12.33 \text{ kJ mol}^{-1}$. The negative value of adsorption enthalpy suggests that high temperatures will decrease adsorption while low temperatures will increase it. Therefore, it is recommended that the entire system for capturing the calibrator output be heated if possible. We note that too high temperatures ($>150^\circ\text{C}$) might result in reduction of Hg^{2+} to Hg^0 which is undesirable; it is crucial to find a balance between lowering Hg^{2+} adsorption rates and preventing Hg^{2+} reduction.

2.7. Good practice guide for field testing of methods for on-line and sorbent-based Hg measurements in stack emissions

In the framework of the MercOx project, emission monitoring was performed at the Marl coal-fired power plant and Salonit cement production plant. Selection of the sampling points depends on the specificity of the system. Sampling points are usually those used for controlling and monitoring operation of a plant's exhausts. In Marl, the most representative sampling points were before flue-gas desulfurization and after selective catalytic reduction. In Salonit, samples were taken directly from the stack gas.

Prior to sampling, calibration of the plants mercury continuous emission monitoring (CEM) system using an evaporative reference gas generator (e.g., HovaCAL) was performed. Based on our experiences within the MercOx project our guidance would be as follows. The typical highest water content in generated reference gas during linearity test should be around 10% (v/v). The temperature of all system parts that are in contact with the reference gas should be 180°C . Total reference gas flow rate should be sufficient to flush the CEM sampling probe and higher than the sample gas flow rate from sampling system to the actual measurement system. Response time of the CEM should have a maximum value of 200 seconds, according to EN 14181 standard. Signal-to-noise ratio, determined as three standard deviations of consecutive concentration readings, should be as low as possible. Linearity of the CEM response should be estimated by assessing consecutive Hg concentrations

injected to the system at variable percentage of the maximum range (e.g., 0 / 70 / 40 / 0 / 60 / 10 / 30 / 90 / 0 %). Any positive offset in the slope of the calibration curve might be explained by response time since zero level concentration might have not been reached.

Commercial Ohio Lumex sorbent traps were used for the collection of samples from the flue gas. The sampling was performed using commercial Ohio Lumex Sorbent Trap Sampling System. The measurements were carried out with sorbent traps for determination of total mercury in accordance with the CEN TS 17286 and the US EPA 30B method (traps were used to collect flue gas for both total Hg, speciation, and stable isotope ratio analysis). Good practice guidance for this type of sampling is as follows. Speciation traps should be sampled at 120 °C using flow rates of 250 - 300 cm³/min, while total mercury traps should be sampled at 130 °C using 1000 cm³/min flow rate. The temperature between the sampling temperature and the stack temperature should be similar to prevent possible changes in Hg speciation. We also recommend making a detailed sampling table to have a complete overview of what/why/where/for whom has been sampled, as possibility of mixing up samples might occur during field work.

Mercury content on sorbent traps was determined using a mercury analyser RA-915M with a PYRO-915+ thermal decomposition attachment. Good practice guidance for this type of measurement is as follows. The calibration curve should be prepared daily by spiking the matrix using a known amount of mercury and determining the corresponding peak area. The regression coefficient of the calibration curve should be always better than 0.999. We recommend recalibration of the instrument whenever there is a considerable change in the recovery of pre-spike on sorbent traps due to detector's drift. Mercury content in each sorbent trap must be determined sequentially, i.e., in each section of the trap separately. The amount of THg on the whole trap should be calculated by summing the contribution of individual sections. The concentration of THg, oxidized, or elemental Hg in the stack gas is determined by dividing the amount of Hg on trap (or trap sections) with the volume of the sampled gas at normal conditions (20 °C and 1 atm). The results should be presented in µg/Nm³. Whenever the stack gas composition significantly differs from the default one (e.g., 7% O₂, 12% CO₂, and 81% N₂), calibration factors for mass flow controllers should be corrected for the corresponding correction parameter.

The CEM performance was compared with THg concentrations in the stack gas obtained using sorbent traps. The resolution of the CEM should be as best as possible (e.g., 1-minute intervals) to account for sudden spikes in Hg concentrations (e.g., 30-minute interval for CEM results in Salonit do not always agree well with the results obtained by sorbent traps during 10-minute collection time; Figure 6).

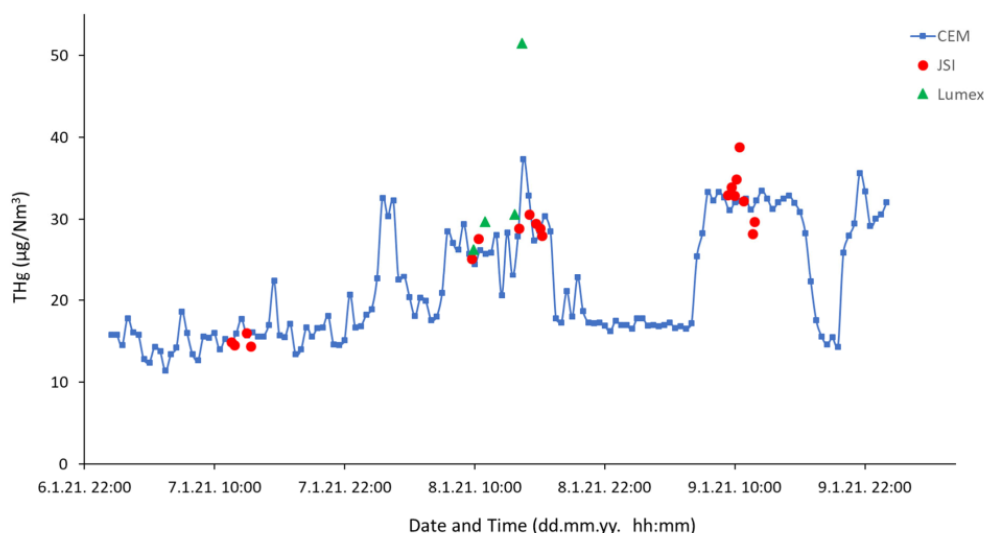


Figure 6. Comparison of THg concentrations in stack gas as determined by CEM (blue squares) and sorbent traps. Some sorbent traps were measured by JSI (red circle) and some by Lumex (green triangle).

A cold vapour generator hyphenated to ICP-MS was used for the quantitative determination of Hg in the sorbent trap samples. Results were obtained using ^{202}Hg due to slightly lower detection limits compared to other isotopes. For ICP-MS determinations, we suggest digestions of the ball-mill homogenized carbon from the C-trap sections using optimized procedure that can completely dissolve the sample (see Deliverable 5). Results showed that up to 50 % of Hg(II) can be trapped on glass wool and acid gas scrubber, and it is mandatory to include this amount of Hg in the budget for oxidized Hg on sorption traps.

EPA method 30B and CEN TS 17286 method are performance standards which allow any analytical technique to be used for the recovery and measurement of mercury from sorbent trap sections. Both methods provide specific analytical tests that must be performed by the testing laboratory. The analytical matrix interference test is a laboratory procedure required only if a liquid digestion or trapping analytical approach is chosen. The purpose of the test is to verify the presence of analytical matrix interferences (e.g., iodine). This test determines the minimum dilution necessary to mitigate matrix effects on the sample digest or extract solutions. The test should be performed using a mass of sorbent material comparable to the sorbent mass typically used in the first section of the sampling trap. The lowest dilution ratio of any solution having a mercury concentration within $\pm 5\%$ of the digest-free solution is the minimum dilution ratio required for analysis of all samples. Before analysing field samples, the laboratory must also demonstrate the ability to recover and accurately quantify Hg^0 and HgCl_2 from the chosen sorbent traps by performing analytical bias test (ABT) for sorbent traps spiked with Hg^0 and HgCl_2 on the first section of the trap. According to CEN TS 17286 the spike recovery range must fall between 90 - 110 % to pass the quality assurance criteria. In accordance with this method, we also suggest to analyse a solid certified reference material (NIST 2445, NIST 2448) as QA/QC standard. It is important to use an equivalent mass of material as used for sorbent trap analysis.

Calibration of the instrument for the determination of THg in cement using thermal decomposition atomic absorption spectrometry can be performed using matrix-matched certified reference materials (CRM) or using spike calibration. The need for several matrix CRMs that differ in Hg content and the uncertainty of the mass fraction are the main drawbacks when choosing to calibrate the instrument

with matrix CRM. From possible alternatives to calibrate the instrument, we recommend using spike calibration that utilizes the addition of the standard calibration solutions to the solid matrix. This approach is preferred because of its simplicity and uncertainty that is smaller compared to the matrix-matched CRM.

2.8. Good practice guide for field testing of methods for on-line and sorbent-based Hg measurements in the atmosphere

Existing methods for on-line Hg monitoring, sorbent trap measurement and biomonitoring of Hg in the atmosphere were tested and validated. These tests were conducted at different sites chosen across Europe to consider the effect of direct sources of Hg and its short- and long-range transportation (i.e., Monte Curcio - MCU, Italy and anthropogenically influenced Anhovo Cement Plant, and former Idrija Hg mine areas).

Active on-line Hg measurements were performed by three different analytical systems using the preconcentration of mercury on sorbent cartridges and analysis with cold vapour atomic fluorescence spectroscopy (CVAFS) (Tekran and Sir Galahad), compared to the direct measurement of elemental mercury in the air using cold vapour Zeeman atomic absorption spectroscopy (CVAAS) (Lumex). Different air sampling and analytical techniques allows to measure different air Hg species. As seen from obtained data at Monte Curcio and Vodarna sites, Hg speciation is important data that shows presence of local Hg sources and their influences on local Hg cycle. As deployed instruments measure different air Hg species (Tekran – GEM, GOM and PBM; Sir Galahad – TGM; Lumex – GEM) at different sampling and measurement frequency direct comparison of the results is rather difficult. Frequency of measurements showed to be an important issue when comparing data. For instance, Lumex produce measurement every second, Tekran on 5 min basis with two-hour cycle for GOM and PBM, and Sir Galahad has 30 min sampling interval. Due to different frequency of data production obtained results have different deviations and therefore it is very important to obtain proper data averages with standard deviations and measurement uncertainty. Compared to the TGM values recorded at MCU (background site) those measured at industrial site with the same active sampling system are about double for the whole period and indicate the importance of the anthropogenic impact on the quality of the air surrounding the industrial complex.

The aspect that has to be taken into an account is the calibration of different instruments. For instance, Tekran uses permeation tube for the calibration, while Sir Galahad is calibrated by injecting a known amount of Hg vapour using syringe. The amount of Hg in the syringe is calculated based on Dumarey equation. Nevertheless, the response of the Tekran detector for a known amount of Hg provided by permeation tube is the same as the response for the same amount of Hg injected by syringe (as external calibration). However, calibration should not only be applied directly to the gold trap used for preconcentration of mercury. Rather, calibration should encompass the whole system, including the sampling system from the sampling inlet. This should be performed for the determination of both GEM and TGM as the responses of the whole system might be different. This is especially important for GOM, due to its sticky nature and possible losses along the sampling systems. Therefore, to assure traceable comparison of the results from the metrological point of view, more work is required not only on the detectors, but also on the whole sampling system.

In addition, the influence of local Hg source and the variability of the concentrations of Hg fractions makes data interpretation difficult without knowing the exact amount and speciation of Hg released. Comparison between Tekran and Sir Galahad shows that we are still not sure which fraction is

measured by these instruments, as there are big differences in the design of respective sampling systems. Particulate matter seems to play an important factor, as Hg released from it can influence the results of the speciation analysis. The uncertainty of the sampling system has to be determined in the future to obtain a better understanding of what is actually being sampled and whether the corresponding results are comparable.

Several types of passive air samplers (PAS) were exposed and tested at locations near Cement Plant and former Hg mine in Idrija. Passive samplers showed trends in concentrations with time and air Hg concentrations and have the potential as cost-effective method for air Hg monitoring. In general, all applied PAS showed highly variable field blanks. The reason for the high and variable field blanks is unknown and we can only assume that it was due to contamination or ineffective storage conditions. The sample repeatability is another important issue considering all used PAS. Overall, all PAS showed lower variability or contribution of field blanks to results at Idrija Uprava site with high Hg air concentrations. The greatest problem accounted for JSI PAS using gold as absorber is their apparent passivation. Therefore, a modified approach should be made. This approach should include a proper sampling time to avoid passivation of the JSI PAS traps, while the exact conditions should be separately determined experimentally. On the contrary, PSA Amasil traps did not show passivation, but rather low uptake rates and therefore required long deployment times. PAS showed the potential as cheap and effective method for long term monitoring of Hg in air. However, further development of PAS designs, absorbers, analytical method and interpretation of obtained results is necessary to assure correct and accurate data.

Air Hg biomonitoring approach was implemented using transplanted lichens (*Hypogymnia physodes*), and in-situ collected lichens (*Punctelia subrudecta* and *Flavoparmelia caperata*). Lichens for transplantation were collected at Pokljuka (Slovenia) that is considered to be remote and clean area, and then transplanted for different time periods at several locations around Cement Plant Anhovo and Idrija Hg mine area. Lichens showed that are very sensitive to air contamination/pollution. As it was seen in previous studies, concentrations of Hg in in-situ and transplanted lichens well correlate with air Hg concentrations and time of exposure (Figure 7).

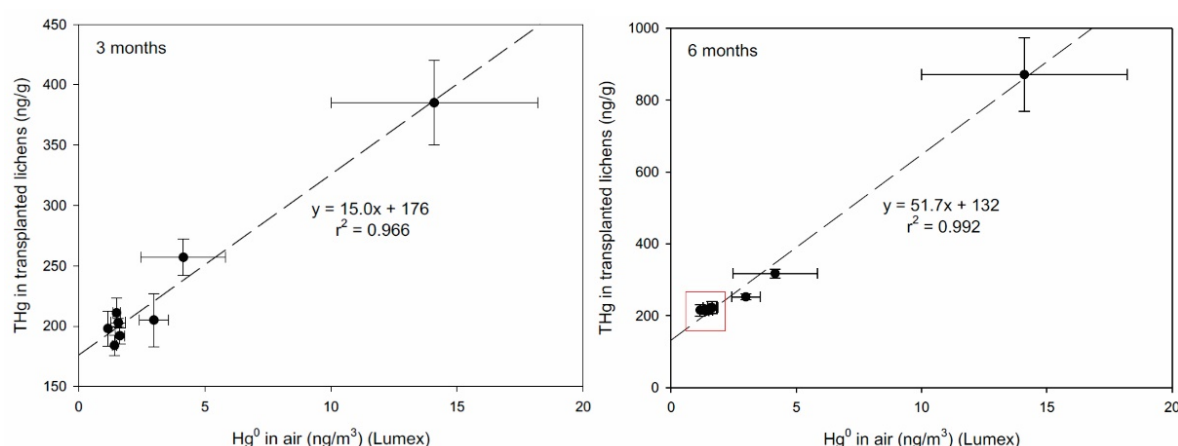


Figure 7. Relation between the amount of total Hg in transplanted lichens following the exposure time of three (left panel) and six months (right panel), and the mean Hg⁰ concentration in the air at selected stations. Error bars represent one standard deviation of measurements.

Variability of obtained results was low and introduce much less measurement uncertainty as for PAS. Therefore, use of epiphytic lichens showed to be prominent and cost-effective method for long term monitoring of Hg in air. To ensure well growth and development of transplanted lichens, and with that stable absorption of Hg from air, sampling and transplantation protocols should be developed.

Estimation of measurement uncertainty and use of proper metrology principles are necessary in all steps, regardless active or passive measurements, or biomonitoring, to assure trustable, accurate, and traceable results.

Final remarks

Good practice guides given in this Deliverable represent a complete overview of the most important findings of the MercOx project. The vast diversity of the methods used and analysis performed in our trying to invent and apply instrumentation, procedures, and analytical protocols for the determination of oxidized Hg in air does not allow writing a simple conclusion. In essence, the good practice guides presented in here are the main conclusions of the entire work performed during this project. Therefore, we would rather like to emphasize the final remarks on the importance of this project and these guidelines in the light of Minamata convention.

The overall goal of the MercOx project was to develop SI-traceable measurements for the monitoring and control of mercury and its different species in gas emission sources and in ambient air. The project wanted to achieve significant improvements in the measurement comparability and uncertainty of Hg measurement results. Traceable calibration methods mainly exist for elemental mercury (Hg^0), but these methods are urgently required also for oxidized Hg species, i.e. Hg(II) , in order to meet the requirements of European Union regulation and the implementation of the Minamata Convention. Therefore, the project aimed at validation and development of traceable oxidized Hg standards and methods for sampling and analysing oxidized Hg species in flue gas emissions and in the ambient air. The measurement of mercury in the atmosphere is recognized as a key indicator for evaluating the effectiveness of the Minamata Convention, a global treaty of the United Nations Environment Program to protect human health and the environment from the adverse effects of mercury. In the future, the results of this project will definitely improve the measurement capabilities of environmental institutions, creating a reliable and consistent basis for reporting mercury emissions, and allowing the legislative levels of control required by the Minamata Convention to be safely met.

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MercOx Deliverable 2. Certification protocol for confirming the output of liquid evaporative HgCl_2 generators.

MercOx Deliverable 3. Report on the comparison of different methods for measuring oxidised Hg (Hg(II)); including methods to accurately compare total mercury (Hg^{tot}) concentrations in generated standard gases for elemental mercury Hg^0 and oxidised mercury (Hg(II)).

MercOx Deliverable 4. Report on bulk species-specific isotope ratio measurements to determine Hg migration pathways, its origin and species interconversion including the use of biomonitors as passive monitors for Hg speciation and isotopic signatures representing the origin and fate of atmospheric Hg.

MercOx Deliverable 6. Optimised and validated sampling methods for gaseous Hg species using traceable reference standards for Hg(0) and Hg(II) .

MercOx Deliverable 7. Validation report on the field testing of new and existing methods for on-line and sorbent-based Hg measurements in stack emissions.

MercOx Deliverable 8. Validation report on the field testing of new and existing methods for on-line and sorbent-based Hg measurements in the atmosphere.

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Appendix A1. Strategies for total Hg and Hg species determination

KCl (as denuders), carbon (as traps) and acids/oxidizing reagents (as impinger solutions) are among the most frequently used media for trapping and preconcentration of Hg and Hg species prior to their quantitative determination. In this section are described the strategies for the determination of Hg^{tot} from the above listed media, as well as the Hg species interaction with the sorbents and other materials used in traps and denuders. Species trapping efficiency and interconversion is discussed as well.

A1.1. Determination of total Hg mercury in carbon rich materials

The determination in Hg in the produced by CENAM coal candidate CRM was described in D3, using the methods developed in A2.1.2. However, employing the reported by LGC MW digestion procedure with HNO₃ acid and H₂O₂ did not result in complete digestion for most of the real trap samples from Marl power plant (see D7) even with sample weights as low as 50 mg. Therefore, LGC has further adapted the developed in A2.1.2 method. The improved digestion procedure includes the use of sulphuric acid pre-mixed with nitric acid to facilitate higher temperature digestion and lower the vapour pressure in the MW digestion vessel. With ratio of 7:3 v/v (HNO₃:H₂SO₄) approximately 0.2 g of activate carbon (iodinated AC) and SRM materials (NIST SRM 2445, and 2448) were completely digested without intermediate venting (pressure <100 bar at all times) and loss of Hg species. The SRM values and the spike recoveries of two spiked AC samples were all within ±3% of the expected values. The HNO₃/H₂SO₄ MW digestion conditions are listed below in Table 1.

Table 1. Single stage MW assisted digestion program suitable for digestion of up to 0.2 g of AC samples with H₂SO₄/HNO₃ acid mixture.

Stage	Time [min]	Temperature [°C]
1. Pre-digestion; slow linear increase from ambient temperature	25	200
2. Digestion of reactive compounds, less steep ramp	15	220
3. Digestion of bulk of the matrix, temperature hold	45	220
4. Cooling step	ND	50

A1.2. Determination of Hg trapped in activated carbon

A1.2.1. Species conversion during the Hg trapping and thermal desorption from activated carbon materials using isotopically enriched Hg standards

The species conversion effect during the trapping and desorption of Hg from selected activated carbon was investigated. For that purpose, a Lumex PYRO-915+ thermal decomposition attachment (referred below as Lumex TD) was coupled to ICP-MS/MS (tandem mass spectrometer) using the forth-concentric tube torch interface, developed for this project and described in details in Deliverable 3. The standard thermal desorption program had to be modified to fractionate Hg⁰ and Hg(II).

For this purpose, initial experiments were performed to establish the relation between the applied electric potential (in volts) and the resulting temperature increase (in °C) in the desorption cell as a function of time. A K-type thermocouple was integrated into the desorption spoon by Lumex and used with continuous data logger. The data was recorded with 0.2 Hz frequency (>150 data points per measurement). Results are present in Figure 8.

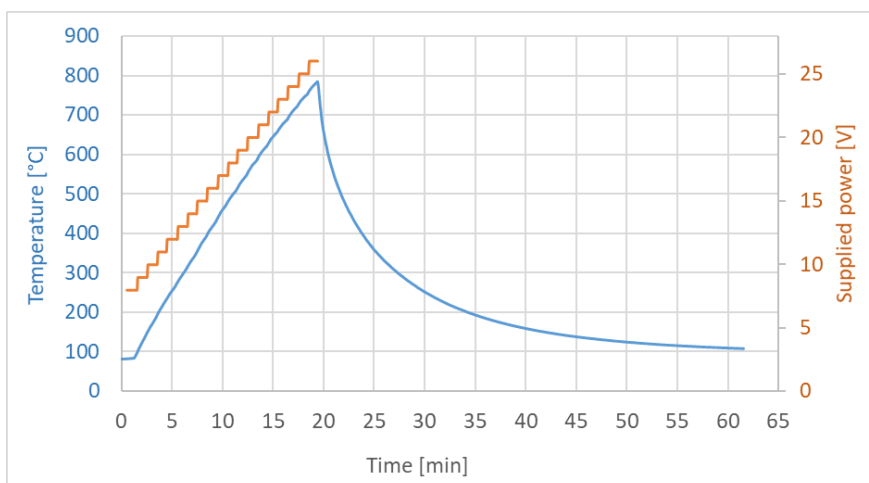


Figure 8. Thermal scanning curve and desorption chamber cooling of Lumex PYRO-915+ module.

Lumex linear scanning program was then tested with activated carbon materials, including non-halogenated and iodized AC. An in-house prepared carbon trap in demountable quartz tube (1/8" ID PEEK fittings) was filled with AC materials and capped with glass wool. Hg^0 was loaded on the trap through a continuous Hg^0 gas (in Ar 1 L/min) using HGX-200 Cold Vapour System (CV). The performance of the CV system coupled to the ICP-MS/MS was estimated before loading the traps. A typical response of the ICP-MS coupled to CV, which output is directed through the TD module, is presented in Figure 9 and the trap loading conditions in Table 2. The CV system was then used to load Hg^0 on AC traps.

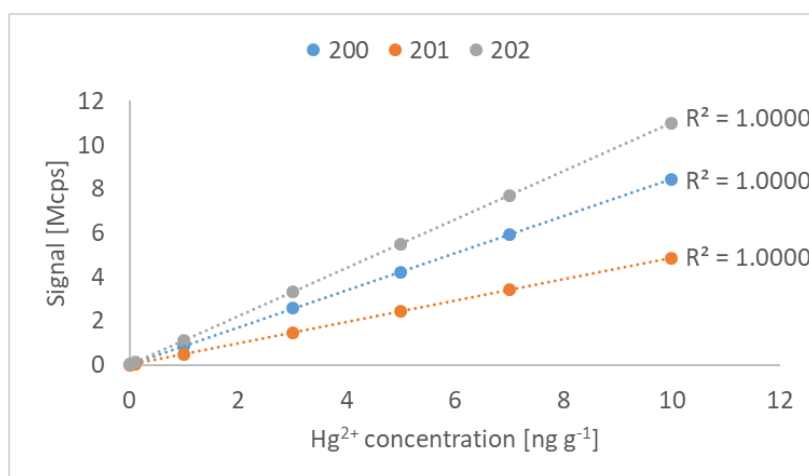


Figure 9. Linearity of CV-Lumex Pyro-ICP-MS/MS response in the range 100 pg/g to 10 ng/g.

Table 2. Trap loading conditions for CV-TD-ICP-MS/MS determination.

Parameter	value	unit
Solution pump speed	0.1	rps
Solution concentration	0.1	ng g ⁻¹
Solution flow rate	0.3	g min ⁻¹
Carrier gas flow	0.5	L min ⁻¹
Loading time	5	min
Loaded Hg	150	pg
Hg concentration, gas	60	ng m ⁻³

Immediately after the loading, a natural abundance Hg(II) was spiked directly on the pre-loaded with Hg⁰ AC trap material. For that purpose, 10 µL standard solutions of HgCl₂ in MeOH with concentration between 6 and 12 ng g⁻¹ were used. The spiked material was then analysed by using LUMEX TD-ICP-MS/MS with linear thermal scanning (Figure 8). Unfortunately, complete species coelution was observed. The thermal program was further modified (Table 3) to produce two plateauing regions around 50-100°C and 300-370°C (Figure 10).

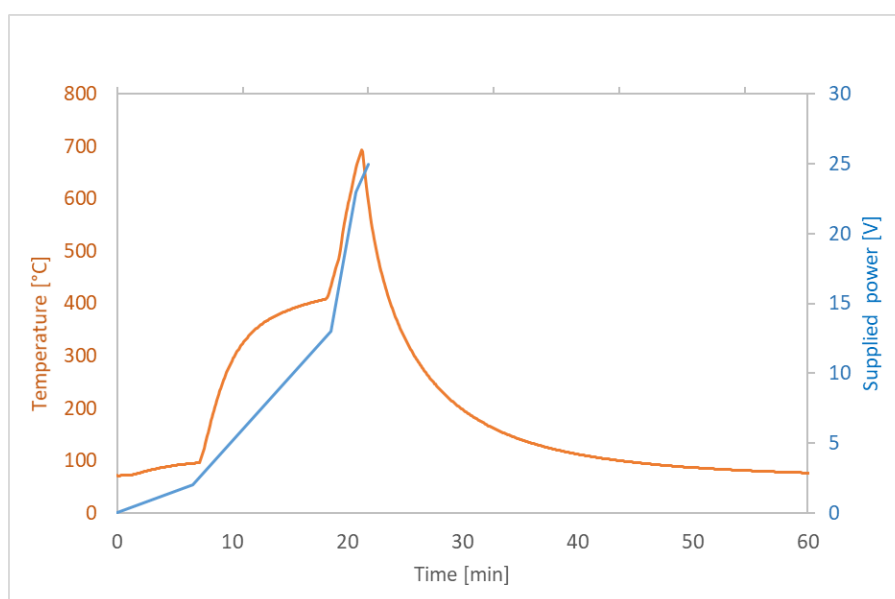


Figure 10. Thermal profile of TD evaporator chamber with time. Total gas flow 0.8 L/min Ar.

Table 3. Thermal desorption program for Hg species fractionation.

Stage	Duration [s]	Relative time [min]	Ue (V)
Initial	--	0	0
1	360	6	2
2	660	17	13
3	60	18	18

4	60	19	23
5	60	20	25

With this program a good linearity ($r^2 > 0.998$) of the LUMEX TD-ICP-MS response was found for Hg(II) when spiked as solution in ranges from 60 pg up to 20 ng Hg(II) but the linearity of the Hg⁰ was impaired when loaded with the use of the CV system. The later could originate from flow variation in the loading setup and incomplete activated carbon recovery from the glass wool, which affects the Hg⁰ recovery. Therefore, results obtained by external calibration can only be considered qualitative with this setup.

To differentiate between Hg⁰ and Hg(II) in the thermogram, a 91.95% ¹⁹⁹Hg enriched Hg(II) solution in MeOH was used to spike Hg⁰ loaded activated carbon (non-halogenated). The trap material was then subjected to TD program as described in Table 3 and the isotopic profile was recorded with ICP-MS/MS monitoring four Hg isotopes. The results are presented on Figure 11. It should be noted that the Hg⁰ content is not designated on the figure due to the non-quantitative Hg⁰ recovery, as discussed above.

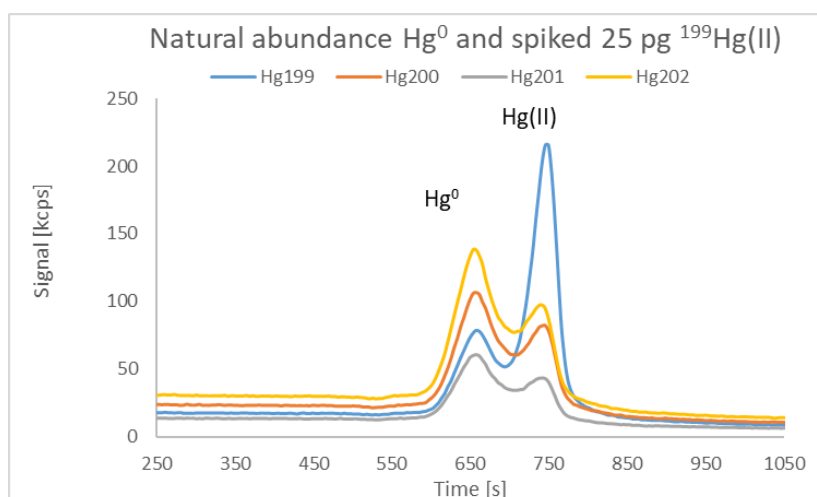


Figure 11. Hg species conversion during trapping and thermal desorption using enriched ¹⁹⁹Hg(II).

As evident from the figure, there is significant transformation of Hg⁰ to Hg(II), which is also confirmed by the distorted isotopic ratio for the Hg(II) peak, while for the Hg⁰ peak, the ratios at the peak maximum as expected match the natural abundance. The latter is a clear indication that Hg(II) did not reduce to Hg⁰ but the Hg⁰ oxidized to Hg(II). These results agree with the monitored Hg⁰ oxidation by Sasmaz et. al. In contrast to the cited work where air (containing oxygen) was used and oxidation upon reaction with air was considered, the carrier gas in our experiments was inert (argon) and it is clear that the Hg⁰ oxidation to Hg(II) is heterogenic. Heterophase oxidation is probable upon an interaction with the activated carbon material. The expected and practically obtained isotope ratios are presented in Table 4. Similar experiments performed with iodised activated carbon. However, on contrast to the non-halogenated AC, the results showed complete Hg⁰ oxidation to Hg(II), i.e. only one peak.

Table 4. Isotope ratios relative to ^{200}Hg for Hg^0 and Hg(II) showing Hg^0 oxidation.

Isotope	Experimental IR	Expected IR
Hg^0		
199	0.73	0.73
201	0.59	0.57
202	1.4	1.3
Hg(II)		
199	3.6	19
201	0.50	0.13
202	1.0	0.15

The monitored differences between experimental and theoretical isotope ratios for the Hg^0 peaks (Table 4) are minimal and within the expected mass bias of the measurement. This work shows that there is species conversion during the trapping and by use of species specific IDMS with Hg^0 and Hg(II) enriched in a different isotope, this conversions can be tracked and potentially corrected for. However, each material and conditions are unique and a general correction factor cannot be recommended to be applied and used with analysis which do not employ isotope dilution calibration.

The results from this study have demonstrated that the application of thermal desorption for speciation analysis of mercury, trapped on activated carbon is not always possible and not applicable with the typically used atomic absorption and atomic fluorescence detectors, unless the species are selectively trapped and therefore temporary resolved.

A1.2.2. Investigation of the species trapping and desorption on activated carbon traps

A thermal desorption system (Markes TD100-xr) was coupled to GC (Agilent 6890) followed by ICP-MS/MS (Agilent 8800) detector for the determination of the different Hg species, selectively trapped on laboratory prepared traps. For that purpose, the typical GC split/splitless injector carrier and septum purge gas lines were cut and directed to the inlet of the TD system. The TD output was directed to the GC through 0.32 mm capillary (inert silica) and to ICP-MS as one-piece capillary with total length of approximately 3.2 meters. The whole sample pathway was heated to 250°C down to 1 mm away from the end of the heated (250°C) ICP-MS injector. This setup was required to avoid species condensation (especially Hg(II)) on the cold surface of the tubing since PFA and PTFA materials could not be used with the GC-ICP-MS setup. Sample traps were prepared from commercially available quartz tubes (Markes Ltd., 4.5 mm ID, 6.0 mm OD, 9 cm length) by filling them with approximately 0.25 g activated carbon between 0.5 cm glass wool (Merck, PN20384) plugs. Iodised blank activated carbon (AC500) was used for that purpose. The trap schematics and flow directions are present on Figure 12.

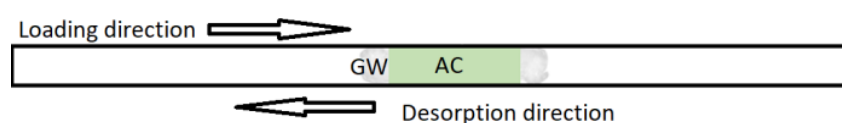


Figure 12. Schematic diagram of carbon trap with loading and desorption flow directions. GW- glass wool, AC – activated carbon.

A thermal desorption program consisting of heating to 220°C and hold (5 min), followed by 380 °C (10 min) and finally 400°C (15min). Three Hg isotopes were monitored (200, 201 and 202-Hg) with 30 min acquisition and 1 second per data point. The first experiment was aimed in the investigation of Hg⁰ trapping and desorbing profile on a carbon trap section. For that purpose, 75 µL gas from bell-jar standard was injected on the manually prepared trap. The trap was then purged with 160 mL of He for 2 min (80 mL min⁻¹ flow). The trap was loaded and analysed with the TD-GC-ICP-MS/MS setup. Similar to what was monitored with LUMEX TD-ICP-MS/MS setup (see section 0) two distinctive peaks were found, with the second one (Hg(II)) eluting at retention time 7.8 min (480 sec, Figure 13, left panel). However, since halogenated AC was used in this case, the second peak (Hg(II)) was more abundant due to the expected oxidation (see section 0). Similar experiment was performed with 1 ng Hg(II) instead of Hg⁰. In this case 1 µL of 1 µg mL⁻¹ Hg(II) as HgCl₂ solution in methanol was injected into the entrance of trap, before the glass wool section (Figure 12). Again, 2 minutes of purging with 80 mL min⁻¹ He followed before the trap was loaded and analysed by TD-GC-ICP-MS. This time, instead of one clear peak as expected from the LUMEX TD-ICP-MS/MS experiment with spiked AC (Figure 11, ¹⁹⁹Hg trace), the Hg(II) mostly appeared at much earlier retention time (split peak between 120 and 172 sec) and at the expected for Hg(II) time of approximately 480 sec. A potential reason for this is the significant absorption of Hg(II) on the glass wool (GW) section as demonstrated in section 0. Further, since the desorption direction is opposite of the loading and the glass wool interaction with Hg(II) is weaker than with the AC, the adsorbed Hg(II) in that section, as expected, is desorbed at lower temperatures and therefore earlier times. However, both set of experiments were performed in clean He gas (4N+ purity) and have to be verified in field conditions with real flue gas matrix, where the species absorption can be higher, lower, or even not present. These experiments are planned as part of the D7 deliverable tests using speciation traps. These traps consist of glass wool sections, acid gas scrubber (AGS) section, KCl section and finally AC sections which all could absorb Hg(II). If the results from these tests confirm those from the model experiments presented in this deliverable, then the structure of the so-called speciation traps has to be reconsidered.

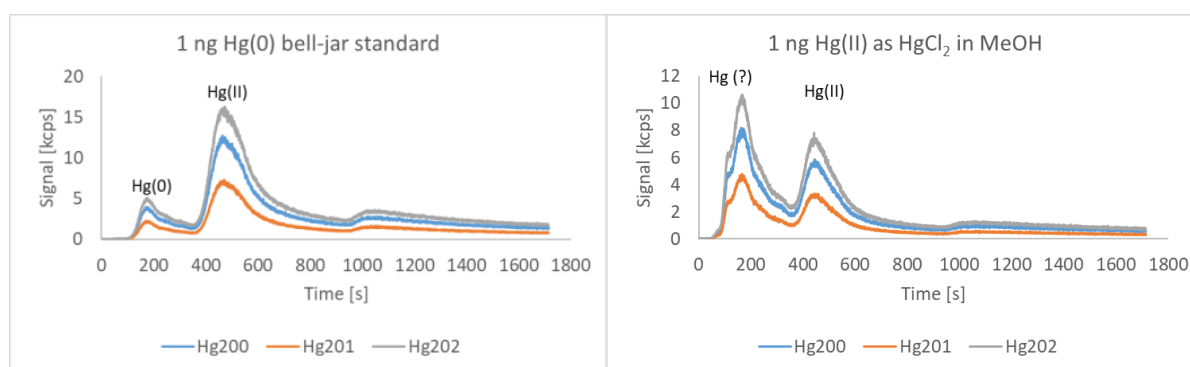


Figure 13. Thermogram of 1 ng Hg⁰ (left) and 1 ng of Hg(II) (right) loaded on AC trap. Determination by TD-GC-ICP-MS.

Based on the shape of the peak at ~170 s, it can be expected more than one adsorption site for Hg(II) be present (e.g. glass wool and quartz tube walls, as reported in the D3 of the project). The expectations were confirmed when injecting higher amount of Hg(II) where clear peak splitting was evident. The experiments were repeated and peak heights matching was 98%. This is also evident from the experiments with ¹⁹⁹Hg(II) enriched and natural abundance Hg⁰, 1 ng g⁻¹ each, sequentially loaded

on the trap. The data is present at Figure 14. The first peak split is present just for Hg(II) and therefore this specie only has absorbed at the beginning of the trap.

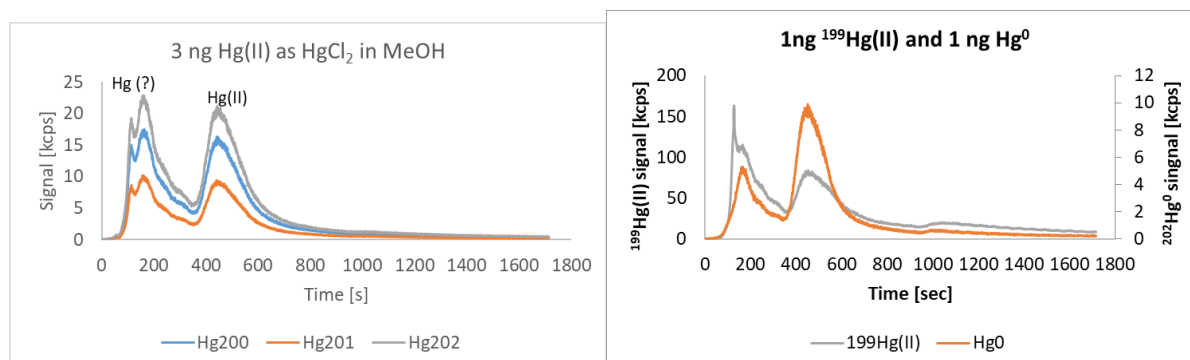


Figure 14. Thermogram of 3 ng Hg(II) loaded on AC trap (left) and 1 ng of each ¹⁹⁹Hg(II) and nat-Hg⁰, right. Determination by TD-GC-ICP-MS.

The experiments presented in sections 0 and 0 provide conclusive evidence of Hg⁰ and Hg(II) species absorption on variety of surfaces and materials and is dependent on multiple parameters like surface type, re-use of material, gas flow rate and Hg species concentration. Moving towards optimal parameter conditions for one of the species (e.g. either Hg⁰ or Hg(II)) have been demonstrated to adversely affect the trapping and recovery of the other. In general, a good practice for both species is to minimise the contact surface areas and avoid cold sampling spots or media that can trap the species. These include the currently frequent used materials like quartz and glass, unless the entire portion trap can be heated and therefore Hg desorbed. However, the species conversion and incomplete trapping at the speciation trap sections have to be overcome by other means.

A1.3. Good laboratory practice of measurement of total Hg in coal using CV-ICP-AES

Due to human health problems arising from mercury emissions and releases to the environment, as an example the carboelectric plants, it is necessary to develop and validate methods for measuring mercury in environmental samples coming from the emissions of the carboelectric plants, to do that, it is necessary to apply good laboratory practices (GLPs) and have certify reference materials (CRM), which are metrological tools to ensure reliable measurement results and provide traceability to the International System of Units (SI), broadening the current outlook in the linking and dissemination of scientific research, thus contributing to generate new approaches or knowledge in science and justifying the need to unify Mexican legislation with existing international standards. The Centro Nacional de Metrología (CENAM) has developed and validated the method of measurement of total mercury in coal by means of acid digestion of accelerated reaction assisted by microwave oven and cold vapour generation system coupled to inductively coupled plasma atomic emission spectrometry (CV-ICP-AES), with the intention of provide a guide of GLPs and certified reference material of mercury in coal, to support to the laboratories that measure mercury in coal samples, in that way, CENAM support the method validation of mercury, and to expand their service capabilities in the metrology field, to establish the traceability to the SI units.

This Section describes some recommendations as good laboratory practices for the measurement of total mercury in coal, to optimize the procedure for sample preparation and measurement of mercury, using the cold vapour generation system coupled to atomic emission spectrometry with inductively coupled plasma (CV-ICP-AES).

A1.3.1. Theoretical principles of the measurement method CV-ICP-AES

The measurement method external calibration with standard addition using a CRM and cold steam system coupled to inductively coupled plasma atomic emission spectrometry (EC-SA-CV-ICP-AES), where the measurement of mercury is carried out using the cold vapour generation system with the flow injection system, which consisted in a reaction cell (Figure 15), where it is combined with the tin chloride reducing solution (SnCl_2), which function is to reduce mercury Hg^{2+} to Hg^0 , the mercury in gas phase is transported from the separation chamber of the reaction cell to the injection system of the atomic emission spectrometer, to be directed to the inductively coupled plasma source, where mercury atoms by electronic transitions effects, emit radiation at a given wavelength, such radiation is proportional to the amount of mercury atoms present in the sample (Jiménez et al., 2020).

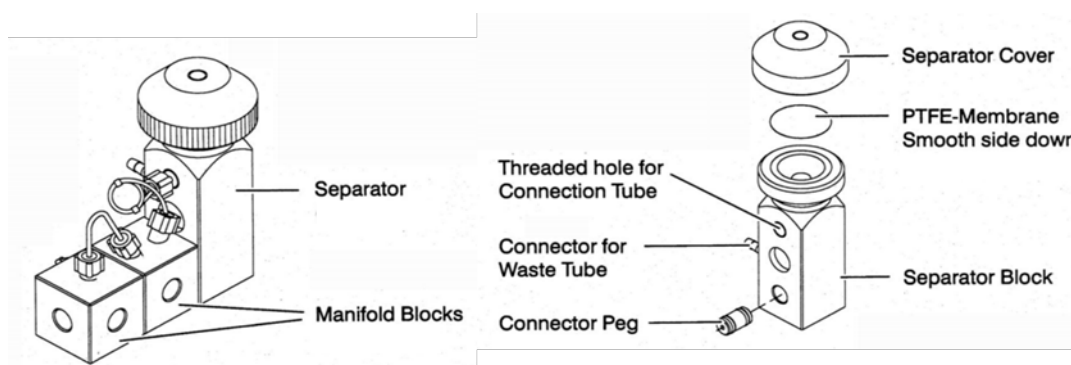
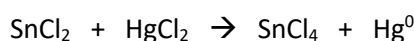


Figure 15. Reaction cell.

A1.3.2. Traceability of measurement results

In order to ensure the traceability to the SI units of measurement results, it is important to include in the development of the working procedure the following aspects:

- a) Use and document the use of certified reference materials (CRM) used as calibrators and for quality control.
- b) Verification of the performance and metrological traceability of measuring instruments. The measuring equipment, analytical instruments and other devices must satisfy the requirements of the measurement methods of the laboratory and the relevant metrological specifications for use, as well as be periodically verified, qualified and/or calibrated to ensure their correct functioning and performance, based on the following concepts:

- Metrological confirmation of physical measuring equipment and other devices, based on the standard UNE-EN ISO 10012:2003, which specifies generic requirements and provides guidance for the management of measurement processes and for metrological confirmation of the measurement

equipment used to support and demonstrate the compliance of metrological requirements. Metrological confirmation should be performed for analytical balances, microwave oven and ultrasonic bath.

- Verify that equipment meets the metrological requirements for its intended use and document in control charts to observe and analyze its behavior over the time.

- *Equipment Qualification of Analytical Instruments (EQ)* (Bedson & Sargent, 1996), to comply with the standards: ISO/IEC 17025:2017 (section 6.4) and ISO 17034:2016 (sections 6.3 and 7.7). EQ is applied to equipment and instruments for measuring the amount of the substance, and for the measurement of mercury the inductively coupled plasma atomic emission spectrometer (ICP-AES) is used, so EQ must be performed in the following stages: Operational qualification (OQ) and Performance Qualification (PQ), to ensure that the atomic emission spectrometer works properly and meets the appropriate specifications for its routine use.

- To evaluate the performance qualification is necessary, the reviews and tests to demonstrate the satisfactory performance of the ICP-AES based on the supplier's specifications. In the performance qualification is included two tests:

- I. The first test is System suitability checks, which is made with control standards. For ICP-AES is made by using Mn solutions at mass fractions of (1 and 10) mg/kg. Perform the measurements at a wavelength of 257.610 nm, in axial mode for (1 mg/kg) and radial mode for (10 mg/kg), perform 3 times the measurement and average the intensity value (I , cps), the value obtained for both measurements must be greater than, or equal to 300,000 cps, this value must be validated because it can vary according to the brand and model of the equipment used.

- II. The second test, the sensibility test is performed with measurements of a solution of mercury to a nearby content to mercury in the sample to be measured. During this measure observe the intensity (I , cps), signal in the equipment, which value obtained is used as a parameter that will be used as a quality control reference test, to be carried out prior the measurement of the analysis samples.

Document both tests in control charts to observe and analyze behavior over the time, which give information on the performance qualification (PQ).

c) Development and validation of the measurement method. Development of the method of measurement of total mercury in coal, by acid digestion of accelerated reaction assisted by microwave oven and external calibration with standard addition with of cold vapour generation system coupled to inductively coupled plasma atomic emission spectrometry (EC-SA-CV-ICP-AES), could be done as described in the manual of the equipment.

- The method development of mercury measuring using EC-SA-CV-ICP-AES is performed by carrying out variations in different instrumental parameters, intending to select those in which the smallest variation is obtained, without compromising the sensitivity of the instrument signal. Therefore, it is recommended to make the necessary adjustments in the instrumental conditions mentioned in Table 5, until favourable conditions of measurement are obtained. The values recorded in the table are for reference. Therefore, they must be verified in the manual of the equipment, because they may vary according to the brand of equipment used. For mercury, the instrumental parameters should be done in axial mode, as it is recommended for low levels.

Table 5. Instrumental parameters.

Parameters	Values
Element / wavelength (λ)	Hg / λ (253.652 nm)
Plasma flow (L/min)	12
Auxiliary gas flow (L/min)	0.2
Nebulizer gas flow (L/min)	0.70
RF power (W)	1500
Read mode	axial
Integration Time (s)	(5 - 10)
Delay time (s)	30
Points per peak	3

- The method validation for measuring mercury using EC-SA-CV-ICP-AES is highly recommended to use the Eurachem Guide, 2014. Where the principal performance characteristics that must be carried out are: limit of detection and limit of quantification, working range, analytical sensitivity, trueness, ruggedness and measurement uncertainty.

A1.3.3. Good laboratory practice for measuring mercury in coal using EC-SA-CV-ICP-AES

The measurement of total mercury in coal sample is highly complex due to the characteristics and properties of the matrix, therefore, it is recommended to follow all the necessary guidelines for the correct planning and execution of the procedure for sample preparation and instrumental measurement of mercury. The analytical challenge is to consider as important each of the stages established in the development of the working procedure, with the intention of avoiding cross-contamination and minimizing errors that ensure the reliability of the method, which will allow reliable measurement results to be asserted with adequate associated uncertainty.

Laboratory and work requirements

- The laboratory must be organized and verify that it complies with all materials, equipment and reagents to operate in a manner that meets the requirements for the development of the procedure for the preparation of the sample and instrumental measurement of mercury.
- Verify that the environmental conditions of the work laboratories, including lighting, energy sources, temperature, humidity and air pressure, are within the metrological requirements and be appropriate for the functions and operations carried out, as described the suggestions in Table 6. The laboratory should ensure that environmental conditions are reviewed, monitored and documented and do not invalidate the results or adversely affect the quality of the measurements.

Table 6. Suggested environmental conditions of laboratories.

Critical parameters	
Temperature	$(20 \pm 2) ^\circ\text{C}$
Relative humidity	$(50 \pm 10) \%$
Atmospheric pressure	Positive pressure with a delta of (5 to 12.5) Pa greater with respect to the corridor
Air quality	-With absolute HEPA filters, with efficiency of 99.97 % in the ducts, with high volume terminal diffusers, that allow to maintain a laminar flow. -Hybrid system with HEPA filters Class ISO 7/5. -Laminar flow (0.5 m/s)
Security parameters	
Extraction	With localized extraction using elephant trunk tube duct systems (dust extraction).
Ventilation	Comfort standard. In sample preparation laboratories (20 to 30) air/hour changes are required.
Illumination	700 lx/m ² (100 lm/ft ²)
Maximum permissible sound levels	Less than 45 dB in 8 hours on a working day, no instruments installed and air conditioning running.
Environmental conditions should be reviewed and controlled in an automated manner, as well as documented in control charts to observe and analyse the behaviour of conditions over the time.	

- Select the staff for the development of the work procedure and ensure precise assignment of responsibilities.
- Establish the appropriate working procedure to avoid exposure and contamination of the sample.
- Establish appropriate safety and hygiene measures for the development of the working procedure, considering the characteristics and properties of coal and mercury, with the intention of safeguarding the integrity of the analyst. Thereby it is important to wear a lab coat, safety shoes, glasses and gloves. It is necessary to use acid vapour mask during the acid digestion stage of the sample.
- It is important to document all activities that involve the development of the working procedure, especially those that are critical such as: sample weighing, addition of reagents, acid digestion and mercury measurement.
- Establish the procedure for the appropriate final disposal of the various types of waste (hazardous and non-hazardous), which are generated at each stage of the development of the working procedure. Mercury residues should be deposited in amber borosilicate containers.
- All activities related to the preparation of acid solutions and addition of acid reagents shall be carried out within the extraction hood.

Material and reagents

- Due to the characteristics and properties of mercury, amber borosilicate bottles should be used for light protection. The cleaning of the bottles is highly recommended carried out as follows:

- a) Clean the bottles with neutral phosphate free detergent and rinse at least 5 times with distilled water (18.2 MΩ cm resistivity).
- b) Fill the bottles with a 20 % solution of hydrochloric acid ϕ_B (HCl), cover the bottles and let stand for 12 hours in the extraction hood.
- c) Rinse the bottles 5 times with distilled water.
- d) Fill the bottles with distilled water, put the bottle caps and let stand for 12 hours.
- e) Subsequently rinse the bottles 3 times with distilled water. The first rinse dispose as waste.
- f) Dry the bottles in a heating oven at a temperature between (80 - 90) °C for 8 hours.
- g) Dry the lids in a heating oven at a temperature between (60 - 70) °C for 4 hours.
- h) Let the bottles and lids cool at room temperature in laminar flow hood and store in hermetically sealed polyethylene bags until use.

- The cleaning of the digestion vessels using the microwave oven is carried out using the closed system under temperature control conditions, as described in the following procedure:

- a) Clean the vessels with neutral phosphate free detergent and rinse at least 5 times with distilled water (18.2 MΩ cm resistivity).
- b) Add 5 mL of concentrated HNO_3 to the vessels. Cover the vessels, place the jacket, and place them on the carousel.
- c) Perform the cleaning in a microwave oven, using a temperature ramp, under the conditions described in the digestion method in Table 7.

Table 7. Temperature method for the material cleaning process in a microwave oven.

Steps	Power (%)	Ramp (min)	Temperature (°C)	Holding (min)
1	100	45	150	30

- d) Let the vessels cool, dispose the acid in the residue container, rinse with distilled water and discard in the residue container, then rinse with distilled water and dry at room temperature under a laminar flow hood.
- e) Store the material in hermetically sealed bags to avoid contamination with particles in the environment.

- Polyethylene bottles used to prepare the tin chloride reducing solution (SnCl_2), the cleaning procedure is as follows:

- a) Clean the bottles with neutral phosphate free detergent and rinse at least 5 times with distilled water (18.2 MΩ cm resistivity).
- b) Fill the bottles with 20 % nitric acid solution ϕ_B (HNO_3) and leave to stand for 12 hours in the extraction hood.
- c) After a period of time, rinse with distilled water and discard as waste, rinse with distilled water and then take the bottles with distilled water and leave to stand for 12 hours.
- d) Discard the water from the bottles and make 5 rinses with distilled water and dry at room temperature in a laminar flow hood.
- e) Store the material in a closed place or sealed bags to avoid contamination with particles in the environment.

- For the measurement of moisture in coal samples, borosilicate weighing low form (50 × 30) mm bottles are used, the cleaning procedure is as follows:

- a) Use phosphate free neutral detergent for cleaning and rinsing at least 5 times with distilled water (18.2 MΩ cm resistivity).
- b) Dry the weighing bottles inside a heating stove at a temperature of $(110 \pm 2)^\circ\text{C}$, for a period of 2 hours.
- c) Remove the weighing bottles at room temperature in a laminar flow hood and place them in a desiccator (with the lid tilted over the mouth of the filters), for 60 min until reaching room temperature $(18 - 22)^\circ\text{C}$.

- All chemical reagents must be of high purity, preferably the acids used must be double-sub-boiling distillate quality:

- Nitric acid (HNO_3)
- Hydrochloric acid (HCl)
- Hydrofluoric acid (HF)
- 30 % hydrogen peroxide (H_2O_2)
- Hydroxylamine hydrochloride ($\text{NH}_2\text{OH HCl}$)
- Boric acid (H_3BO_3)
- Tin chloride (SnCl_2)
- CRM "Mercury spectrometric solution".

- The water used must be deionized or double-distilled quality.

- As far as possible, ensure that the control CRM to be used is alike to the coal matrix.

- It is important to verify the expiration date of the reagents before use, as well as ensure that they comply the storage conditions indicated by certificate. Similarly, it is important to assess the quality of water and reagents used.

- It is advisable to use tin chloride (SnCl_2), with no more than two years of life. It is important to avoid its hydration. If the reagent has approximately more 6 months or one year without being used, the superficial part must be removed and discarded; and always after use it, it should be stored in the absence of light in an inert atmosphere adding high purity argon gas before closed the cap, then sealed.

- All prepared solutions must be identified with labels containing specific information such as: preparation date, solution name indicating the chemical reagent, name of the analyst that prepared it and the content value of the substance.

- A nitric acid 2 % aqueous solution [ϕ_B (HNO_3)] must be prepared for use as: matrix of sample, blank and/or blank calibrating sample, as well as rinsing solution. It is recommended to prepare enough solution of 2 % nitric acid and use it on throughout the measurement process, to keep same conditions of the process and to avoid as far as possible, to change the solution, this is done with the intention of avoiding contamination and variations in the measurements of blanks and samples, due the contamination impact caused by reagents and solutions.

- The Hg(II) usually is kept stable in an oxidant solution, but for measuring it, it is important to minimize the excess of oxidant substances content, which minimize the signal of Hg in the instrument (ICP-AES). A hydroxylamine chlorate aqueous solution of ϕ_B ($\text{NH}_2\text{OH HCl}$) of 20 % is highly recommended and required to remove the excess of oxidizing agent in samples for its measurement. The solution must be prepared in an amber borosilicate flask and preserved under cooling conditions between (4 - 10) °C. The proper amount of the solution must be prepared, to take care of any instability of this solution.

- The reducing tin chloride solution (SnCl_2) is prepared in a ϕ_B (HCl) of 3 % hydrochloric acid aqueous solution matrix in a polyethylene bottle. The proper amount of the solution to use in the measurement must be prepared, due the instability of this solution. This solution must be prepared fresh every day for use it.

- Hydrogen peroxide (H_2O_2) must be stored under cooling conditions between (4 - 10) °C and absence of light.

- The presence of high silicon content in the coal sample must be removed, the recommendation for removing the silicon is to use in excess hydrofluoric acid, the excess of hydrofluoric acid could be neutralized with boric acid aqueous solution γ (H_3BO_3) of 45 g/L, which complexing the fluorine, forming tetrafluoroboric acid in solution. The boric acid solution should be prepared with distilled water at 70 °C of temperature in a polyethylene bottle and store it at room temperature. The proper amount of the solution must be prepared, to take care of any instability of this solution.

Sample preparation

- Studies are required to determine the size of the coal sample. The studies must be conducted varying the size of the sample and determine the smallest amount of the sample in which mercury can be measured, as well as a compromise, to determine the largest amount of the sample, to ensure the least signal instrumental variation during the Hg measurements.

- It is important to consider during the process of weighing the coal sample directly into the reaction vessels for the microwave oven, to place the sample directly on the bottom of the vessel and avoid the adhesion of the sample on the walls.

- Immediately after the coal sample has been taken for analysis, the sample should be taken for moisture measurement. It is suggested to take 1 g of sample and weigh directly on the weighing bottle previously taken at constant weight. It is important to select weighing bottles of suitable size like (50 × 30) mm, so that when the sample is placed, the height of the sample will not be greater than 1 cm.

- It is advisable to use more than one desiccator if more than six samples, CRMs for control and blank samples are going to be measured, then it is recommended to use at least three desiccators in order to have enough space and have a better efficiency of lost moisture.

- Carry out the measurement of moisture n samples within a heating oven at a temperature of $(110 \pm 2) ^\circ\text{C}$ for at least a period of 2 hours and cooling at room temperature in a desiccator for a period between (45 to 60) min. Perform the measurements until reaching the constant weight criterion: it is suggested to use: (0.0001 or 0.001) g, which depend of analytical balance having in the laboratory and the uncertainty that is needed.

- During the measurement of the moisture of coal samples it is suggested to place the weighing bottles in the same position in the desiccator and in the heating oven, as well as apply at mass values of the samples the correction indicated by certificate of the balance and the buoyancy correction.

- Due to the characteristics and properties of the coal, it tends to agglomerate, so prior to the acid digestion stage, it is suggested to apply a sonication stage in ultrasonic bath. This step must carry out after weight the sample in reaction vessels and placed them in extraction fume hood, then have the addition of 6 mL of nitric acid (HNO_3), then take the samples to ultrasonic equipment, then applying agitation for approximately 45 min. It is very important apply a uniform sonication as well as all samples being subjected to sonication at the same time, to ensure the breakup of the agglomeration of the coal and in order to moisturize the coal particles to achieve a total absorption of the acids during acid digestion.

- It is very important to add the same amount of acid reagents to the samples, to ensure the complete acid digestion of the matrix in them. It is suggested for 0.1 g of coal sample to use 5 mL of HCl, 2 mL of HF, 4 mL of H_2O_2 and 0.5 mL of H_3BO_3 solution (of 45 g/L), close the reaction vessels under pressure and carry out digestion acid with microwave accelerated reaction system.

- The digestion acid of accelerated microwave-assisted reaction is performed in order to have the mercury in solution and to facilitate the stage of introduction of the sample to the measuring instrument (CV-ICP-AES). The acid digestion process involves taking care to keep under control the conditions of temperature, pressure and time during the acid digestion, in order to allow the mercury to be in total solution. First, it is highly suggested to apply as a good laboratory practice, a pre-treatment stage as for example see Table 8, and then followed by several digestion stages as you can see as example the Table 9. The pre-treatment acid digestion is very important, due to the coal sample is very reactive at low temperature and because of the above, the pressure is rapidly increased due the presence of high level of carbon content. Therefore, it is important to keep these conditions under control in order to prevent the rupture of the protective membranes of the reaction vessels, to prevent mercury loss through.

Table 8. Instrumental conditions of pre-treatment in microwave oven.

Steps	Max power (W)	Power (%)	Ramp (min)	Pressure (psi)	Temperature (°C)	Holding (min)
1	1600	100	60	250	120	40
2	1600	100	40	280	150	60

Table 9. Instrumental conditions of digestion in microwave oven.

Steps	Max power (W)	Power (%)	Ramp (min)	Pressure (psi)	Temperature (°C)	Holding (min)
1	1600	100	60	250	160	60
2	1600	100	60	300	180	60
3	1600	100	60	350	200	60
4	1600	100	60	400	210	60

- After digestion it is important to keep the samples in cooling conditions (using ice) overnight, before opening the reaction vessels, in order to avoid the loss of mercury vapours present in the vessel samples.

- It is important to consider in the mercury measurement using the cold vapour generation method, that Hg should be in the oxidation form of cation Hg^{2+} , in order to provide the reduction chemical reaction of Hg^{2+} to elemental mercury (Hg^0), this is always achieved in an acidic medium. Therefore, studies to find the optimum amount of oxidizing reagent to maintain Hg^{2+} should be carried out; then, when it is measuring the Hg in coal sample, the mass of the suitable oxidant reagent to maintain stable the Hg^{2+} in aqueous solution should be added. Also, it is recommended when the measurement of Hg in coal samples is carried out, must be done on the same day, after sample preparation is finished; if it is not possible, make studies to check if could be necessary to use oxidant reagents solutions, as for example, solution of ϕ_B (HNO_3) of 2 % with ($\text{K}_2\text{Cr}_2\text{O}_7$), but it is important to consider the necessary amount of ϕ_B ($\text{NH}_2\text{OH HCl}$) of 20 % during the instrumental measurement of Hg using CV-ICP-AES.

- The addition of hydroxylamine hydrochloride ϕ_B ($\text{NH}_2\text{OH HCl}$) of 20 % must be done just before to measure Hg, to remove excess of oxidizing agent. Therefore, it is necessary to carry out previous studies to determine the amount to be added.

- It is important to perform the preparation of blank samples that will be included in the measurement:

- Blank digestion sample: sample that does not contain the analyte of interest (B) and has the same preparation treatment as the samples are given. It should be prepared at the same time when the samples are prepared.

- Reagent blank sample: aqueous solution sample containing the same matrix than the calibration solution.

Instrumental measurement by ICP-AES

- It is important to verify the coupling of the reaction cell, called “cold vapour generation” to the sample introduction system of the ICP-AES, to rule out leakage of liquid or gas, as well as to ensure a continuous flow in the residues, in order to avoid loss of mercury present in the sample.
- Adjust the flow for reducing agent (SnCl_2), for the sample and for the residues, in such a way that the highest sensitivity of the mercury is obtained in the instrument, as example could be adjusted for reducing reagent (SnCl_2) to 4 mL/min, for sample to 7 mL/min and for residues to obtain a constant flow. It is necessary to ensure that constant flows are maintained in order to improve repeatability during the measurement sequence of the samples.
- To minimize the memory effect, it is suggested to apply rinses with a solution of ϕ_B (HNO_3) of 2 % between each measurement of samples, calibration solutions, and blank samples with a minimum time of 1 min, based on the established measurement sequence.
- It is advisable to measure blank samples at the beginning of the run sequence, in the intermediate position between the measurement of the sample and control certified reference materials and at the end of the run sequence.
- It is important to check for interferences caused by matrix effects or spectral interferences due overlapping emission lines coming from atomic, ionic or molecular emission lines of the components of the matrix, which could be affects the mercury content at low level.
- Perform the measurement for calibration curve with mercury solutions prepared from CRM, which will be in the working range. Prepare at least five points and execute the measurement with five replicates of each.
- Apply the measurement of the samples and the control CRM with at least five replicates each, in order to improve the repeatability of the measurements, performing the measurement sequence in a random order.
- Check for instrumental drift of the Hg measurements during the measurement sequence; and if it is present, could be necessary correct it by increase the rinsing time between sample measurements. If the drift is significative, apply correction for drifting using the correction factor for drifting (f_{cd}). The correction factor could be applied in blocks of measurements (could be blocks of 4 or 5 measurements) using one of the calibration solutions of mercury, which it is near to the sample content, see Table 10 as example, where the number of blocks depend of the number of samples. The factor f_{cd} is calculated by Equation 1.

$$f_{cd} = \frac{w_{\text{PCRM}_x}}{w_{\text{ECRM}_x}}$$

Equation 1

where:

f_{cd} is correction factor for drifting of instrument of interested element.

w_{PCRM_x} is mass fraction of mercury in solution prepared from a CRM, with content value near to the sample.

$\overline{w_{\text{EMRC}_x}}$ is average mass fraction value of mercury obtained by calculate the mean value of the measurements w_{ECRM_x} in each block during measurement.

To calculate the fc_d , use the measured w_{ECRM_x} values (see Table 10) and calculate the mean value per block $\overline{w_{\text{ECRM}_x}}$ (first, second, until last block of measurements), then divide it by the value of the prepared w_{PCRM_x} , according to Equation 1.

Table 10. Example of blocks of measurements.

Sequence	Sample	Measures	Mean value
	CRM-(f_{dc})-1	$w_{\text{ECRM-1}}$	w_{ECRM}
	Sample 10	w_{S10}	
	Sample 3	w_{S3}	
Block 1	Sample 5	w_{S5}	
	Sample 9	w_{S9}	w_{ECRM}
	CRM-(f_{dc})-2	$w_{\text{ECRM-2}}$	
	Sample 2	w_{S2}	
	Sample 4	w_{S4}	
Block 2	Sample 12	w_{S12}	w_{ECRM}
	Sample 7	w_{S7}	
	CRM-(f_{dc})-3	$w_{\text{ECRM-3}}$	
	Sample 1	w_{S1}	
	Sample 6	w_{S6}	w_{ECRM}
Block 3	Sample 11	w_{S11}	
	Sample 8	w_{S8}	
	CRM-(f_{dc})-4	$w_{\text{ECRM-4}}$	

Mathematical model for determining Hg in coal using CV-ICP-AES

The mathematical model for determining the mass fraction of mercury $w(\text{Hg})$ present in coal is given in Equation 2:

$$w_{\text{Hg}} = (w_x - w_B) \cdot fc_d \cdot fr \cdot \frac{m_{d1}}{m_{x1}} \cdot \frac{m_d}{(m_x \cdot fw_{dry})}$$

Equation 2

where:

- $w_{(x)}$ obtained value from external calibration curve
- w_B mass fraction of Hg in the blank sample
- fc_d drift factor, if it is applied
- fr recovery factor, if it is applied
- m_{x1} mass of the subsample aliquot
- m_{d1} mass of the final solution
- m_x mass of coal sample
- m_d mass of the first solution
- fw_{dry} dry mass factor

The results of measurement of mercury in coal can be statistically evaluated to determine whether they are consistent and meet the measurement method specifications. The evaluation of results should consider the results of all trials. Whenever doubtful (atypical) results are obtained, they should be investigated for decision-making.

A1.3.4. Measurement uncertainty

The measurement of uncertainty should be estimated according to the Measurement Uncertainty Expression Guide (GUM, 2008), known as GUM. Equation 3 presents the expression to calculate uncertainty when no correlation exists.

$$u[y(x_{i,j,k},...)] = \sqrt{\sum_{i=1} \left(\frac{\partial y}{\partial x_i} \cdot u(x_i) \right)^2}$$

Equation 3

where:

c_i is sensibility coefficient,

y describes the variation of $y(x_i, x_j, x_k, ...)$ with variations of each term.

The contribution of each uncertainty source to the total uncertainty should be included in a table called the uncertainty budget, which is a summary table of the contribution of each parameter of the measurement model as input (or influence) quantities, this table allows to identify which sources are the main contributors, so it should be included in a measurement report following the indications of the GUM.

Sources of uncertainty in Hg in coal measurement

The purpose of this section is to summarize how the user could estimate the standard uncertainties associated with the input quantities on the example of Hg mass fraction measurement in coal using CV-ICP-AES. The mathematical model used is shown in the Equation 4.

$$w_{Hg} = (w_x - w_B) \cdot f_{c_d} \cdot f_r \cdot \frac{m_{d1}}{m_{x1}} \cdot \frac{m_d}{(m_x \cdot f_{w_{dry}})} \cdot \beta$$

Equation 4

The uncertainty budget for mercury measurement should consider contributions from the following sources:

Mass fraction of mercury obtained by calibration curve, including the calibration CRM

Mass fraction of mercury measured in white sample

Instrumental drift factor

Recovery factor

Mass of the final solution

Mass of the first solution

Mass of coal sample

Moisture factor of coal

Method coefficient (β)

The Table 11 describes the approach for estimation of standard uncertainty for each input quantity, an example on how the uncertainty could estimate, based on the mathematical model of the Equation 4. The uncertainty combination could be estimate using the Equation 5.

$$u_{w_{Hg}} = w_{Hg} \cdot \sqrt{\left(\frac{u_{w_x - w_B}}{w_x - w_B}\right)^2 + \left(\frac{u_{f_{cd}}}{f_{cd}}\right)^2 + \left(\frac{u_{f_r}}{f_r}\right)^2 + \left(\frac{u_{m_{d1}}}{m_{d1}}\right)^2 + \left(\frac{u_{m_{x1}}}{m_{x1}}\right)^2 + \left(\frac{u_{m_d}}{m_d}\right)^2 + \left(\frac{u_{m_x}}{m_x}\right)^2 + \left(\frac{u_{\beta}}{\beta}\right)^2}$$

Equation 5

Table 11. Approach for estimation of standard uncertainty in Hg in coal by CV-ICP-AES.

Quantity		Standard uncertainty	Source of information
1	$w_{(x)} - w_B$	$u_{w_{(x-B)}} = \sqrt{(u_{w_{(x)l}}^2) + (u_{w_B}^2) + (u_{w_{MRC}}^2)}$	Data of calibration curve, CRM and blank samples
1.1	$w_{(x)}$	$u_{(w_x)} = \frac{s}{b_1} \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(w_{X_i} - \bar{w}_{MRC})^2}{S_{xx}}}$	Linear regression
1.2	w_B	$u_{bco} = \frac{s_{bco}}{\sqrt{n}}$	From repeatability of blank measurement
1.3	$w_{(Hg, MRC)}$	$u_{(w_{Hg,MRC})} = w_{Hg,MRC} \cdot \sqrt{\left[\frac{u(w_{MRC})}{w_{MRC}}\right]^2 + \left[\frac{u(m_1)}{m_1}\right]^2 + \left[\frac{u(m_2)}{m_2}\right]^2 + \left[\frac{u(m_3)}{m_3}\right]^2 + \left[\frac{u(m_4)}{m_4}\right]^2}$	Masses of CRM of Hg from solution preparation
1.3.1	m_1, m_2, m_3, m_4	$u_{m_i} = \sqrt{(u_{err})^2 + (u_{rep})^2}$	Maximum permissible error of balance and repeatability of the analyst
1.3.2	$w_{(MRC)}$	$u_{w_{MRC}} = \frac{U_{w_{MRC}}}{k}$	Certificate of CRM, mass fraction of Hg
2	fc_d	$u_{(fc_d)} = fc_d \cdot \sqrt{\left[\frac{u(w_{PCRmx})}{w_{PCRmx}}\right]^2 + \left[\frac{u(w_{PCRmx})}{w_{PCRmx}}\right]^2}$	From experimental Hg in prepared CRM measure, and Certificate of CRM mass fraction of Hg
3	f_r	$u_{(f_r)} = \frac{s_{fr}}{\sqrt{n}}$	From repeatability of recovery factors
4	m_{d1}, m_{x1}, m_d, m_x	$u_{m_i} = \sqrt{(u_{err})^2 + (u_{rep})^2}$	Maximum permissible error of balance and repeatability of the analyst
5	β	$u_{(\beta)} = \frac{s_{\beta}}{w_{Hg} \cdot \sqrt{n}}$	Method repeatability, selectivity (interfering elements), method imperfection

A1.4. Determination of Hg trapped in KCl crystals

A1.4.1. $^{197}\text{Hg}^0$ retention on various KCl sorbent traps

One of the crucial factors that considerably influence sampling methods for atmospheric Hg speciation is the specificity of sorbent traps. Hg^{2+} -specific sorbent traps should therefore have high level of specificity towards Hg^{2+} and low affinity for other Hg species (mainly Hg^0) (Jaffe et al., 2014). A set of experiments was performed at JSI to assess whether Hg^{2+} -specific KCl sorbent traps also retain considerable amounts of Hg^0 which would represent an artefact during Hg atmospheric speciation. For this purpose, ^{197}Hg radiotracer was used enabling work with ambient level Hg. The use of ^{197}Hg radiotracer was applied since it eliminates blank problems (radioisotope ^{197}Hg is not present in the environment) and enables lower detection limits than the use of stable isotopes and isotope dilution ICP-MS. This is due to the high specific activity of ^{197}Hg which can be obtained by the irradiation of ^{196}Hg enriched material with thermal neutrons (thermal neutron cross section of 3080 barns for ^{196}Hg , one of the highest of all nuclides).

Hg enriched to 51.58% in the ^{196}Hg isotope (natural abundance is 0.15%) was purchased from Isoflex, San Francisco, USA. 2 mL of solution of enriched ^{196}Hg in 2% HNO_3 acid (v/v) was sealed into a quartz ampoule and irradiated for 12 h in the central channel of the TRIGA Mark II (250 kW) reactor core channel (JSI, Ljubljana, Slovenia). Because of the nuclear reaction of ^{196}Hg with high neutron flux ($10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$) in the reactor core, ^{197}Hg was produced in the solution after irradiation. Prior to irradiation, Hg concentration was determined by cold vapour atomic absorption spectrometry (CV AAS). Obtained concentration ($102 \mu\text{g mL}^{-1}$) was the reference for Hg amounts that were spiked in the following experiments. After irradiation, the Hg solution was transferred from the irradiated vial and diluted to appropriate Hg concentrations for spiking experiments.

A1.4.2. Determination of ^{197}Hg using gamma detector

Two different types of detectors were used for the determination of ^{197}Hg . If ^{197}Hg was present in a solution, an aliquot was taken into a measurement vial and measured using a well type HPGe (high purity germanium) detector. If ^{197}Hg was present on a gold trap, it was measured using a coaxial type HPGe detector.

To obtain standards for gamma well measurement, triplicates of the standard solution (8 mL, 2% HNO_3 (v/v)) were transferred into measurement vials. Standard solution was always diluted in such a way that the obtained activity was similar to the activity of the measured sample. Activity (γ -rays and X-rays) of standards in vials was measured using a well type HPGe detector.

To obtain standards for coaxial well measurement, a known amount of $^{197}\text{Hg}^{2+}$ in 100 mL solution was reduced to $^{197}\text{Hg}^0$ using SnCl_2 solution (2 mL, 10% (w/v) in 10% HCl (v/v)) in a bubbler and purged for 10 min with N_2 carrier gas (flowrate of 1 L min^{-1}). Purged $^{197}\text{Hg}^0$ was transferred to a gold trap by the carrier gas. Triplicate measurements were performed to obtain standards for the gamma coaxial detector. When a new gold trap was prepared, new triplicate standards were always prepared. Gold traps were prepared in quartz tubes (170 mm long, 6 mm inner diameter) by placing 15 mm in length of the absorbing material (Au bound to corundum, Al_2O_3 , 0.60 – 0.85 mm grain size) fixed in place by quartz wool. Activity (γ -rays and X-rays) of $^{197}\text{Hg}^0$ on gold trap standards was measured using a coaxial type HPGe detector. In order to re-use gold traps, they were heated to 300°C for 30 s which released the bounded $^{197}\text{Hg}^0$.

The amount of ^{197}Hg in samples were determined by peak area comparison of the characteristic γ -ray and X-ray emissions for ^{197}Hg (two doublet peaks: $67.0 + 68.8 \text{ keV}$ and $77.3 + 77.9 \text{ keV}$). All obtained activities were re-calculated to a reference time by applying Equation 6 derived from the exponential

law of radioactive decay. Equation 6 was applied for calculation of both A_0 (activity at reference time) of the sample and A_0 of the standard. The recoveries were calculated using Equation 7 (Ribeiro Guevara et al., 2013; Žižek et al., 2008).

$$A_{0,sample} = \frac{A_{sample} * \frac{\ln 2}{t_{1/2}}}{e^{-\left(\frac{t_{passed} * \ln 2}{t_{1/2}}\right)} * \left[1 - e^{-\left(\frac{t_{measurement} * \ln 2}{t_{1/2}}\right)}\right]}$$

Equation 6

$$R = \frac{A_{0,sample}}{A_{0,std.}} * \frac{m_{Hg,std.}}{m_{Hg,sample}} * f_{dillution} * 100$$

Equation 7

where:

$A_{0, sample}$ is sample activity at reference time $t=0$ [Bq],

$A_{0, std}$ is standard activity at reference time $t=0$ [Bq],

A_{sample} is sample activity at the time of measurement [Bq],

$t_{1/2}$ is half-life of ^{197}Hg [s],

t_{passed} is time passed since reference time $t=0$ till the start of measurement [s],

$t_{measurement}$ is time passed during the measurement [s],

R is recovery [%],

$m_{Hg,std.}$ is mass of Hg used for standard [pg],

$m_{Hg, sample}$ is mass of Hg used for sample, assuming 100% recovery [pg],

$f_{dillution}$ is dilution factor in case sample and standard were not diluted in the same way.

A1.4.3. Experimental design for $^{197}\text{Hg}^0$ retention on various KCl sorbent traps

The goal in the following experiments was to evaluate the extent of undesirable Hg^0 retention on KCl traps. This was achieved by transferring a known amount of Hg^0 in the carrier gas through a Hg^{2+} -specific sorbent trap (where Hg^0 retention is undesirable). Simplified scheme of the experimental setup is shown in Figure 16. First, $^{197}\text{Hg}^{2+}$ (usually from 0.1 to 1 ng) was reduced to $^{197}\text{Hg}^0$ in the bubbler using SnCl_2 solution (10% (w/v) SnCl_2 in 10% HCl solution (v/v)). $^{197}\text{Hg}^0$ was then purged out with N_2 carrier gas (flowrate of 1 L min^{-1}) for 10 minutes, passed through various types of KCl sorbent traps (described below) and captured on the end by a gold trap. Three different types of KCl sorbent traps were used:

KCl crystal,

KCl crystal + Al_2O_3 catalyst,

quartz wool impregnated with KCl.

All sorbent traps were prepared in quartz tubes (170 mm long, 6 mm inner diameter). In design 1 (Figure 16), KCl crystal was 15 mm long and fixed using quartz wool. In design 2, KCl crystal was 5 mm long and Al_2O_3 catalyst part was 65 mm long. In design 3, quartz wool impregnated with KCl was 70 mm long. Quartz wool impregnated with KCl was prepared by soaking quartz wool in 1 mol L^{-1} KCl for

24 h, draining the excess solution and drying at 130 °C for 24 h. All three types of sorbent traps were tested fresh (no prior heating of the traps) and re-used, resulting in six tested variations.

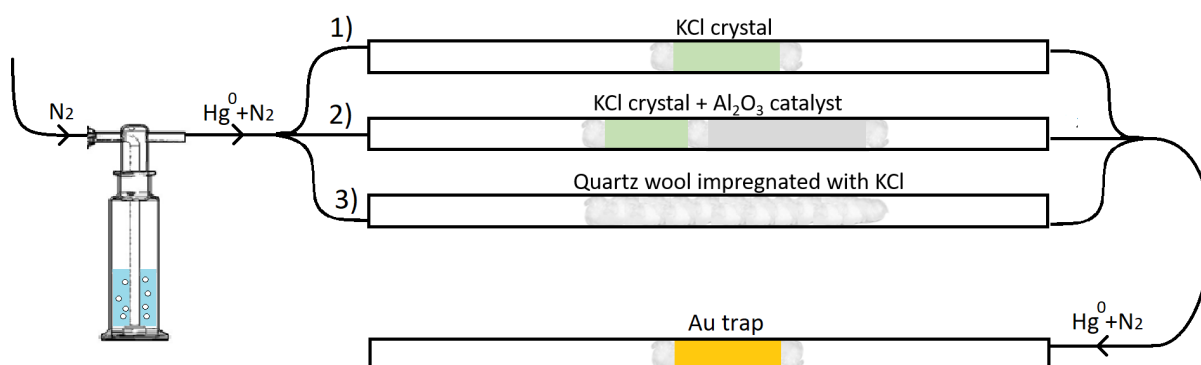


Figure 16. Simplified scheme of the experimental setup for $^{197}\text{Hg}^0$ retention on three different KCl sorbent trap designs.

To determine the amount of $^{197}\text{Hg}^0$ adsorbed on KCl sorbent traps, they were leached with 20 mL of 10% HNO_3 (v/v) + 5% HCl (v/v) solution and measured using gamma well detector. $^{197}\text{Hg}^0$ on gold traps was measured using gamma coaxial detector. The results of the above described experiments are shown in the Table 12. Column “retained Hg^0 ” presents $^{197}\text{Hg}^0$ that was retained on the KCl sorbent part of the experimental trap. Column “mass balance” represents sum of $^{197}\text{Hg}^0$ on a KCl sorbent trap and $^{197}\text{Hg}^0$ on a gold trap.

Table 12. $^{197}\text{Hg}^0$ retention on various KCl sorbent traps, comparison of fresh and re-used designs. Results are presented in percentage of the initially purged Hg^0 amount. Less than 1 ng of Hg was used.

trap description	retained Hg^0 [%]	mass balance [%]
re-used KCl crystal + Al_2O_3 catalyst	11.5	102
	18.0	101
	23.8	101
	9.46	101
fresh KCl crystal + Al_2O_3 catalyst	0.00	99.1
	0.00	96.7
re-used KCl crystal	4.10	95.4
	7.12	92.7
	2.41	94.5
fresh KCl crystal	0.13	95.9
	0.14	102
	0.20	96.2
re-used quartz wool impregnated with KCl	0.35	100
	0.10	101
	0.64	100
fresh quartz wool impregnated with KCl	0.05	98.2
	0.23	109
	0.23	93.3

Evidently the designs containing KCl crystal (KCl crystal + Al_2O_3 catalyst and KCl crystal traps) retained much more Hg^0 when they were re-used (which is not desired; Hg^{2+} specificity is required). The retained amount also varied highly for re-used sorbent traps. Possible explanation for this could be that the surface of sorbent trap material is changed after being heated to high temperatures ($> 500\text{ }^\circ\text{C}$), in a way that increases binding of Hg^0 . Fresh traps design always retained very small Hg^0 amounts ($< 0.3\%$ for all designs). Mass balances were in all cases quantitative; therefore, these results can be trusted with a high degree of confidence. From these findings it can be concluded that fresh traps are superior to re-used traps and should be therefore always used fresh to ensure artefact-free Hg atmospheric speciation. It is not necessary to correct the measured values for the obtained recovery as losses are regularly lower than the variability of the recovery (standard deviation up to 4%, losses up to 0.2%). In future, morphology difference of fresh and re-used sorbent material will be used to obtain additional information about these results.

A1.4.4. Stability of $^{197}\text{Hg}(\text{II})$ on various KCl sorbent traps during exposure in ambient airflow

To obtain a coherent insight into Hg atmospheric speciation it is important to know the stability of $\text{Hg}(\text{II})$ on speciation traps in addition to knowing their specificity. Prolonged sampling and preconcentration time might result in losses of $\text{Hg}(\text{II})$ or reduction to Hg^0 . These processes can represent an additional source of artefacts resulting in biased Hg atmospheric speciation. With this purpose JSI tested the stability of $\text{Hg}(\text{II})$ on various KCl sorbent traps while being exposed to the flow of ambient air. Similar as in section 0, ^{197}Hg radiotracer was used to exploit its high specific activity for ambient Hg concentration experiments.

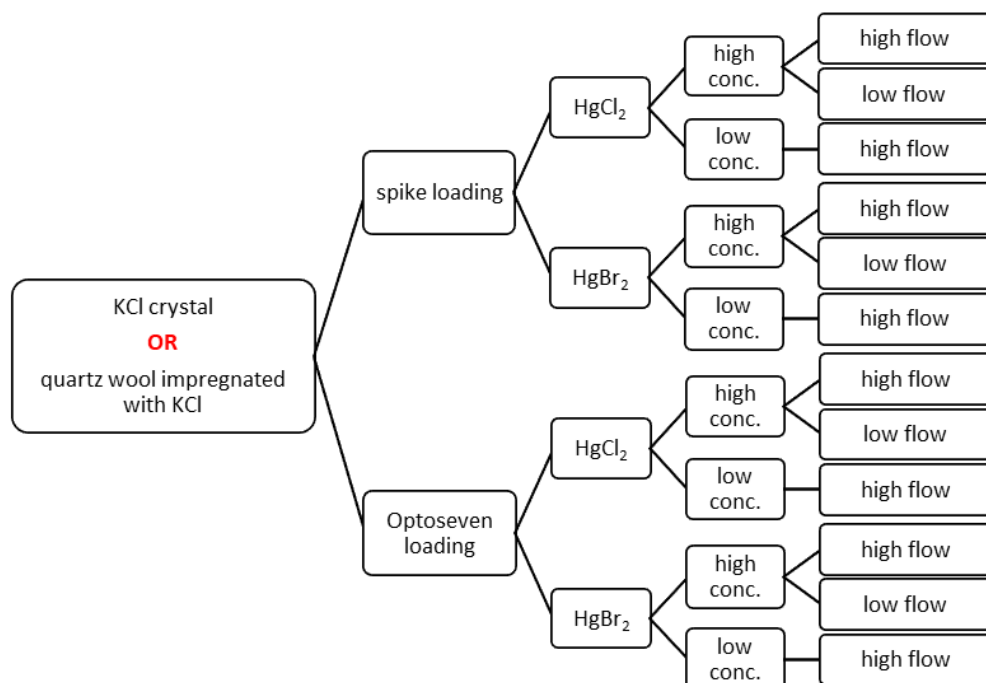


Figure 17. Variations of performed experimental conditions for $^{197}\text{Hg}^{2+}$ stability on KCl sorbent traps during exposure in ambient airflow.

In order to test $^{197}\text{Hg(II)}$ stability on KCl sorbent traps, the traps were exposed to ambient airflow for 30 min intervals. Potential $^{197}\text{Hg}^0$ artefact was captured downstream of the KCl sorbent trap by Au trap (Au trap preparation is described in section 0). After each 30 min exposure interval, Au traps with $^{197}\text{Hg}^0$ were measured in the gamma coaxial detector. KCl sorbent traps were loaded with $^{197}\text{Hg(II)}$ again (to imitate sampling where new Hg(II) is constantly adsorbed) and the procedure was repeated 4 to 5 times. Figure 17 shows a diagram of all performed variations of the stability tests.

Two types of $^{197}\text{Hg(II)}$ loadings were applied. First one was a direct spike of $^{197}\text{Hg}^{2+}$ onto the sorbent traps. Second type of loadings was using Optoseven evaporative gas calibrator. This instrument enabled traceable Hg(II) loadings by evaporating Hg^{2+} solution and injecting it into a carrier gas (Saxholm et al., 2020). More information on Optoseven evaporative gas calibrator are available in Deliverable 1 and Deliverable 2. Calibration gas was comprised of evaporated 0.07 mL min^{-1} of $^{197}\text{Hg}^{2+}$ solution ($^{197}\text{Hg}^{2+}$ concentration was dependent on concentration level tested) and 5 L min^{-1} of carrier gas N_2 . Obtained calibration gas had $^{197}\text{Hg}^{2+}$ concentration of 4.74 ng m^{-3} for low concentration tests and 947 ng m^{-3} for high concentration tests.

Two Hg^{2+} species were tested for stability, HgCl_2 and HgBr_2 . In cases when $^{197}\text{Hg}^{2+}$ was spiked, 4% HCl (v/v) + 3% HNO_3 (v/v) solution was used for HgCl_2 , and 4% HBr (v/v) + 3% HNO_3 (v/v) solution was used for HgBr_2 . Acids and their corresponding percentages were chosen based on the acid composition of NIST 3177 standard reference material (Mercuric Chloride Standard Solution). In cases when $^{197}\text{Hg}^{2+}$ was loaded with Optoseven calibrator, 0.1% HCl (v/v) + 0.1 % HNO_3 (v/v) solution was used for HgCl_2 , and 0.1% HBr (v/v) + 0.1 % HNO_3 (v/v) solution was used for HgBr_2 .

These approaches were used because direct irradiation of Hg(II) halogenides is not recommended due to high halogen activation in the nuclear reactor. Theoretically, to compensate for the absence of two halogenide equivalents for each Hg equivalent, the exact amount of corresponding halogenide should be added in form of its conjugated acid. However, this additional amount was usually so small (in nanolitre range) and within the uncertainty of the pipette used for the preparation of acid solutions. In addition to two loading types and two Hg species, two different KCl sorbent trap materials were tested: KCl crystal and quartz wool impregnated with KCl (preparation and dimensions of the traps are described in section 0). Each trap material was then tested under different experimental conditions: high concentration ($> 50 \text{ ng}$) / low concentration ($< 1 \text{ ng}$) and high airflow (400 mL min^{-1}) / low airflow (100 mL min^{-1}). All variations of experimental conditions, trap types, Hg species and loading types were tested as shown in Figure 17.

Exposure of loaded sorbent trap to airflow changes the geometry of the loaded $^{197}\text{Hg(II)}$. This affects the measurement resulting in biased results as shown in Figure 18. Figure illustratively shows a sorbent trap that is placed over a coaxial gamma detector before and after exposure to airflow. Airflow shifts the position of loaded $^{197}\text{Hg}^{2+}$ and longer airflow exposures causing higher shifts. The measurement after airflow would therefore result in greater apparent sample activity than the measurement before airflow exposure. Because of this observation and since measured losses were within the uncertainty of $^{197}\text{Hg(II)}$ measurement on KCl sorbent traps, it was impossible to constantly check for complete mass balance. On the other hand, measurement of $^{197}\text{Hg(II)}$ losses captured on Au trap was not affected by this since Hg forms a strong amalgamation with Au. Therefore, only measured losses are presented in the tables below.

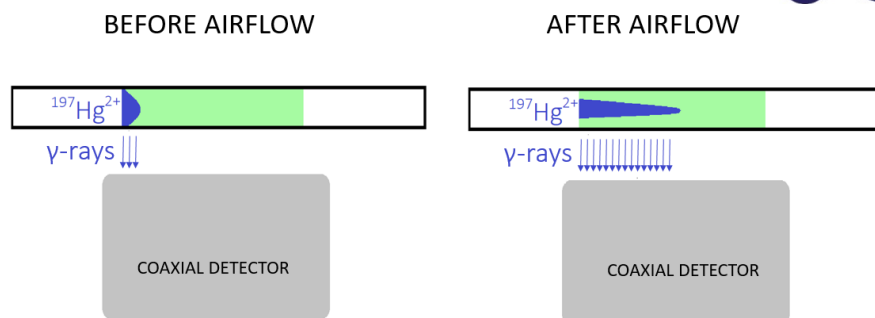


Figure 18. Effect of changed geometry on the activity measurement after ambient airflow exposure.

To make sure that no $^{197}\text{Hg(II)}$ breakthrough occurred and that measured losses were only $^{197}\text{Hg}^0$, additional KCl crystal trap was placed between KCl sorbent trap and Au trap to filter the potential $^{197}\text{Hg}^{2+}$ breakthrough. Since this filter KCl trap was always free of ^{197}Hg , only Teflon connector placed after KCl sorbent trap was regularly checked for $^{197}\text{Hg(II)}$ breakthrough in later experiments ($^{197}\text{Hg(II)}$ would be found there if breakthrough occurred due to the highly adsorptive nature of Hg(II)). Even though the connector was not possible to properly calibrate, the obtained signals were always within the noise of the gamma well detector.

Preparation of standards and calculation of results was performed using the same procedures and equations as in section 0. Results of the above described stability test variations are shown in the tables and figures below. Losses are presented in percentages relative to the cumulative Hg amount that was spiked up till that time period. Some results have 4 time periods and others have 5 time periods due to time limitations of each measurement day. If the radiotracer was more decayed, longer measurement times were required and longer loading times in case of Optoseven loading; all leading to less time periods performed for the individual stability test.

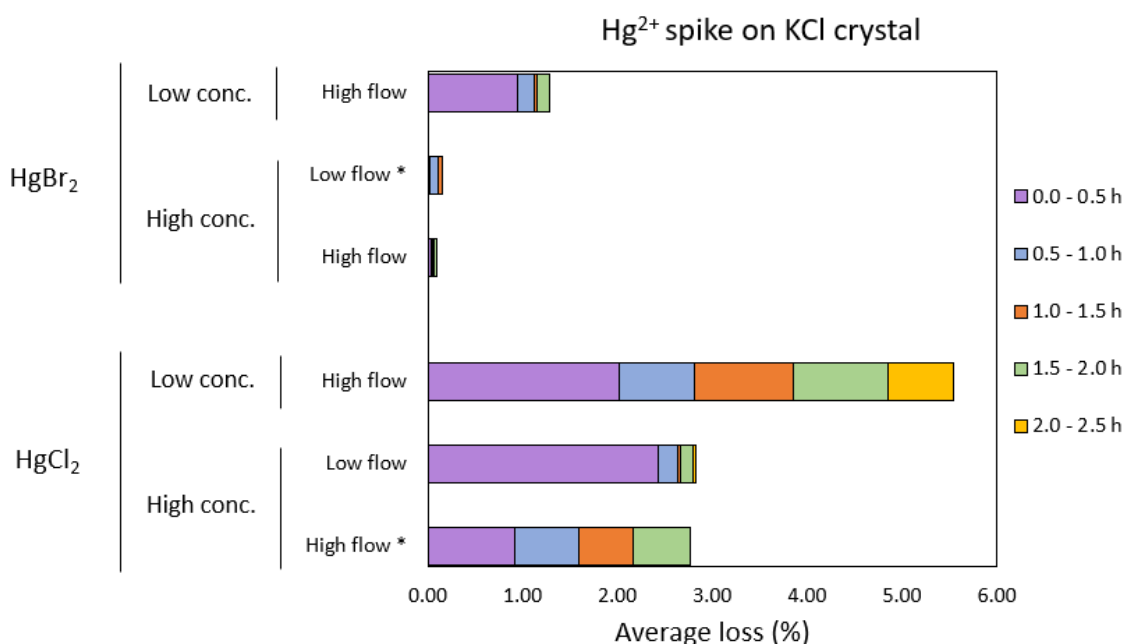


Figure 19. Stability test results for $^{197}\text{Hg}^{2+}$ (radiotracer) spike on KCl crystal. Low concentration variations were loaded with under 1 ng of Hg per time period and high concentration variations were loaded with over 50 ng of Hg per time period. Low gas flow variations were exposed to 100 mL min^{-1} airflow and high gas flow variations were exposed to 400 mL min^{-1} airflow.

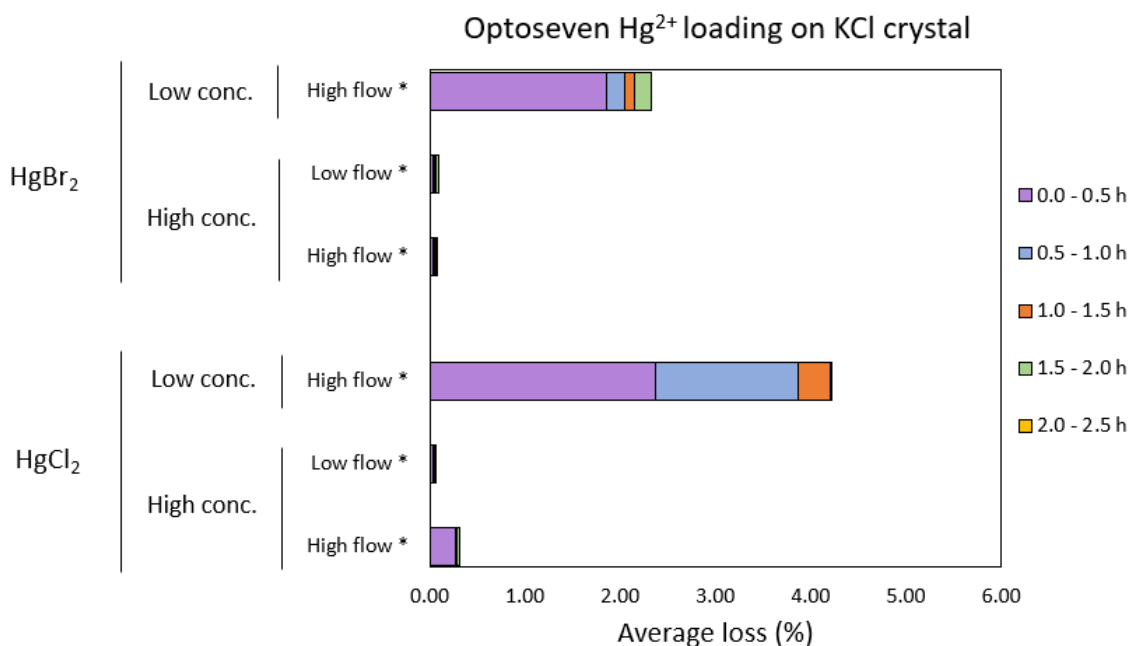


Figure 20: Stability test results for Optoseven loading of ¹⁹⁷Hg²⁺ (radiotracer) on KCl crystal. Low concentration variations were loaded with under 1 ng of Hg per time period and high concentration variations were loaded with over 50 ng of Hg per time period. Low gas flow variations were exposed to 100 mL min⁻¹ airflow and high gas flow variations were exposed to 400 mL min⁻¹ airflow.

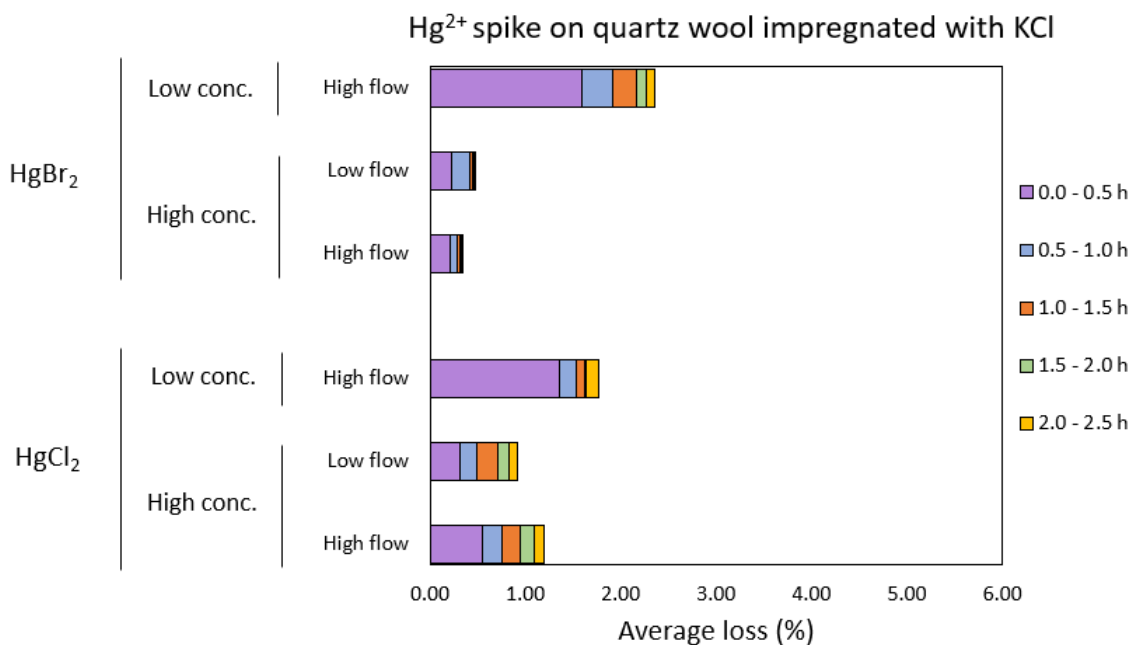


Figure 21. Stability test results for ¹⁹⁷Hg²⁺ (radiotracer) spike on quartz wool impregnated with KCl. Low concentration variations were loaded with under 1 ng of Hg per time period and high concentration variations were loaded with over 50 ng of Hg per time period. Low gas flow variations were exposed to 100 mL min⁻¹ airflow and high gas flow variations were exposed to 400 mL min⁻¹ airflow.

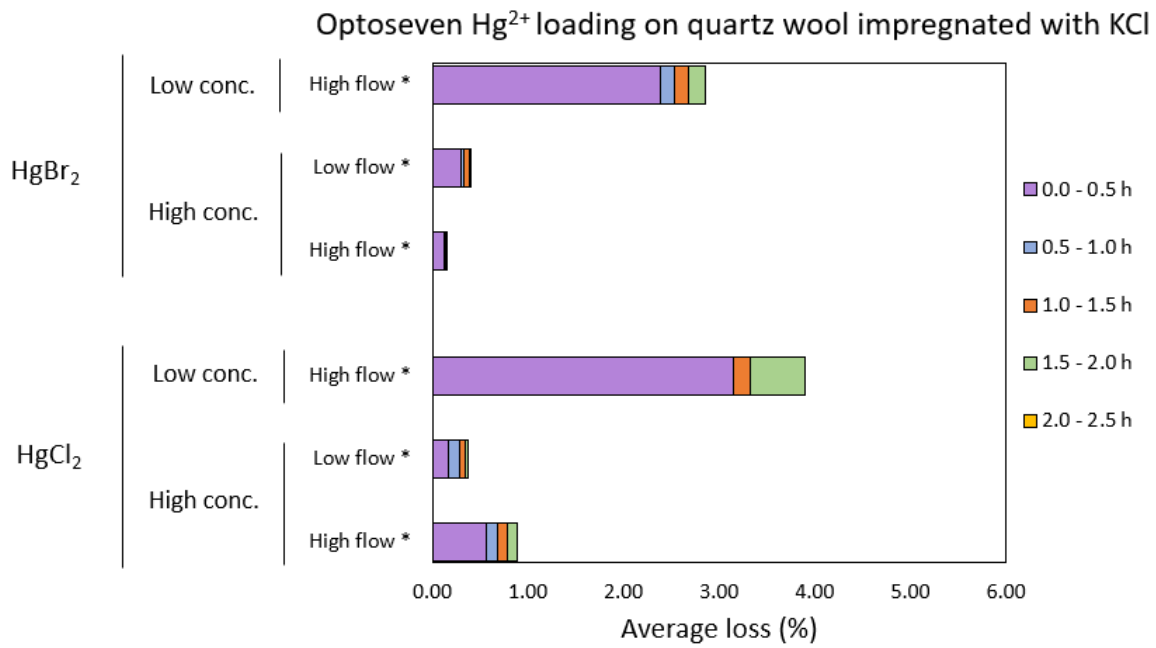


Figure 22. Stability test results for Optoseven loading of $^{197}\text{Hg}^{2+}$ (radiotracer) on quartz wool impregnated with KCl. Low concentration variations were loaded with under 1 ng of Hg per time period and high concentration variations were loaded with over 50 ng of Hg per time period. Low gas flow variations were exposed to 100 mL min^{-1} airflow and high gas flow variations were exposed to 400 mL min^{-1} airflow.

Table 13. Stability test results for $^{197}\text{Hg}^{2+}$ (radiotracer) spike on KCl crystal. Low concentration variations were loaded with under 1 ng of Hg per time period and high concentration variations were loaded with over 50 ng of Hg per time period. Low gas flow variations were exposed to 100 mL min^{-1} airflow and high gas flow variations were exposed to 400 mL min^{-1} airflow.

Species	Concentration	Gas flow	Time period	0.0 - 0.5 h	0.5 – 1.0 h	1.0 - 1.5 h	1.5 – 2.0 h	2.0 – 2.5 h
HgCl_2	High	High	Average loss (%)	0.92	0.67	0.57	0.61	×
			SD (%)	0.52	0.46	0.14	0.23	×
			RSD	56.7	68.6	24.0	37.9	×
		Low	Average loss (%)	2.43	0.21	0.03	0.12	0.03
			SD (%)	1.45	0.26	0.03	0.10	0.03
			RSD	59.8	126	115	86.6	88.4
	Low	High	Average loss (%)	2.01	0.80	1.04	1.00	0.69
			SD (%)	1.25	1.07	1.50	1.70	1.04
			RSD	62.1	133	143	169	152
HgBr_2	High	High	Average loss (%)	0.04	0.01	0.02	0.02	0.00
			SD (%)	0.05	0.03	0.02	0.02	0.00
			RSD	104	199	100	118	0.00
		Low	Average loss (%)	0.02	0.09	0.04	0.00	×
			SD (%)	0.03	0.03	0.06	0.00	×
			RSD	173	31.9	173	509	×
	Low	High	Average loss (%)	0.95	0.17	0.03	0.13	0.00
			SD (%)	0.76	0.17	0.05	0.21	0.00
			RSD	80.1	103	173	154	173

Table 14. Stability test results for Optoseven loading of $^{197}\text{Hg}^{2+}$ (radiotracer) spike on KCl crystal. Low concentration variations were loaded with under 1 ng of Hg per time period and high concentration variations were loaded with over 50 ng of Hg per time period. Low gas flow variations were exposed to 100 mL min^{-1} airflow and high gas flow variations were exposed to 400 mL min^{-1} airflow.

Species	Concentration	Gas flow	Time period	0.0 - 0.5 h	0.5 – 1.0 h	1.0 - 1.5 h	1.5 – 2.0 h	2.0 – 2.5 h
HgCl_2	High	High	Average loss (%)	0.27	0.01	0.01	0.02	×
			SD (%)	0.27	0.00	0.01	0.02	×
			RSD	101	41.9	141	141	×
		Low	Average loss (%)	0.03	0.01	0.01	0.01	×
			SD (%)	0.02	0.01	0.02	0.01	×
			RSD	72.1	94.6	165	72.9	×
	Low	High	Average loss (%)	2.37	1.50	0.33	0.02	×
			SD (%)	0.61	1.06	0.56	0.02	×
			RSD	25.7	70.7	173	97.0	×
HgBr_2	High	High	Average loss (%)	0.04	0.01	0.01	0.01	×
			SD (%)	0.02	0.01	0.00	0.01	×
			RSD	41.7	70.3	18.9	43.7	×
		Low	Average loss (%)	0.03	0.02	0.02	0.02	×
			SD (%)	0.02	0.02	0.02	0.02	×
			RSD	78.2	103	85.1	82.2	×
	Low	High	Average loss (%)	1.86	0.19	0.10	0.18	×
			SD (%)	0.95	0.33	0.17	0.26	×
			RSD	51.4	173	173	147	×

Table 15. Stability test results for $^{197}\text{Hg}^{2+}$ (radiotracer) spike on quartz wool impregnated with KCl. Low concentration variations were loaded with under 1 ng of Hg per time period and high concentration variations were loaded with over 50 ng of Hg per time period. Low gas flow variations were exposed to 100 mL min^{-1} airflow and high gas flow variations were exposed to 400 mL min^{-1} airflow.

Species	Concentration	Gas flow	Time period	0.0 - 0.5 h	0.5 – 1.0 h	1.0 - 1.5 h	1.5 – 2.0 h	2.0 – 2.5 h
HgCl_2	High	High	Average loss (%)	0.55	0.21	0.19	0.14	0.10
			SD (%)	0.22	0.09	0.18	0.10	0.09
			RSD	40.4	40.0	96.4	75.8	93.9
		Low	Average loss (%)	0.31	0.18	0.22	0.12	0.08
			SD (%)	0.17	0.13	0.28	0.08	0.10
			RSD	53.1	76.5	127	71.6	115
	Low	High	Average loss (%)	1.36	0.17	0.09	0.02	0.12
			SD (%)	0.47	0.27	0.10	0.04	0.05
			RSD	34.8	164	109	173	40.2
HgBr_2	High	High	Average loss (%)	0.21	0.07	0.03	0.02	0.02
			SD (%)	0.06	0.03	0.01	0.02	0.02
			RSD	31.2	47.8	44.7	122	121
		Low	Average loss (%)	0.23	0.18	0.03	0.02	0.01
			SD (%)	0.18	0.12	0.04	0.02	0.01
			RSD	77.1	68.6	131	90.5	86.9
	Low	High	Average loss (%)	1.59	0.32	0.25	0.11	0.08
			SD (%)	1.21	0.35	0.22	0.08	0.06
			RSD	76.1	107	87.3	74.6	75.1

Table 16. Stability test results for Optoseven loading of $^{197}\text{Hg}^{2+}$ (radiotracer) spike on quartz wool impregnated with KCl. Low concentration variations were loaded with under 1 ng of Hg per time period and high concentration variations were loaded with over 50 ng of Hg per time period. Low gas flow variations were exposed to 100 mL min⁻¹ airflow and high gas flow variations were exposed to 400 mL min⁻¹ airflow.

Species	Concentration	Gas flow	Time period	0.0 - 0.5 h	0.5 – 1.0 h	1.0 - 1.5 h	1.5 – 2.0 h	2.0 – 2.5 h
HgCl_2	High	High	Average loss (%)	0.57	0.11	0.11	0.10	×
			SD (%)	0.07	0.11	0.13	0.04	×
			RSD	12.5	95.8	122	41.7	×
		Low	Average loss (%)	0.17	0.12	0.05	0.03	×
			SD (%)	0.15	0.11	0.07	0.03	×
			RSD	86.0	89.3	135	96.5	×
	Low	High	Average loss (%)	3.15	0.00	0.18	0.56	×
			SD (%)	0.67	0.00	0.32	0.72	×
			RSD	21.3	0.00	173	130	×
HgBr_2	High	High	Average loss (%)	0.12	0.00	0.02	0.01	×
			SD (%)	0.05	0.01	0.01	0.01	×
			RSD	46.0	173	70.9	104	×
		Low	Average loss (%)	0.30	0.03	0.05	0.02	×
			SD (%)	0.22	0.04	0.03	0.02	×
			RSD	74.8	140	59.7	120	×
	Low	High	Average loss (%)	2.38	0.15	0.15	0.17	×
			SD (%)	1.60	0.13	0.26	0.22	×
			RSD	67.2	86.6	173	129	×

The most obvious trend observed in the presented tables is that the relative losses were almost in all cases higher for low concentration experiments. Nevertheless, the absolute losses (tables and graphs above present relative values) were still higher for high concentration experiments than for low concentration experiments. Additionally, the first interval (0 – 0.5 h) has statistically significant the greatest relative losses during the whole stability test (Kruskal–Wallis test, $p < 0.001$; pairwise multiple comparison procedures (Dunn’s Method), $p < 0.05$ for 0 – 0.5 h period against others). Since low/high airflow variation did not result in significant differences in the overall average $^{197}\text{Hg}^{2+}$ losses (paired t -test, $p = 0.471$), tests with low airflow were abandoned for low concentration stability tests. $\text{HgCl}_2/\text{HgBr}_2$ and Optoseven/spike loading variations also did not result in any relevant differences in $^{197}\text{Hg}^{2+}$ losses during the stability tests.

Longer sampling times are often used for low concentrations of Hg^{2+} (the amount of Hg^{2+} collected from the ambient atmospheric samples is in order of picograms) and therefore such losses as observed in upper experiments should be considered when evaluating atmospheric Hg speciation measurement results. For Hg speciation, Hg^{2+} reduction to Hg^0 during sampling could result in a positive bias for Hg^0 (gaseous elemental mercury, GEM) measurement and negative bias for Hg^{2+} (gaseous oxidized mercury, GOM). All of this must be considered, especially when longer sampling times are required.

A1.4.5. Stability of $^{197}\text{Hg}(\text{II})$ on $\text{KCl} + \text{Al}_2\text{O}_3$ trap loaded with non-thermal plasma

Oxidation of Hg^0 to Hg^{2+} can be effectively achieved with non-thermal plasma, but was previously used mostly as a potential Hg^0 removal tool for flue gas (Wang et al., 2010; Byun et al., 2008). JSI developed a SI-traceable calibration using non-thermal plasma oxidation of Hg^0 to $\text{Hg}(\text{II})$ during the work in the MercOx project (Deliverable 1). As described in Deliverable 3, Al_2O_3 was chosen as the best catalyst for $\text{Hg}(\text{II})$ to Hg^0 thermal reduction, having the highest and most repeatable conversion efficiencies. To accompany these developments, we conducted stability tests of non-thermal plasma loaded $^{197}\text{Hg}(\text{II})$ on $\text{KCl} + \text{Al}_2\text{O}_3$ trap (trap and its preparation described in section 0). Since this SI-traceable calibration is meant for use at ambient concentration levels, ^{197}Hg radiotracer was used to enable work at such low Hg concentrations.

In order to test stability of non-thermal plasma loaded $^{197}\text{Hg}(\text{II})$, a set of $\text{KCl} + \text{Al}_2\text{O}_3$ traps were loaded with 3 ng of $^{197}\text{Hg}(\text{II})$. After loading, the traps were sealed and left under daylight conditions or in darkness for 3 days. Both fresh (never exposed to high temperatures) and re-used (traps that were heated to 600 °C) were examined. After the storage, $^{197}\text{Hg}(\text{II})$ on traps was reduced to $^{197}\text{Hg}^0$ by thermal conversion. Thermal conversion was conducted by heating KCl crystal and the Al_2O_3 part to 600 °C in the flow of N_2 for 20 s using a heating coil. The trap was left on the flow of N_2 carrier gas (flowrate of 370 mL min⁻¹) for 60 s after the end of heating to ensure all $^{197}\text{Hg}^0$ was transported downstream where it was captured by a gold trap. $^{197}\text{Hg}^0$ on the gold trap was measured using gamma coaxial detector to obtain the $^{197}\text{Hg}(\text{II})$ losses that occurred during storage.

Preparation of standards for gamma coaxial measurement and calculation of results was performed using the same procedures and equations as in section 0. Results of the above described stability test are shown in Table 17. Values are presented in percentage relative to the loaded $^{197}\text{Hg}(\text{II})$ amount.

Table 17. Stability of non-thermal plasma loaded $^{197}\text{Hg}^{2+}$ during different exposure conditions.

Trap conditions	Losses during storage [%]	Average [%]	St.Dev. [%]	RSD [%]
fresh traps, darkness	25.9	23.6	10.9	46.3
	33.3			
	11.7			
fresh traps, daylight	29.8	28.8	1.39	4.83
	27.8			
	5.61			
re-used traps, daylight	2.00	4.15	1.93	46.6
	5.94			

The difference between daylight and dark conditions was small (5.2% difference) and within the standard deviation of replicate measurements (10.9% standard deviation of replicates for fresh traps in darkness). The difference between the re-used and fresh KCl + Al₂O₃ traps was considerable and large (Table 17); re-used traps had much lower losses than the fresh traps. In contrast, results for KCl + Al₂O₃ traps showed that re-used traps retain relatively high amounts of Hg⁰ (15% on average) in comparison to fresh traps which did not retain Hg⁰. This is not desirable as Hg⁰ retention on Hg(II)-specific trap results in biased Hg speciation. Indications are therefore conflicting and suggest that if fresh KCl + Al₂O₃ traps are used for Hg(II) loading, they should not be stored for longer time periods. If the longer storage time period is inevitable, it is best to pre-condition it by heating it to 600°C since the $^{197}\text{Hg(II)}$ loading is much more stable.

A1.4.6. Stability of $^{197}\text{Hg}^{2+}$ solution in the Optoseven gas evapourative calibrator

Optoseven gas evapourative calibrator is an instrument that enables traceable Hg(II) loadings by evaporating Hg²⁺ containing solution and injecting it into a carrier gas. This way, calibration gas is comprised of Hg²⁺ solution flow and carrier gas flow. More information about the calibrator is available in Deliverable 1 and Deliverable 2. To have reliable instrument calibration, it is important to be certain about the stability of the calibrator output which is connected to the stability of the calibration solution (in addition to other factors that influence the stability of calibrator output). ^{197}Hg radiotracer was used for the purpose of studying stability of the Hg²⁺ calibration solution that is used in Optoseven calibrator.

To test the stability of $^{197}\text{HgCl}_2$ solution in the Optoseven gas evapourative calibrator, 4.5 ng mL⁻¹ of $^{197}\text{Hg}^{2+}$ in 0.1 % HCl (v/v) + 0.1 HNO₃ (v/v) solution was prepared in accordance with Optoseven protocol. Freshly prepared solution was measured immediately in triplicate and used as a reference value for 100 % recovery.

Calibration solution stability was tested using three different measurement approaches. First, 8 mL of freshly prepared $^{197}\text{Hg}^{2+}$ calibration solution was taken for gamma well measurement. Second, the calibration solution was left in operating Optoseven calibrator for 24 h and after that 8 mL of the solution was taken for gamma well measurement. Finally, a 24-hour old calibration solution was purged with a flow of He (370 mL min⁻¹) prior to gamma well measurement. All three approaches were repeated in duplicate. Preparation of standards for gamma well measurement and calculation of results was performed using the same procedures and equations as described in section 0. Results of

the described stability test are shown in Table 18. Values are presented in percentage of the activity of freshly prepared $^{197}\text{HgCl}_2$ standard solution.

Table 18. Stability of $^{197}\text{HgCl}_2$ standard solution used for Optoseven gas evaporative calibrator.

Calibration solution description	Individual run recovery [%]	Average recovery [%]
fresh	102	101
fresh	99.6	
24 hours old	97.8	100
24 hours old	103	
24 hours old, purged for 15 min	99.8	98.3
24 hours old, purged for 15 min	96.9	

All standard solution stability experiments gave satisfactory results. A small loss was observed in calibration solutions that were purged for 15 min prior to measurement which might be due to formation of Hg^0 in the HgCl_2 solution. Described calibrator does not purge the calibration solution and therefore there should be little concern regarding the solution stability within each individual measurement/sampling day. The formed Hg^0 could present a problem for the calibration itself, which was described in Deliverable 6.