19NMR03 SI-Hg
Metrology for traceable protocols for elemental and oxidised mercury concentrations

Panayot Petrov, Sophie Page, Philip J.H. Dunn, Heidi Goenaga-Infante

Project Partners

National Metrology Institute

Jožef Stefan Institute

National Research Council of Italy

Chief stakeholder: David Graham, Uniper

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Introduction

- SI-Hg project overview
- Technical work packages
  - WP1: elemental mercury
  - WP2: oxidised mercury
  - WP3: performance evaluation
- Project outcomes

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Project overview – drivers and needs

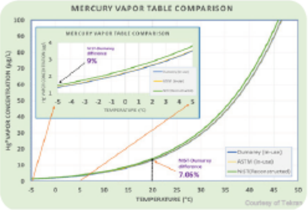
- Direct response to CEN/TC264/WG8 need for metrological research on mercury measurements

Drivers

- **European Directives**
  - Industrial emissions
  - Air quality
  - Waste incineration
- **Minamata Convention ↘**
  Global treaty to protect human health and the environment from the adverse effects of mercury

Need

- **CEN/TC264/WG8 ↘**
  Sound metrological validation of protocols for the certification of mercury concentrations produced by gas generators (CEN/CENELEC priority research topics)
- **Global Mercury Observation System (GMOS) ↘**
  Need for harmonized mercury measurement results



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Objectives

1. To develop and validate a protocol for the SI-traceable certification of **elemental mercury (Hg^0)** gas generators used in the field. (*WP1*)
2. To validate a certification protocol for the certification of **oxidised mercury Hg(II)** gas generators used in the field. (*WP2*)
3. To organise a **performance evaluation** to gather data on the characteristics of at least three Hg^0 and three Hg(II) gas generators on the market. (*WP3*)
4. To **support the development of a suitable calibration system** for mercury measurements in the atmosphere, as part of the global mercury observation system used to measure the effectiveness of the implementation of the Minamata Convention. (*WP4*)
5. To facilitate **the take up of protocols, methods, technology and measurement infrastructure** developed in the project by the standards developing organisations and end-users. (*WP4*)

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Project overview – outputs and impact

Scientific excellence

Validated protocols for SI-traceable certification of mercury gas generators

Elemental mercury (Hg^0)

Primary Hg^0 standards → **certify Hg^0 gas generators** used in the field → Bring SI-traceability to industry

Validation data → certification of Hg^0 gas generators used in the field → currently no data available

Applicable to mercury measurements at **emission sources** and challenging background levels in the **atmosphere**

Improved comparability and uncertainty → SI-traceability → Metrology is KEY!

Oxidised mercury (Hg^{II})

- **Quantify essential characteristics** of state-of-the-art dual analysers and Hg^{II} gas generators:
  - Thermal converter efficiency
  - Species selectivity
  - Transport efficiency

Establish SI-traceability for Hg^{II}

Primary Hg^0 standards → **certify Hg^{II} gas generators** used in the field

Validation data → certification of Hg^{II} gas generators used in the field → for **emission sources** and the **atmosphere**

Performance evaluation of Hg^0 and Hg^{II} gas generators on the market

- **Assessment of Hg^0 and Hg^{II} gas generators** available on the market (collaboration with at least three instrument manufacturers)
- **Data** on the characteristics
  - Performance requirements → protocols → fit-for-purpose
  - Benchmark mercury gas generators
  - Improve and develop new equipment

Based on primary standards and calibration methods developed in EMRP PartEmission and MeTra and EMPIR MercOx

Impact

Normative → This project will provide CEN/TC264/WG8 with validated certification protocols:
- Production of new **documentary standards**
- **Include metrological traceability** concepts in new and existing documentary standards
- **New work item proposal** submitted to CEN/TC264

Industry
- Changes the calibration of mercury instruments in laboratories and in the field with **improved SI-traceability and uncertainty**
- Improved corporate social responsibility
- Control and reduce mercury emissions
- Compliance with ISO/IEC 17025

Science
- Improved measurement capabilities → **Testing and calibration laboratories**
- Support GMOS → KEY in **effectiveness evaluation** of the Minamata Convention

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WP1: Elemental mercury

Development and validation of a SI-traceable certification protocol for elemental mercury gas generators used in the field

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Certification protocol scope

- This protocol specifies the procedures for establishing traceability to the SI units for the quantitative **output of elemental Hg generators** that are employed in regulatory applications for emission monitoring or testing.

- This protocol provides methods for
  - Determining the output of a mercury gas generator by comparison with a reference standard;
  - Calculating the uncertainty of the mercury concentration generated with the gas generator in relation to the known uncertainty of the reference standard.

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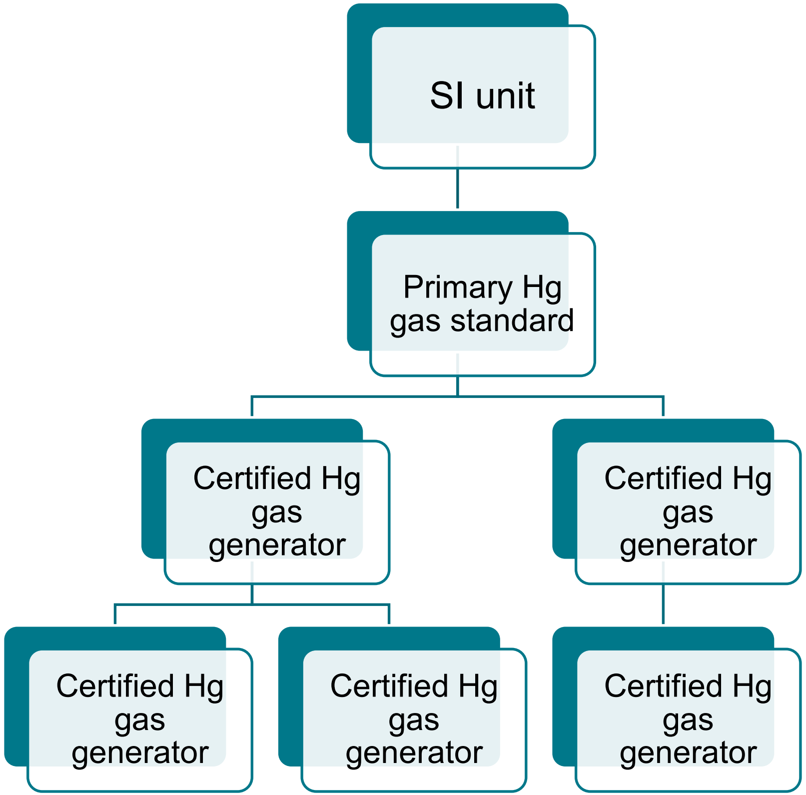
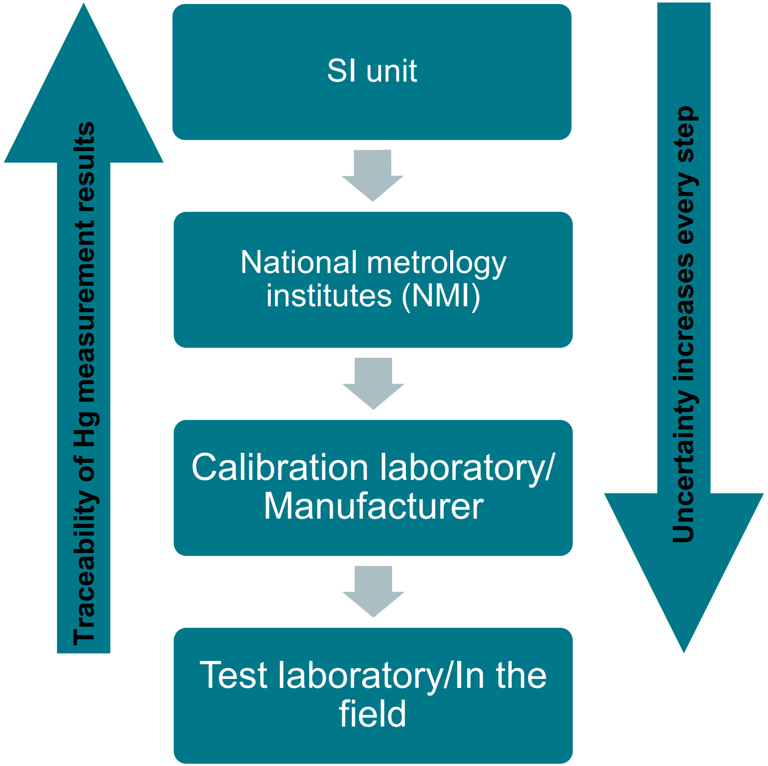
Traceability chain





WP2: Oxidised mercury

Validation of certification protocols for oxidised mercury gas generators used in the field

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Summary of goals within the WP2

- To validate a certification protocol for the certification of oxidised mercury [Hg(II)] gas generators used in the field for low mercury concentrations present in the atmosphere and higher concentrations from emission sources.

- Evaluate state-of-the-art dual analytical systems (analysers) used for the quantitative determination of Hg^0 and Hg(II).
- Evaluate state-of-the-art Hg(II) gas generators.
- Adjust the certification protocol to determine the output of liquid evaporative $HgCl_2$ gas generators developed within the EMPIR 16ENV01 MercOx project, to obtain a protocol which is fit-for-purpose for a wider range of Hg(II) gas generators used in the field.
- Validate the developed traceable certification protocols for oxidised mercury gas generators for mercury concentrations present in the atmosphere at low ng/m^3 levels and higher concentrations from emission sources for repeatability, reproducibility, bias and measurement uncertainty

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Determination of converter efficiency

- **Method development for the determination of converter efficiency based of parallel determinations**
  1. Requires a detector capable of measuring the total Hg concentration
  2. Requires a detector, capable of measuring the Hg^0 concentration, only
  3. Hg^0 source
  4. Hg(II) source

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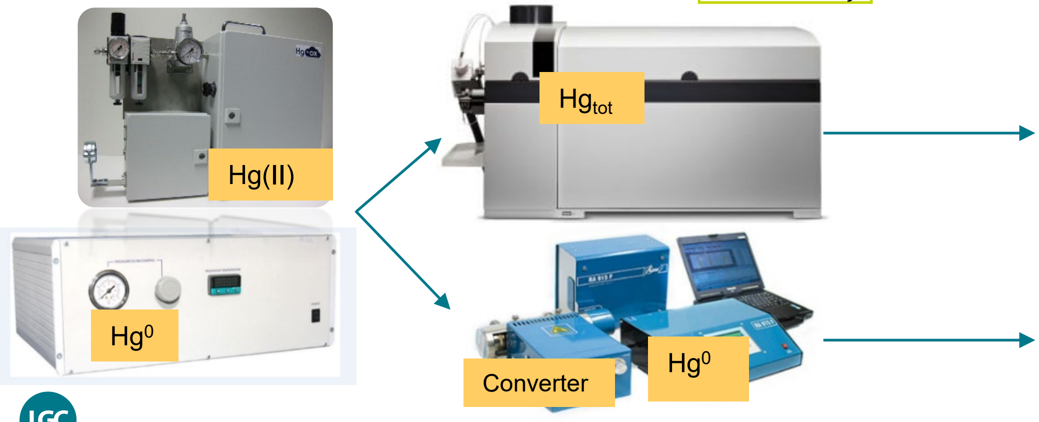
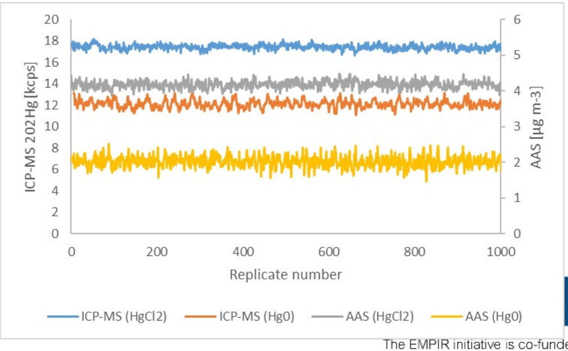
Schematic diagram of instrumental setup for converters efficiencies estimation

1. A source of elemental Hg is split and directed to:
   - ICP-MS which provides the total Hg concentration (Hg_{tot})
   - Thermal converter → AAS (which measures Hg^0)
2. The ratio $\boldsymbol{R_{ref}}$ of the AAS to ICP-MS signals is calculated.
   - Since only Hg^0 species is supplied, this is taken as a reference ratio (i.e. equivalent of 100% conversion)
3. Hg^0 generator is replaced with Hg(II) generator. After stabilisation time (2-3 hours at least) the same ratio is measured, $\boldsymbol{R_C}$
4. The converter efficiency is calculated as:

$$E_C = \frac{R_C}{R_{ref}}$$





R(c)	1.30E-04
R(ref)	1.69E-04
Ec	77%

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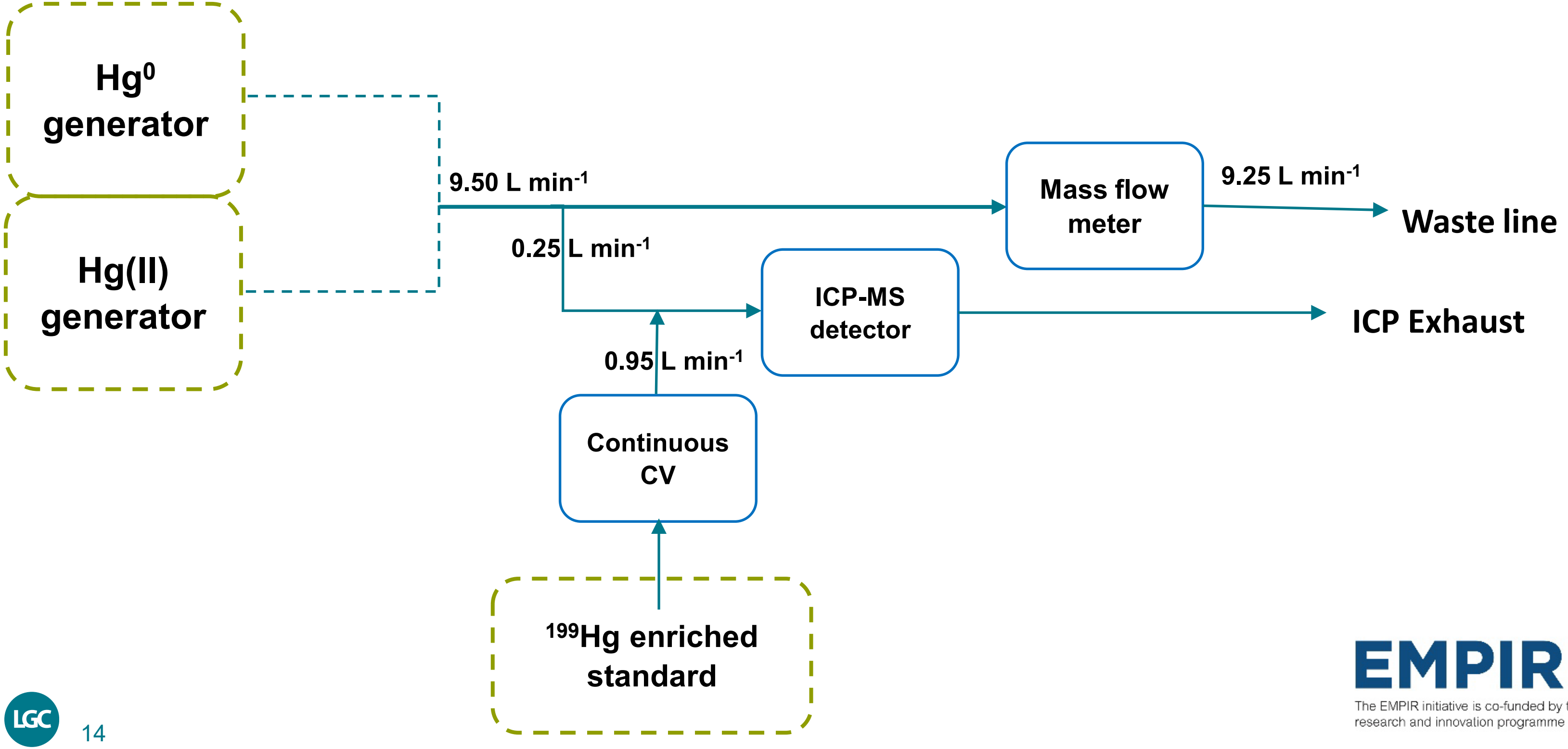
Gas phase CV-ICP-IDMS online calibration for Hg(II) and Hg^0 generators with traceability to SI



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Gas phase CV-ICP-IDMS online calibration for Hg(II) and Hg^0 generators with traceability to SI

- Liquid Phase IDMS and Reverse IDMS for enriched standard mass fraction calculation (^{199}Hg):

$$C_t = C_n \cdot \frac{m_n}{m_t} \cdot \frac{W_t}{W_n} \cdot \frac{A_n^a}{A_t^b} \cdot \left(\frac{1 - R_n \cdot R_m}{R_m - R_t} \right)$$

- Gas-phase online mass-flow IDMS

$$MF_n = MF_t \cdot \frac{W_n}{W_t} \cdot \frac{A_t^b}{A_n^a} \cdot \left(\frac{R_m - R_t}{1 - R_n \cdot R_m} \right) \cdot f_t$$

t	Tracer (i.e. ref to enriched ^{199}Hg)
n	Natural Abundance Standard i.e. referes to NIST 3133
a	Major Isotope in natural abundance standard (i.e. 202Hg)
b	Major Isotope in enriched standard (i.e. 199Hg)
C_n (pg g^{-1})	Concentration of Hg in the natural abundance standard (n)
C_t (pg g^{-1})	Concentration of Hg in the enriched standard (n)
m_n (g)	Mass of the natural abundance standard (n) added to prepare the mixture
m_t (g)	Mass of the spike or tracer added to prepare (t) the mixture
W_t (g mol^{-1})	Atomic weight of Hg in the spike or tracer (t)
W_n (g mol^{-1})	Atomic weight of Hg in the natural abundance standard (n)
A^a_n	Isotopic abundance of the major isotope (^{202}Hg) in the natural abundance standard (n)
A^b_t	Isotopic abundance of the major isotope (^{199}Hg) in the isotopically-enriched standard (t)
R_n	Isotope Ratio $^{199}Hg/^{202}Hg$ in the natural abundance standard (n)
R_t	Isotope Ratio $^{202}Hg/^{199}Hg$ in isotopically-enriched tracer
R_m	Experimental Isotope Ratio ($^{202}Hg/^{199}Hg$) in the gas mixture (m)
Mfi [g min^{-1}]	mass flow of the enriched standards and Hg gas generator
f_t	Cold vapour generator efficiency

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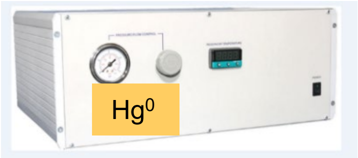
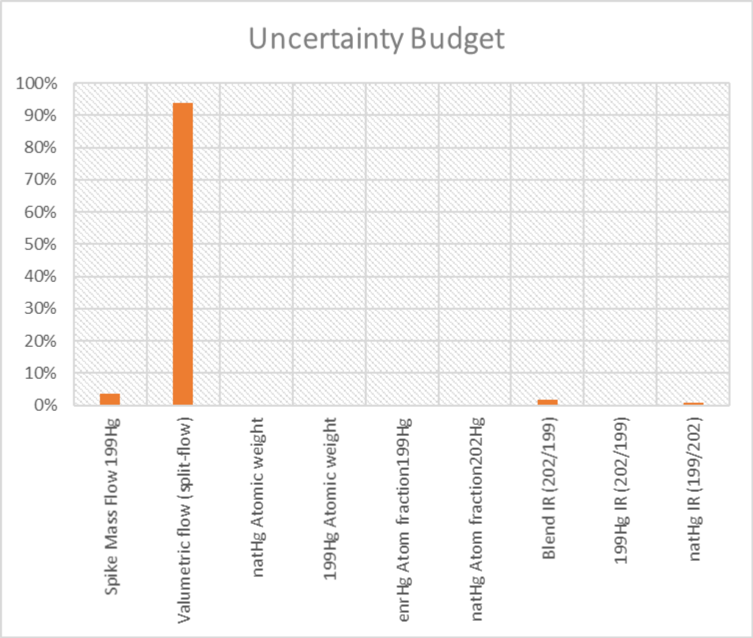
Case study - Gas phase CV-ICP-IDMS online calibration of saturated vapours Hg^0 generator

$$MF_{GEN} = \frac{MF_{t\_e}}{V_f} \cdot \frac{Aw_{(Hg\_n)}}{Aw_{(Hg\_e)}} \cdot \frac{A_{(199Hg)\_e)}}{A_{(202Hg)\_n}} \cdot \left(\frac{R_{b(\frac{202Hg}{199Hg})} - R_{e(\frac{202Hg}{199Hg})}}{1 - R_{b(\frac{202Hg}{199Hg})} \cdot R_{n(\frac{199Hg}{202Hg})}} \right)$$



Parameter	Anotation	Unit	Value	Uncertainty
Enriched std Mass Flow ^{199}Hg	MFt_e	pg min^{-1}	13.2	0.2
Valumetric flow (split-flow)	Vf	sl min^{-1}	0.25	0.02
natHg Atomic weight	Aw(Hg_n)	g mol^{-1}	200.592	0.002
^{199}Hg Atomic weight	Aw(Hg_e)	g mol^{-1}	199.1	0.1
enrHg Atom fraction ^{199}Hg	A(199Hg)_e	-	91.95	0.05
natHg Atom fraction ^{202}Hg	A(202Hg)_n	-	29.7	0.1
Blend IR (202/199)	Rb(202Hg/199Hg)	-	0.820	0.004
^{199}Hg IR (202/199)	Re(202Hg/199Hg)	-	0.0079	0.0001
natHg IR (199/202)	Rn(199Hg/202Hg)	-	0.570	0.005
Generator mass flow (natHg)	MFgen	ng m^{-3} (pg L^{-1})	246	22
			RSU	8.9%

Gas-phase IDMS – Uncertainty budget*



$$MF_{GEN} = \frac{MF_{t\_e}}{V_f} \cdot \frac{Aw_{(Hg\_n)}}{Aw_{(Hg\_e)}} \cdot \frac{A_{(199Hg)\_e)}}{A_{(202Hg)\_n}} \cdot \left(\frac{R_{b(\frac{202Hg}{199Hg})} - R_{e(\frac{202Hg}{199Hg})}}{1 - R_{b(\frac{202Hg}{199Hg})} \cdot R_{n(\frac{199Hg}{202Hg})}} \right)$$

u_C=8.9%

*u_C – combined measurement uncertainty (k=1)

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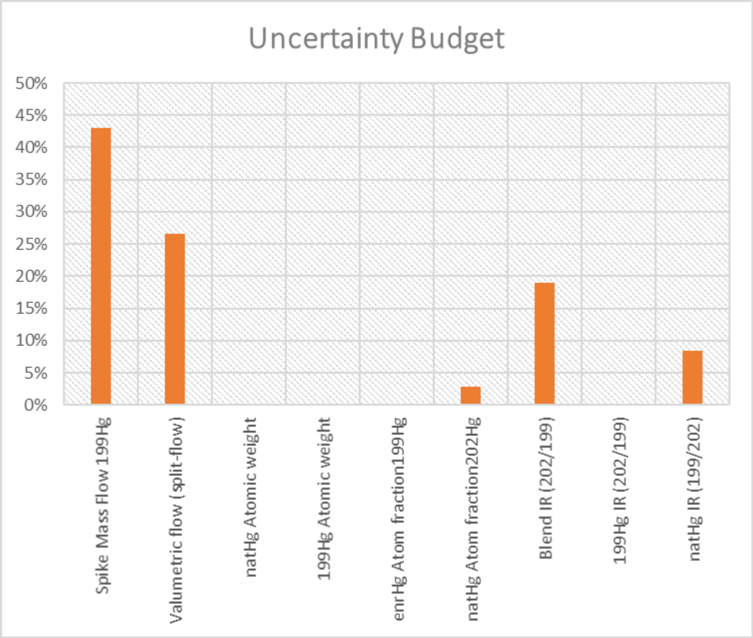
Gas-phase IDMS – V_f improvement



$$MF_{GEN} = \frac{MF_{t\_e}}{V_f} \cdot \frac{Aw_{(Hg\_n)}}{Aw_{(Hg\_e)}} \cdot \frac{A_{(199Hg)\_e)}}{A_{(202Hg)\_n}} \cdot \left(\frac{R_{b(\frac{202Hg}{199Hg})} - R_{e(\frac{202Hg}{199Hg})}}{1 - R_{b(\frac{202Hg}{199Hg})} \cdot R_{n(\frac{199Hg}{202Hg})}} \right)$$

u_C=2.6%

Improvement by measuring smaller differences in *Vf* with accurate mass-flow meter providing lower uncertainty

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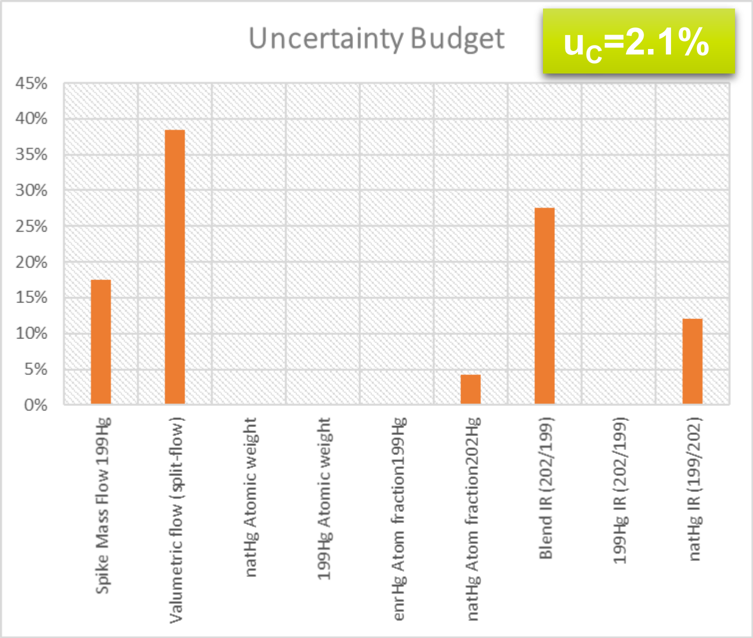
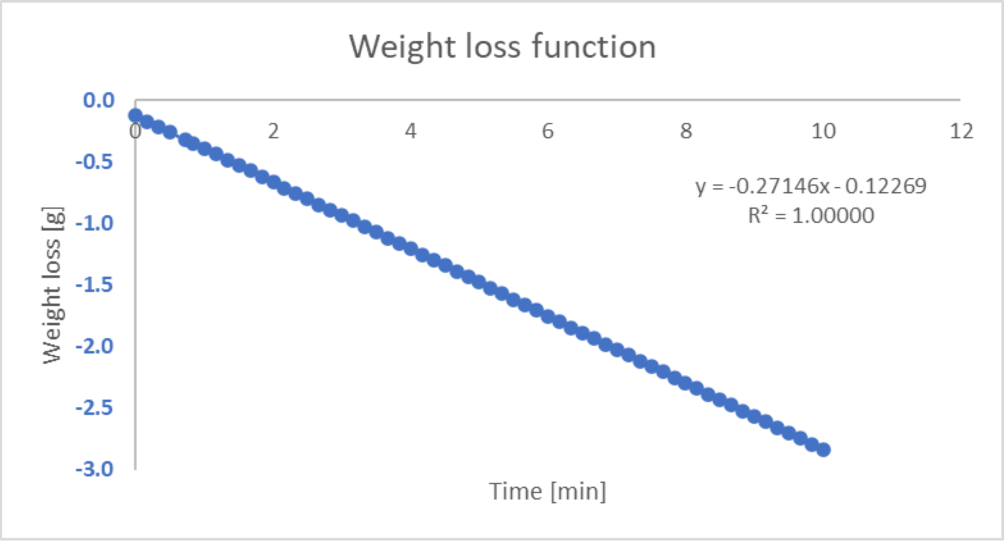
Gas-phase IDMS – MF_{t_e} improvement

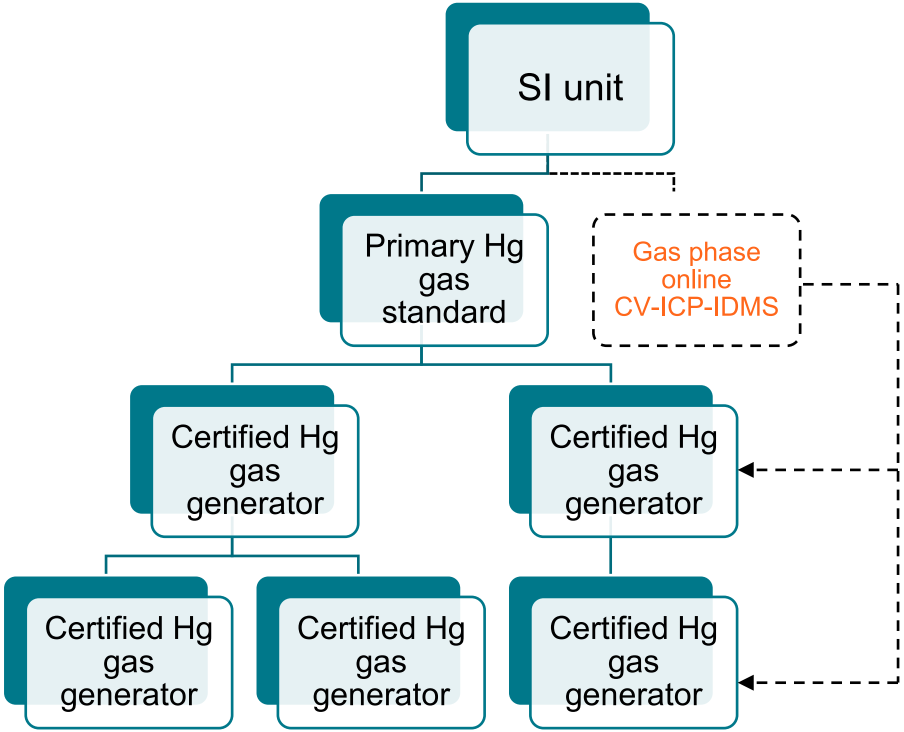


$$MF_{GEN} = \frac{MF_{t\_e}}{V_f} \cdot \frac{Aw_{(Hg\_n)}}{Aw_{(Hg\_e)}} \cdot \frac{A_{(199Hg)\_e}}{A_{(202Hg)\_n}} \cdot \left(\frac{R_{b(\frac{202Hg}{199Hg})} - R_{e(\frac{202Hg}{199Hg})}}{1 - R_{b(\frac{202Hg}{199Hg})} \cdot R_{n(\frac{199Hg}{202Hg})}} \right)$$

Improvement by using weight-loss function for MF_{t_e}



Traceability chain



WP3: Performance evaluation of elemental and oxidised mercury generators on the market

Start-up

- ✓ Collaborators selected
- ✓ Experimental approaches determined in WP1 (Hg^0) and WP2 (Hg^{II})
- ✓ Protocols for the campaign under development

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Project outcomes and future work

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- Improved traceability of Hg measurements at global level
- Improved comparability through certification of gas generators (GMOS system)
- Novel approach for generators certification with direct traceability to SI units through the use of IDMS

Future work :

- Performance Evaluation Hg^0 and Hg(II) gas generators (field measurements, WP3)
- To **support the development of a suitable calibration system** for mercury measurements in the atmosphere, as part of the global mercury observation system used to measure the effectiveness of the implementation of the Minamata Convention.
- To facilitate **the uptake of protocols, methods, technology and measurement infrastructure** developed in the project by the standards developing organisations and end-users. (*WP4*)
- Knowledge transfer between NMIs, organise CCQM studies, support CMCs

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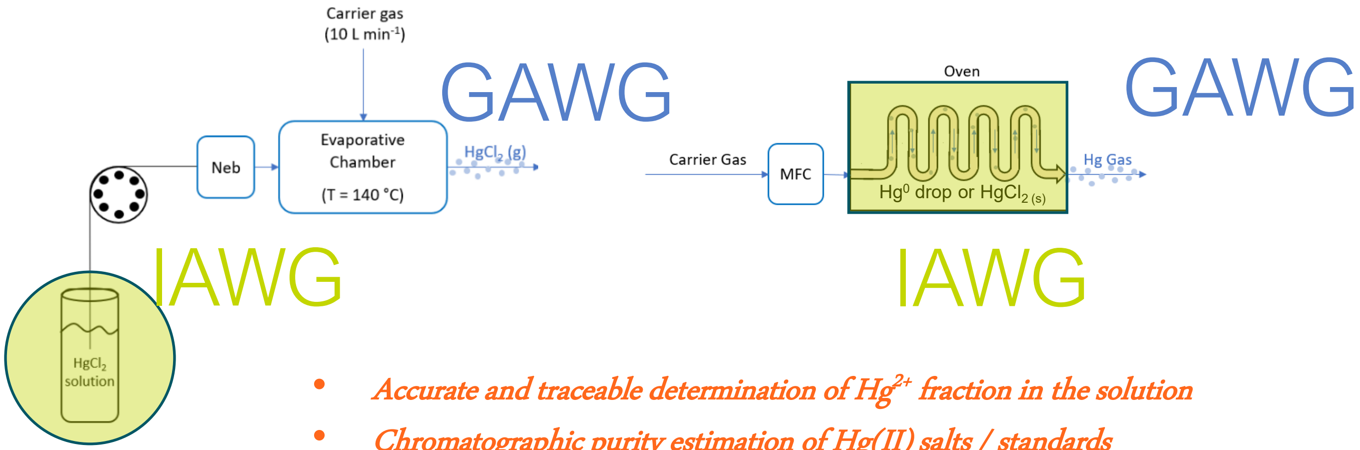
19NMR03 SI-Hg common areas IAWG ↔ GAWG



- *Accurate and traceable determination of Hg^{2+} fraction in the solution*
- *Chromatographic purity estimation of Hg(II) salts / standards*
- *Elemental impurities determination in pure Hg(II) standard*
- *Elemental impurities determination of pure Hg-salts*
- *Elemental impurities determination in ultra-pure Hg drop*

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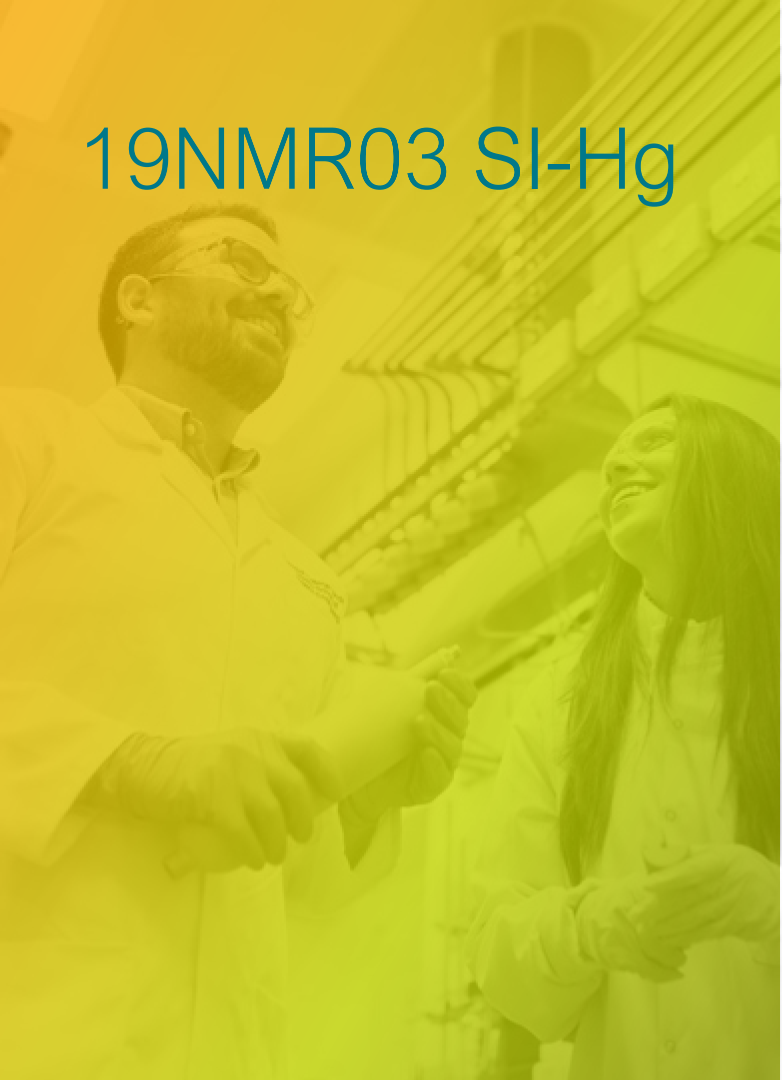

SI-Hg

Thank you

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