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19NRM03 SI-Hg Webinar

Metrology for traceable protocols for elemental and oxidised mercury concentrations

04-03-2022

Iris de Krom

Agenda SI-Hg Webinar

- Welcome (Iris de Krom, VSL)
- MercOx results and impact (Milena Horvat, JSI)
- SI-Hg project overview (Iris de Krom, VSL)
- Introduction, progress, and further approach WPs
  - WP1 – Elemental mercury (Iris de Krom, VSL)
  - WP2 – Oxidised mercury (Panayot Petrov, LGC)
  - WP3 – Performance evaluation (Timo Rajamäki, VTT)
- Discussion

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Partners

Thanks to our stakeholders and chief stakeholder: **David Graham Uniper**

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EMPIR
European Metrology Programme for Innovation and Research

Goals

- It is about improving measurement to drive innovation and competitiveness and to support societal challenges and regulation
- It enables European metrology institutes, industrial organisations and academia to collaborate on joint research oriented projects

Organisation

- Implemented by EURAMET (European Association of National Metrology Institutes)
- Jointly funded by the EMPIR participating countries and the European Union
- Budget of approximately 600 M€ over seven years (H2020)

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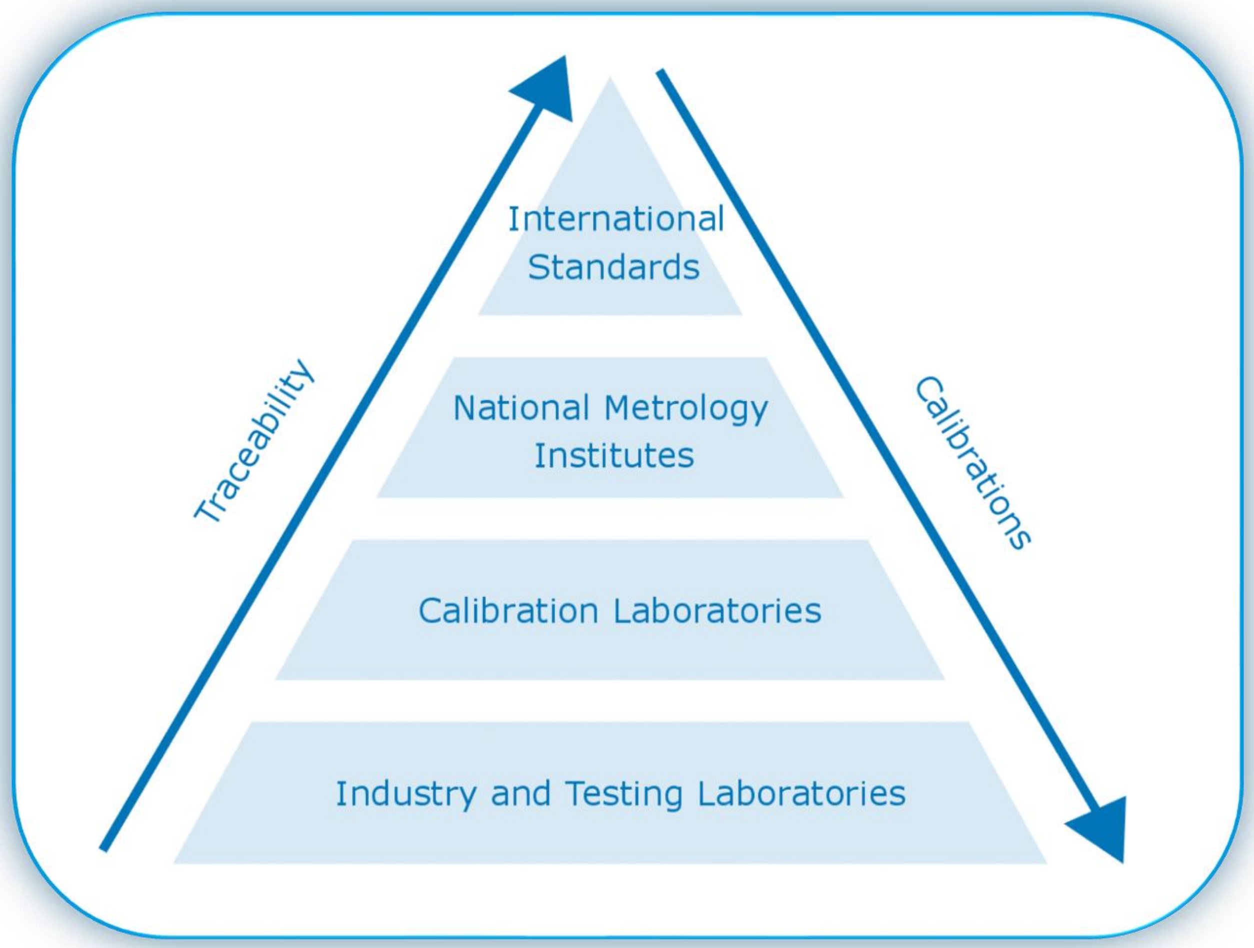
SI-traceability



National Metrology Institute

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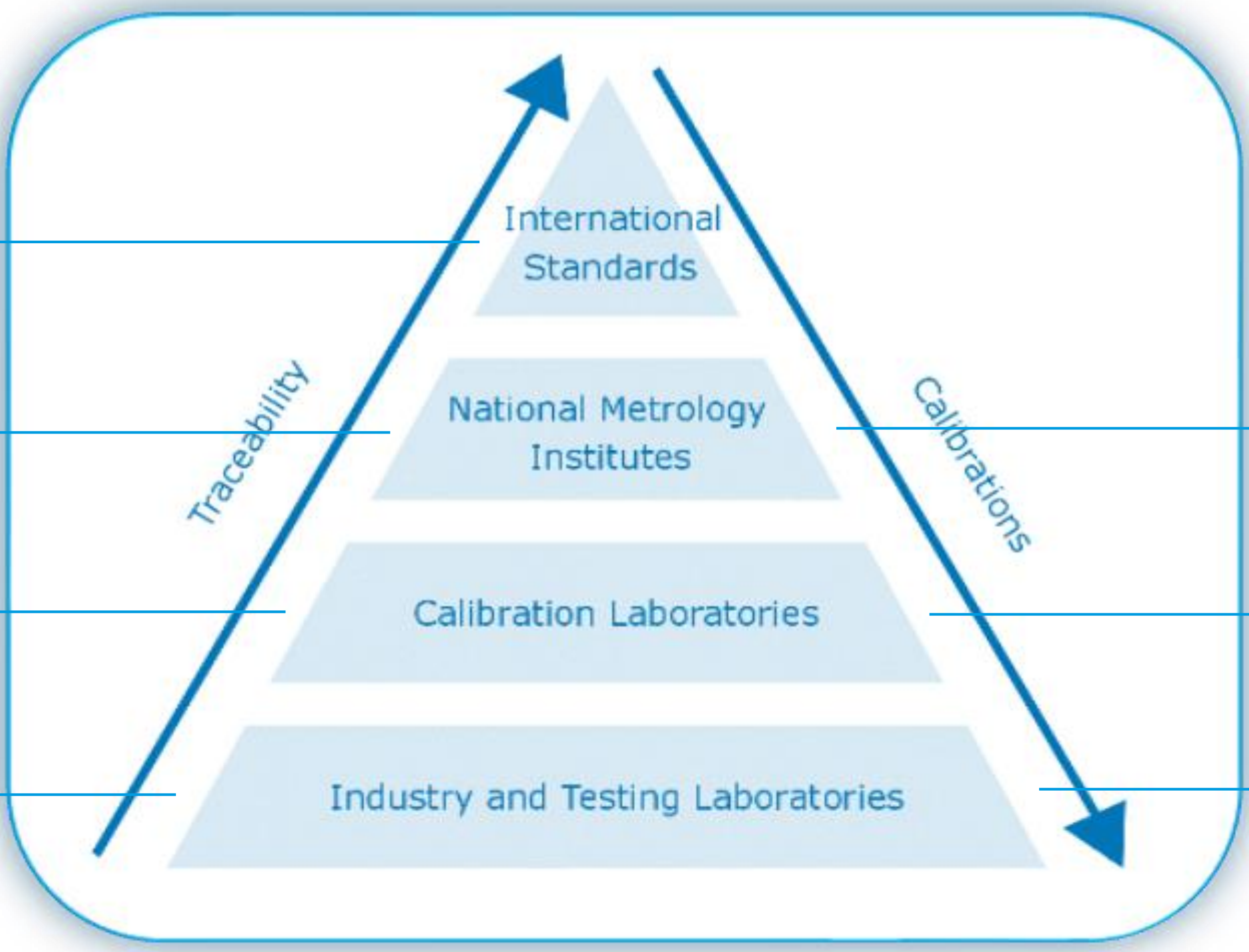
SI-traceability of mercury measurement results in air

Kg (BIPM)

Development of primary standards and working standards (NMI)

Calibration of standards and equipment; currently not SI-traceable

Field measurements; Currently not SI-traceable



EMRP and EMPIR Projects

PartEmission, MeTra and MercOx

Bring present NMI state of the art to industry

SI-Hg → validated protocols → to improve SI-traceability

Metrological traceability requires an established calibration hierarchy

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SI-Hg – Metrology for traceable protocols for elemental and oxidised mercury concentrations – 19NRM03

- 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

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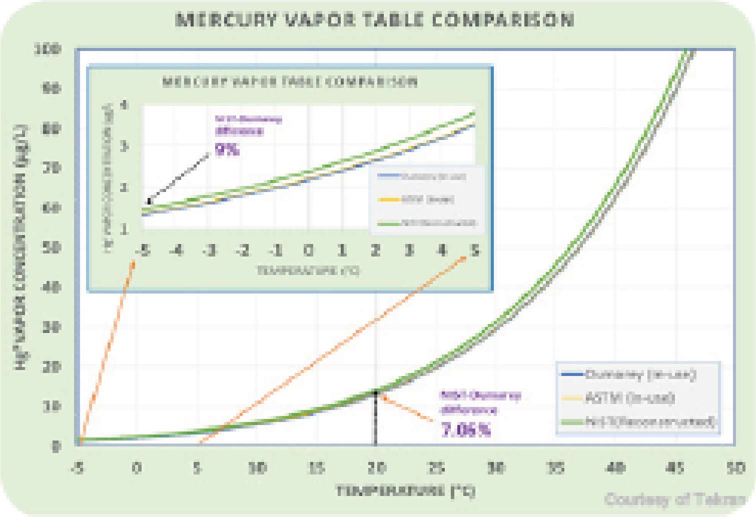
SI-Hg – Metrology for traceable protocols for elemental and oxidised mercury concentrations – 19NRM03

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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SI-Hg – Metrology for traceable protocols for elemental and oxidised mercury concentrations – 19NRM03

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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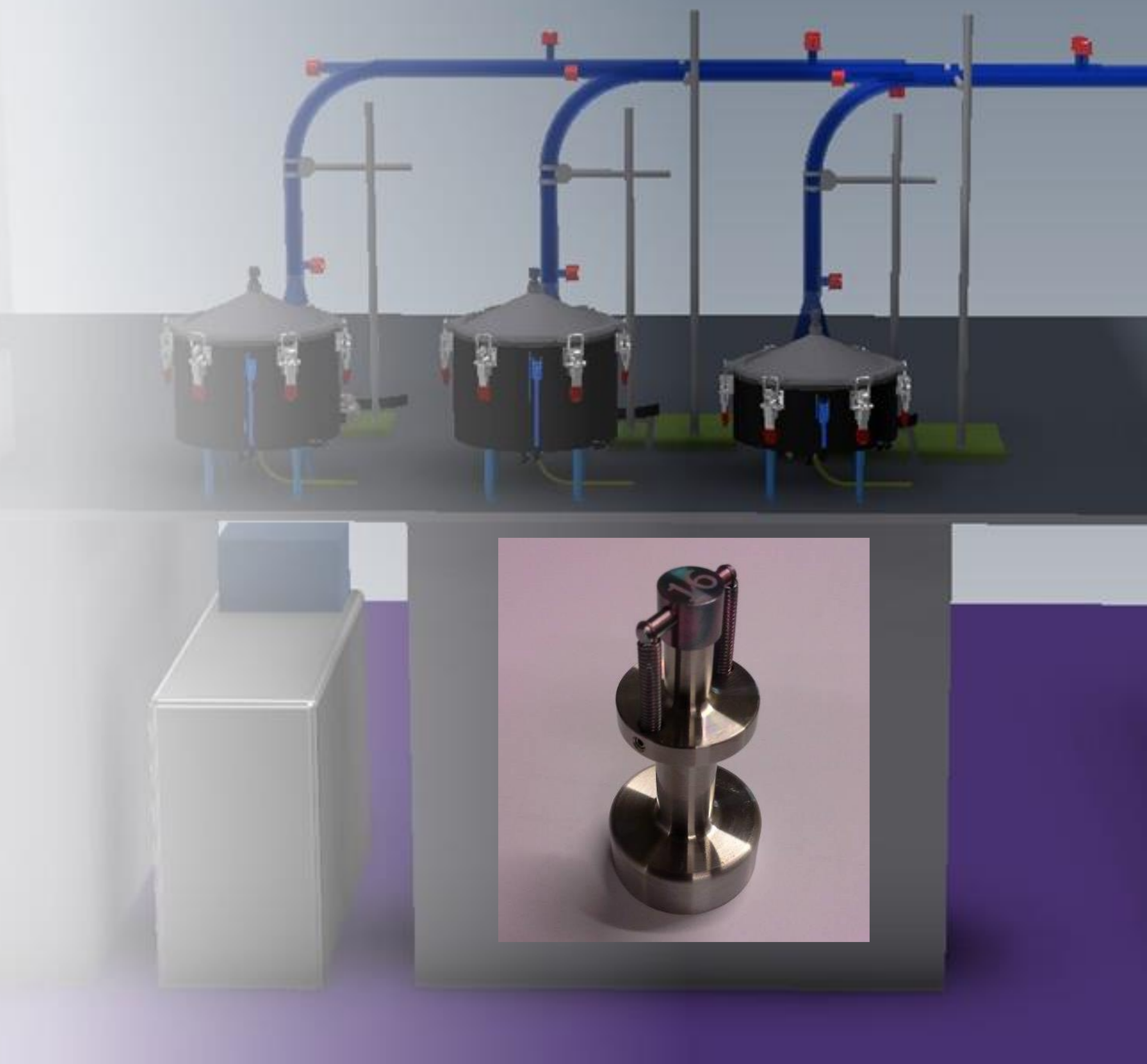
VSL

Primary Mercury Gas Generator

- Based on first principles
  - Diffusion according to ISO 6145-8
  - Gravimetry
  - Volumetry

- Stainless steel diffusion cells
  - Elemental mercury

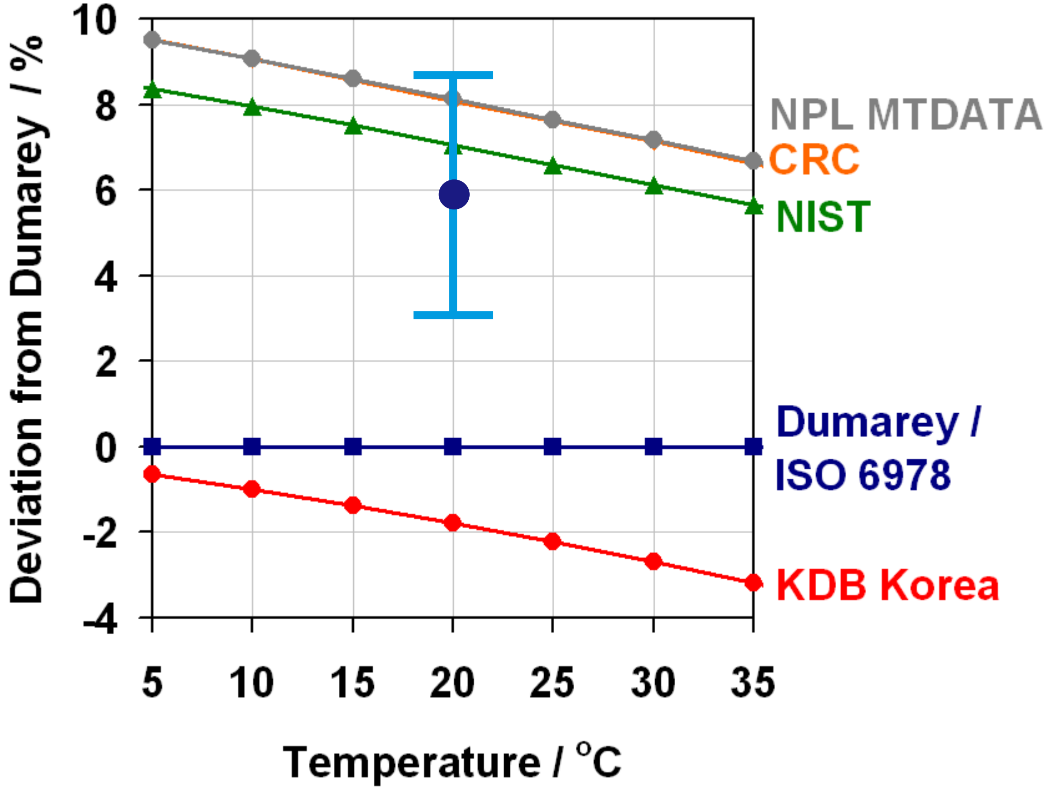
- Range
  - 10 – 500 ng m^{-3} (under validation)
  - 0.1 – 2.1 µg m^{-3} (U = 3 % (k =2))
  - 0.7 – 16 µg m^{-3} (under validation)
  - 5 – 100 µg m^{-3} (U = 1.8 % (k =2))



de Krom et al. Measurement 169 (2021) 108351
doi: https://doi.org/10.1016/j.measurement.2020.108351

Traceability for mercury measurement results

- Traceability for elemental mercury
  - In emission sources and the atmosphere
  - Comparisons between current calibration facilities
    - Dumarey equation
    - NIST SRM
- Future
  - Comparison with NIST
  - SI traceability in written standards
    - EMPIR 19NMR03 SI-Hg (www.si-hg.eu)



de Krom et al. Atmos. Meas. Tech., 14 (2021) 2317-2326
doi: https://doi.org/10.5194/amt-14-2317-2021

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19NRM03 SI-Hg WP1

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

Webinar 04-03-2022

Iris de Krom

WP1: Development and validation of a SI-traceable certification protocol for elemental mercury gas generators used in the field

- **Task 1.1:** The aim of this task is to **develop** a traceable **certification protocol** for elemental mercury gas generators used in the field traceable to SI.
- **Task 1.2:** The aim of this task is to **validate** the traceable certification protocol developed in A1.1.4 for Hg^0 gas generators, through direct comparisons at concentration levels, which are valid for mercury measurements from **emission sources**.
- **Task 1.3:** The aim of this task is to **validate** through indirect comparisons the certification protocol for elemental mercury gas generators developed in A1.1.4, at concentration levels which are relevant for **atmospheric mercury** measurements in the sub ng/m^3 range.
- **Task 1.4:** The aim of this task is to determine the consistent quality of mercury measurements during a **comparison**. Participants will perform field measurements using elemental gas generators and methods for the simultaneous determination of the mercury concentration at the **Monte Curcio Climatic-Environmental Observatory**, an official **European GMOS mercury speciation site**.

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Scope certification protocol

- 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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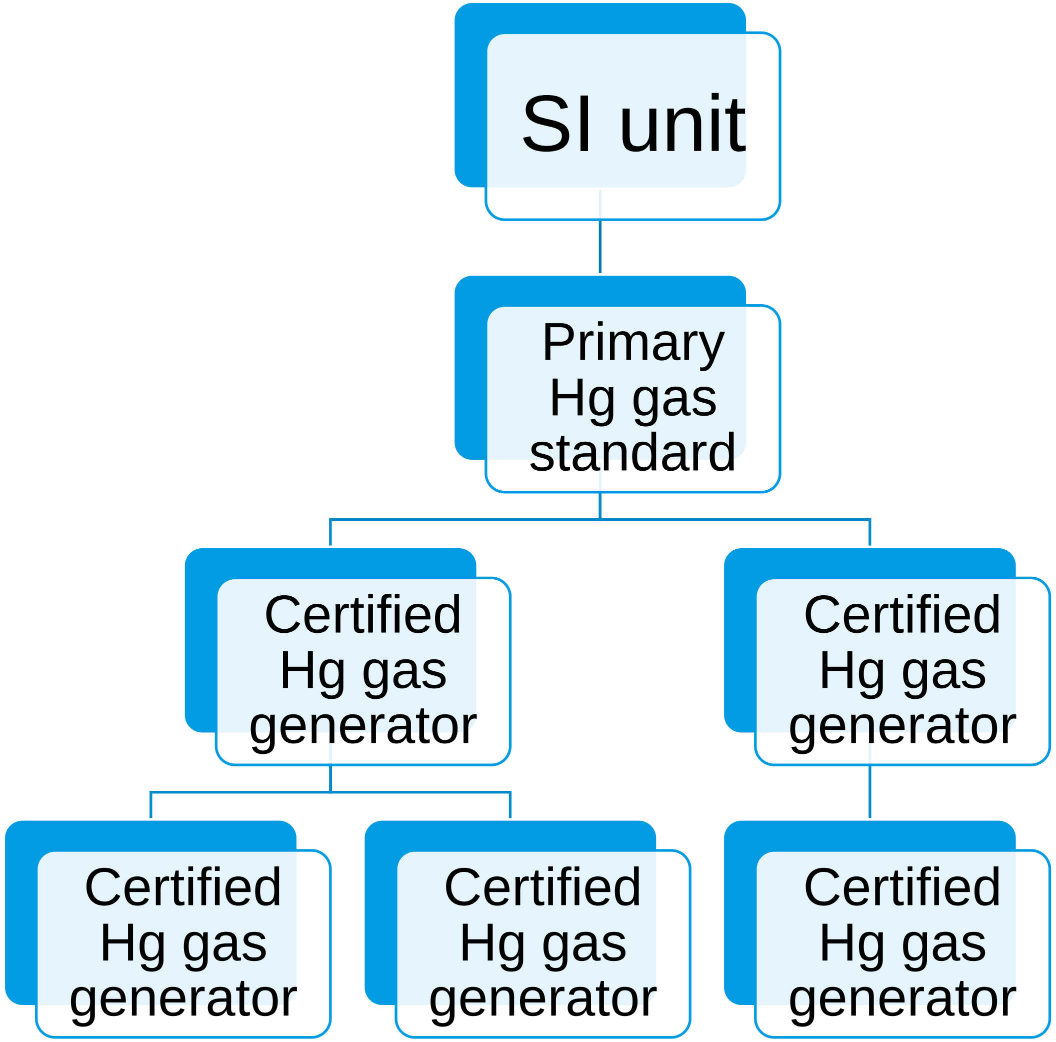
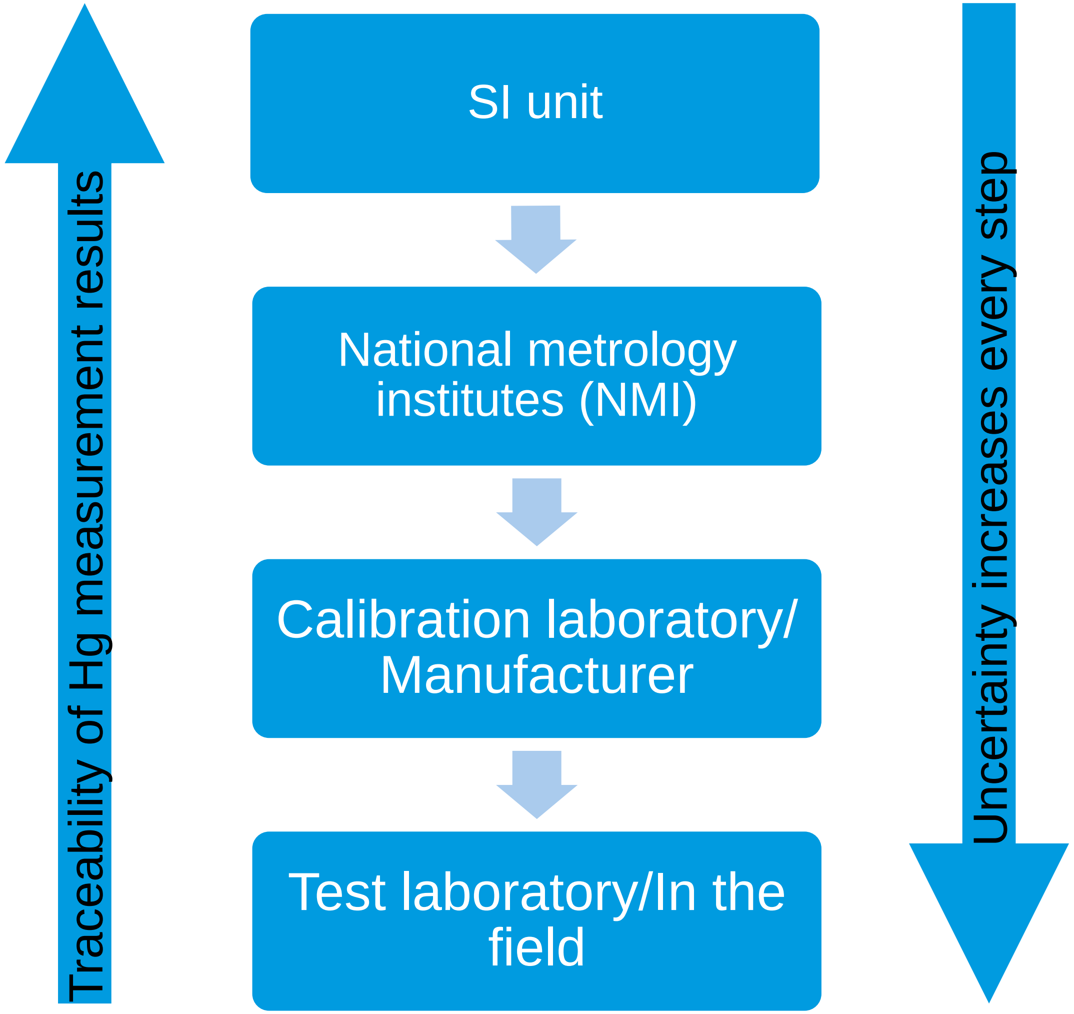
Traceability chain





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Principle certification protocol

- The mercury concentration in a gas mixture prepared with a mercury gas generator is determined by comparison with a metrologically traceable reference standard to calibrate the output of a candidate gas generator.
  - At one concentration level – single-point calibration
  - At several concentration levels – multipoint calibration
- Bracketing measurement sequence

Generator ID	Response ID
Reference standard	RS_1
Candidate	C_1
Reference standard	RS_2
Candidate	C_2
Reference standard	RS_3
Candidate	C_3
Reference standard	RS_4

- There are two approaches for the data processing
  - Without zero correction
  - With zero correction

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Equipment

- The method is applicable for different types of mercury gas generators:
  - Bell-jar generator, working according to ISO 6145-9
  - Saturation gas generators, working according to o ISO 6145-9
  - Permeation gas generators, working according to ISO 6145-10
  - Mercury amount fractions in high-pressure cylinders, prepared according to ISO 6142-1
  - Reduction gas generators of Hg(II) to Hg(0)

- Mercury reference standard:
  - The metrological traceable reference standard can either be a 1) primary mercury standard or 2) a metrologically calibrated reference standard, e.g., a calibrated mercury gas generator or a calibrated gas mixture in a high-pressure cylinder.

- Analyser equipment
  - AFS or AAS
  - Direct measurement system or pre concentration system

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Stepwise procedure

Step A: Zero the detector by injecting zero gas and making any necessary zero adjustments. Alternatively, obtain the response of the zero gas from the detector (r_z).

Step B: Direct the output of the reference standard to the detector and obtain a response (r_{rs1}).

Step C: Direct the output of the candidate gas generator to the detector and obtain a response (r_{u1}).

Step D: Switch back to direct the output of the reference standard to the detector and obtain a response (r_{rs2}).

Step E: Repeat steps C and D two more times to achieve triplicate responses for the mercury concentration from the candidate generator and quadruple responses for the mercury concentration from the reference standard.

Step F: In case the deviation between RS_1 and RS_4 is bigger than 1 % at least one extra repeat of steps C and D shall be performed.

Step G: When applying a multipoint calibration repeat steps B through E for the second, third and following concentration levels.

Step H: Check the zero response of the detector, without making any adjustments.

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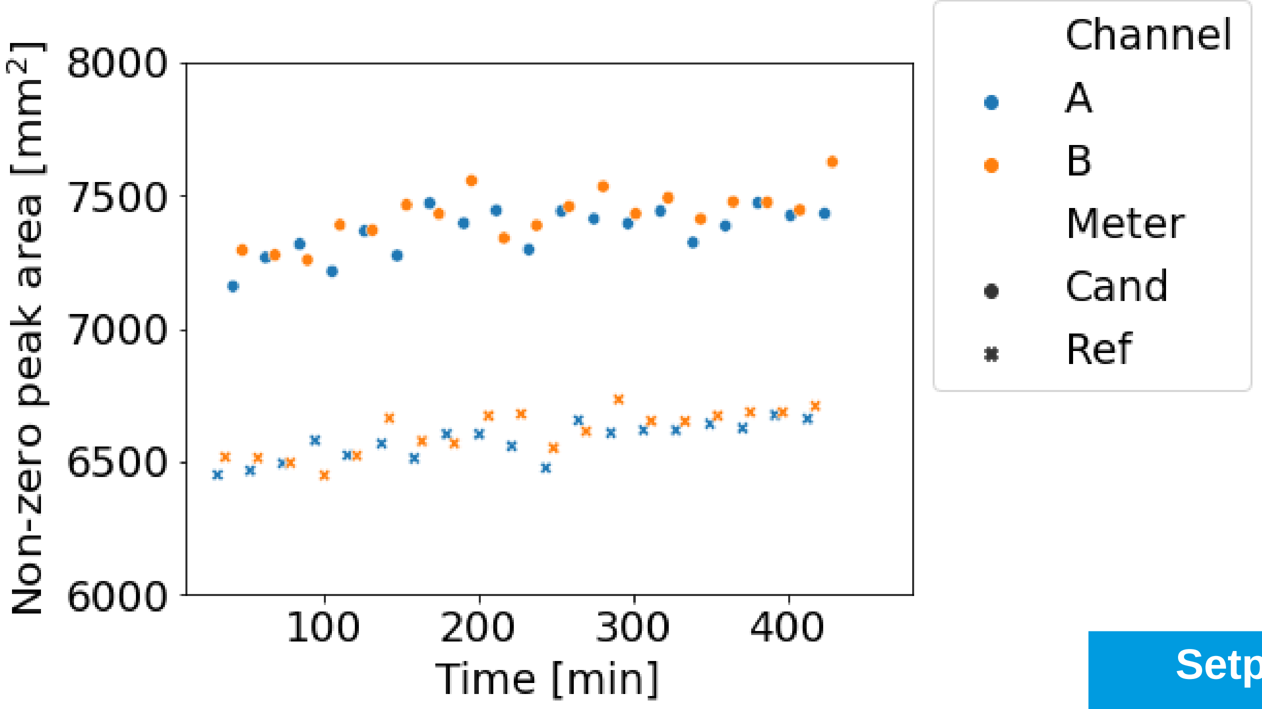
First validation measurements – Single point calibration



Setpoint candidate (µg m^{-3})	2.571
Reference standard ± U (µg m^{-3}, k = 2)	2.167 ± 0.065

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Data processing
Single-point calibration **with** zero correction (1/3)

Step L: To determine the actual output of the User generator, first correct each response for any zero offset of the detector. Calculate the interpolated zero offset based on the time when a specific response was recorded according to equation (3):

$$r_{zi} = r_{z1} + \left[(t_i - t_1)\frac{(r_{z1} - r_{z2})}{(t_1 - t_2)}\right] \quad (3)$$

Step M: then, correct the response at t_i for the zero offset using equation (4):

$$r_{u_{corr}} = r_u - r_{zi} \quad (4)$$

Time (min)	y_{rs}	$y_{rs_{corr}}$	y_u	$y_{u_{corr}}$
140	6539	6522		
150			7270	7254
161	6523	6507		
172			7331	7315
182	6521	6506		
193			7293	7278
203	5649	6534		
214			7354	7339
225	6601	6587		
235			7439	7425
246	6643	6630		

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Data processing
Single-point exact-match calibration **with** zero correction (2/3)

Step N: Next, calculate the output ratio (R) for each value of r_{corr} according to equation (5):

$$R = \left[\frac{r_{u_{corr}}}{\frac{r_{rs1_{corr}} - r_{rs2_{corr}}}{2}}\right] \quad (5)$$

Step O: Next, average the three calculated output ratios arithmetically.

Step P: Finally, use Equation (6) to determine Y_{c_i}, the calculated candidate gas generator output mercury concentration.

$$Y_{c_i} = c_{rs}\,\bar{R} \quad (6)$$

Step R: For each concentration level calculate the relative standard deviation (RSD) of the output rations. The RSD shall not exceed 1.0 %. If the RSD value is exceeded, the test is invalid and shall be repeated.

Step S: Determine the uncertainty of the mercury concentration from the candidate gas generator

Time (min)	r_{rs}	$r_{rs_{corr}}$	r_u	$r_{u_{corr}}$	Output ratio (R)
140	6539	6522			
150			7270	7254	1.113
161	6523	6507			
172			7331	7315	1.124
182	6521	6506			
193			7293	7278	1.116
203	5649	6534			
214			7354	7339	1.119
225	6601	6587			
235			7439	7425	1.124
246	6643	6630			

Mean R	1.119
RSD [%]	0.42

Setpoint (µg m^{-3})	2.571
Y_{c_i} (µg m^{-3})	2.427
U (%) (*k* = 2)	3.0
D (%)	-5.6

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Difference compared to NIST procedure

Interim EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators - 2009

- Single procedure for both user generator and field reference generator
- Data processing with and without zero correction
- Multipoint calibration is added to enable interpolation with use of regression
- Integrated with ISO and EN standards

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Next steps

- Elaborate calculations to determine calibration function and uncertainty (*2022*)
- Validation protocol (*2022*)
- Performance evaluation of elemental mercury generators on the market (*2022/2023*)
- Finalize protocol based on validation and performance evaluation (*2023*)
- Software available for data processing and uncertainty calculations (*2023*)
- Protocol converted into a written documentary standard (*2025*)

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Comparison at the climatic-Environmental Observatory MCU

- The Monte Curcio CNR-IIA station is a Climatic-Environmental Observatory located in a strategic and isolated position within the Sila Grande area. The operative station is situated at 1780 m a.s.l. on a southern Apennine mountain peak with completely free horizon.
- CRN will invite companies regularly performing mercury measurements at air monitoring sites, in contact with regional and global monitoring programmes. 2 – 5 participants will be selected for the comparison exercise.

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