VSL

National Metrology Institute

Metrology for traceable protocols for elemental and oxidized mercury concentrations

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CEM 2023 – 22nd September 2023 – Barcelona – Spain

Session: Mercury

SI-Hg

Introduction

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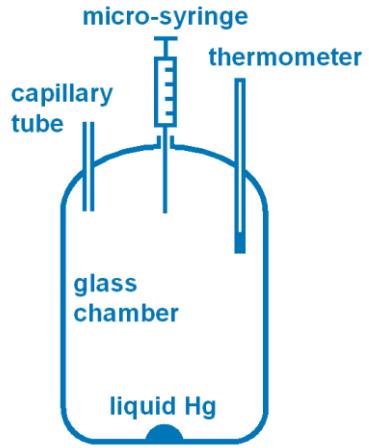
Standardisation

- **EN 14181** *Quality assurance of automated measuring systems*
  1. Requirements for the calibration and validation → **QAL 2**
     - With guidance specific for mercury measurements **EN 14884** *determination of total mercury – automated measuring systems*
       - 6.2.2 **Zero and span check** (EN 14181:2014, A.7): Elemental mercury shall be used for the independent span check provided that the reference material generator used by the test laboratory is calibrated with metrological traceability to the SI.
       - 6.2.3 **Linearity test** (EN 14181:2014, A.8 and Annex B): Linearity tests shall be performed by passing gaseous reference materials through the entire automated measuring systems
       - 6.2.4 **Response time** (EN 14181:2014, A.11): Response time tests shall be performed by passing gaseous reference materials through the entire automated measuring systems
       - 6.2.5 **Converter efficiency**: The converter efficiency shall be tested to confirm that oxidized mercury is converted to elemental mercury. Oxidized mercury reference materials shall be introduced (e.g.; $HgCl_2$).
     - **EN 13211** *Manual method of determination of the concentration of total mercury SRM manual method*
       - based on wet chemistry
  2. Requirements for quality control→ **QAL 3**
     - **Zero and span check**
- **US EPA** traceability protocol for qualification and certification of elemental and oxidised mercury gas generators

Mercury gas generators

- Saturation gas generators (ISO 6145-9)
  - Manually with syringe injection (bell-jar)
  - Automatically
- Permeation gas generators (ISO 6145-10)
- Mercury amount fraction in cylinders (ISO 6142-1)
- Continuous injection (ISO 6145-4)
  - Based on vaporization of a mercury chloride solution



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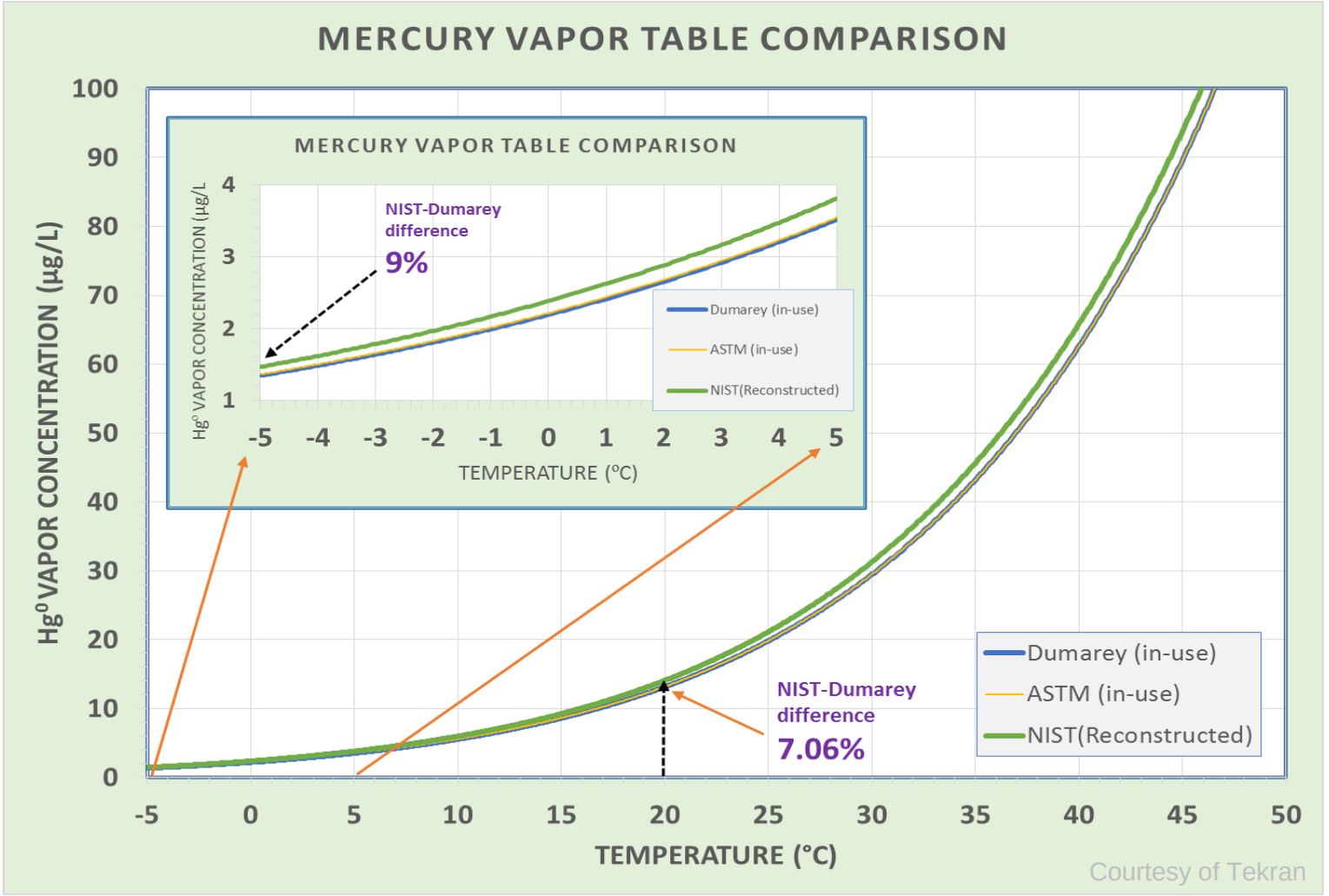
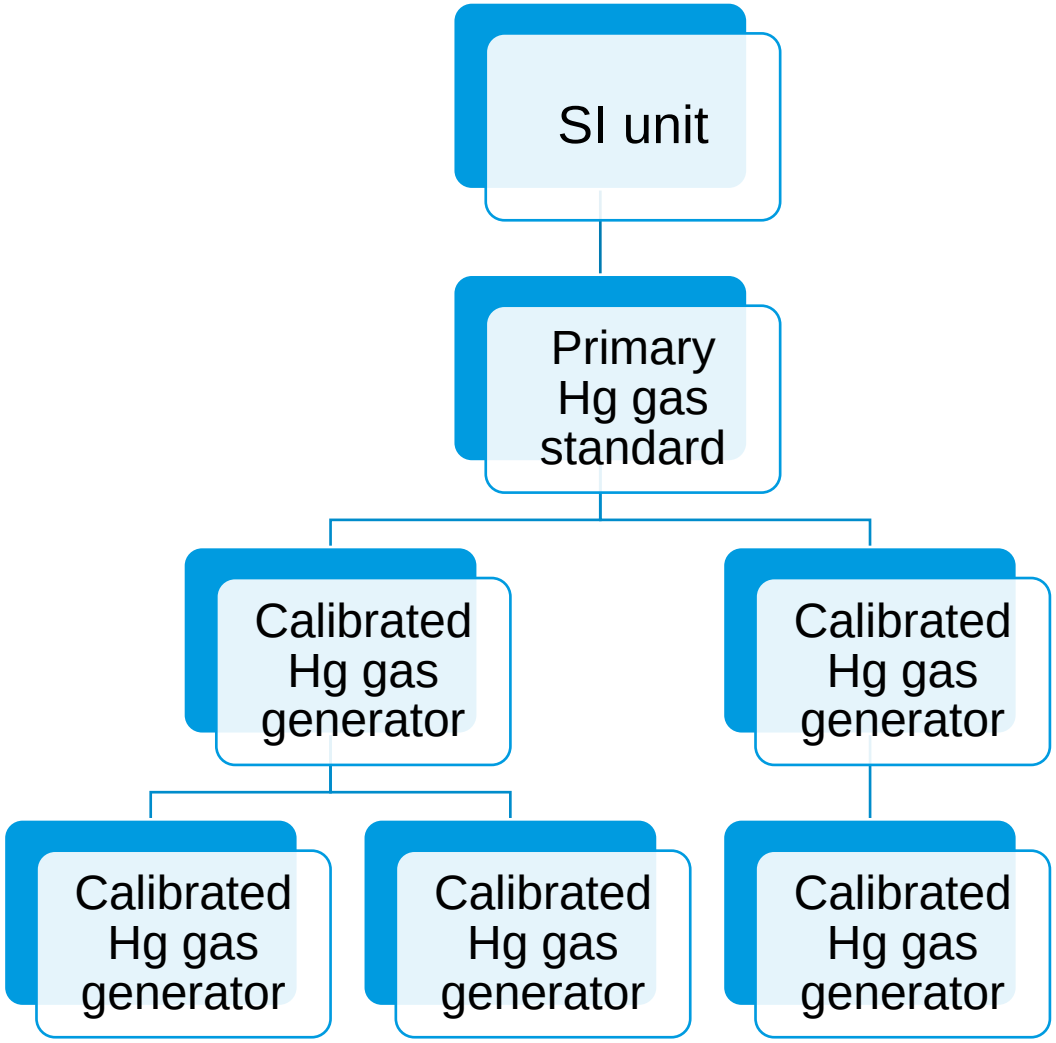
Vapour pressure equations

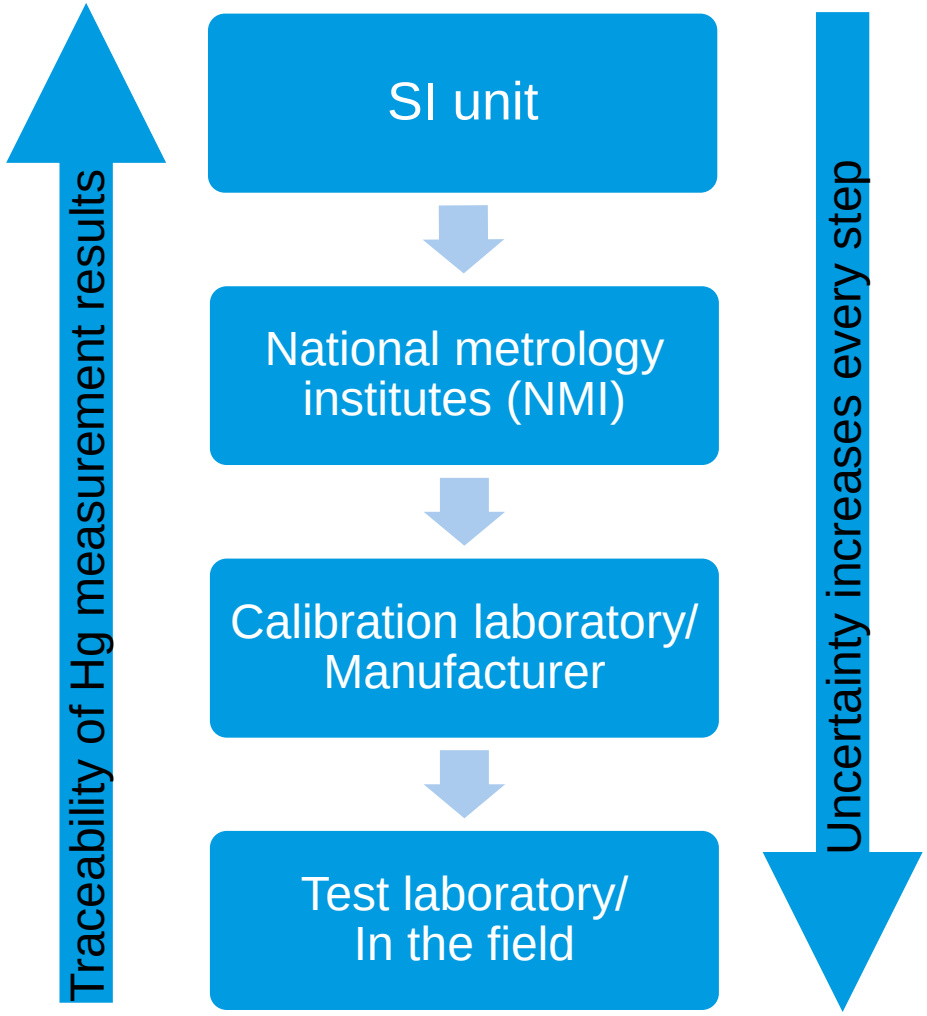
- Mercury concentration dependent upon vapour pressure equation used



Courtesy of Tekran

Traceability chain





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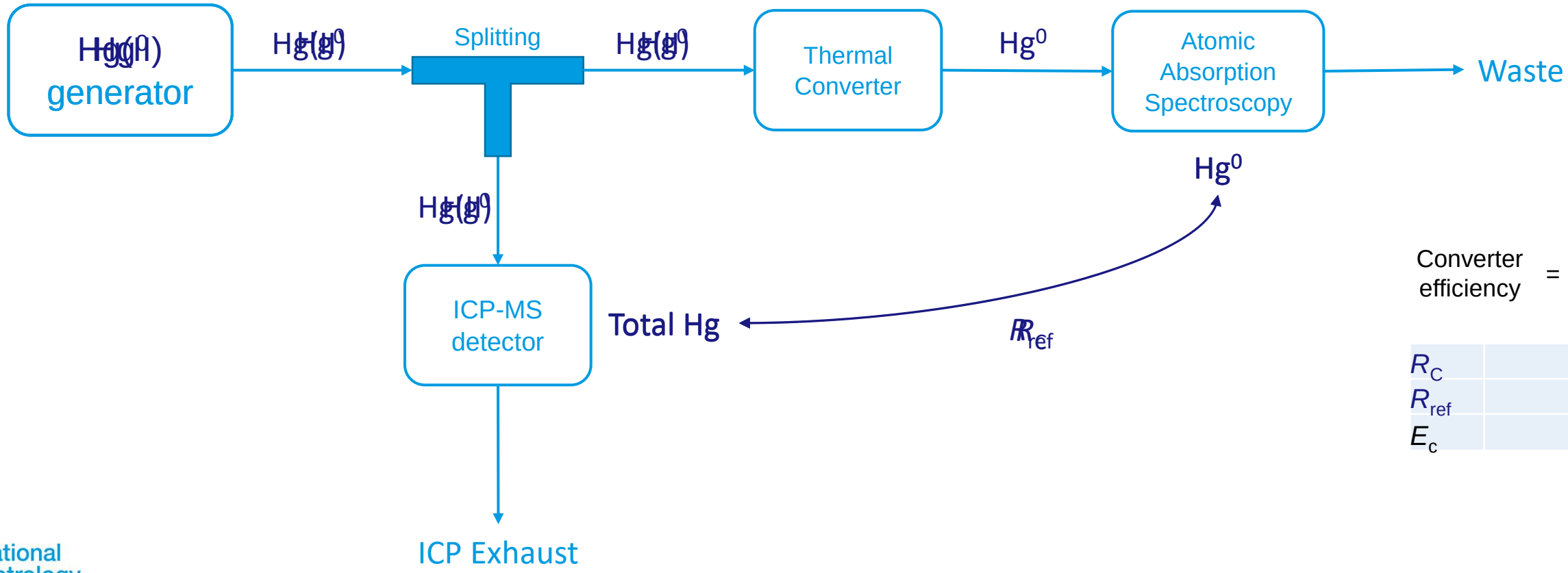
Oxidised mercury converter efficiency



$$\text{Converter efficiency} = \frac{R_C}{R_{ref}}$$

R_C	343
R_{ref}	392
E_c	88%

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Calibration protocol

- This protocol specifies the procedures for establishing **traceability to the SI** for the **quantitative output of mercury gas generators** that are employed in regulatory applications for emission or ambient air monitoring.

- This protocol provides methods for
  - Calibrating 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.

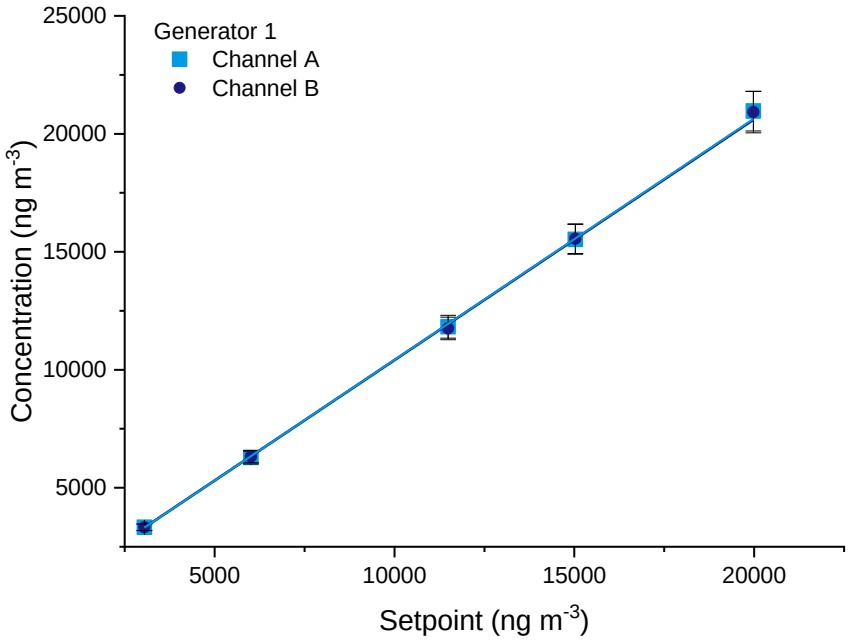
Performance evaluation

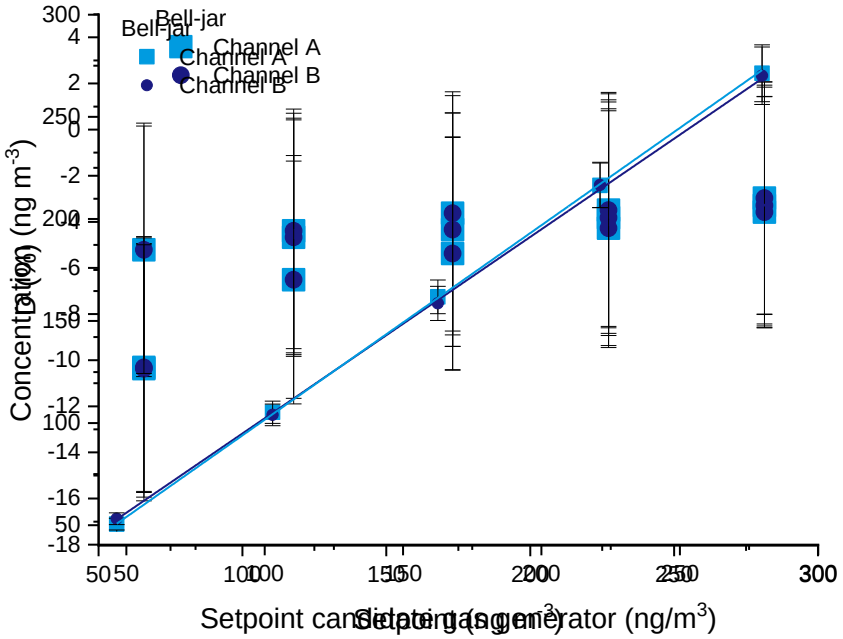
- Goal
  - making sure the developed calibration protocol is fit for purpose
  - establish a benchmark
  - encouraging the use of the best available methods

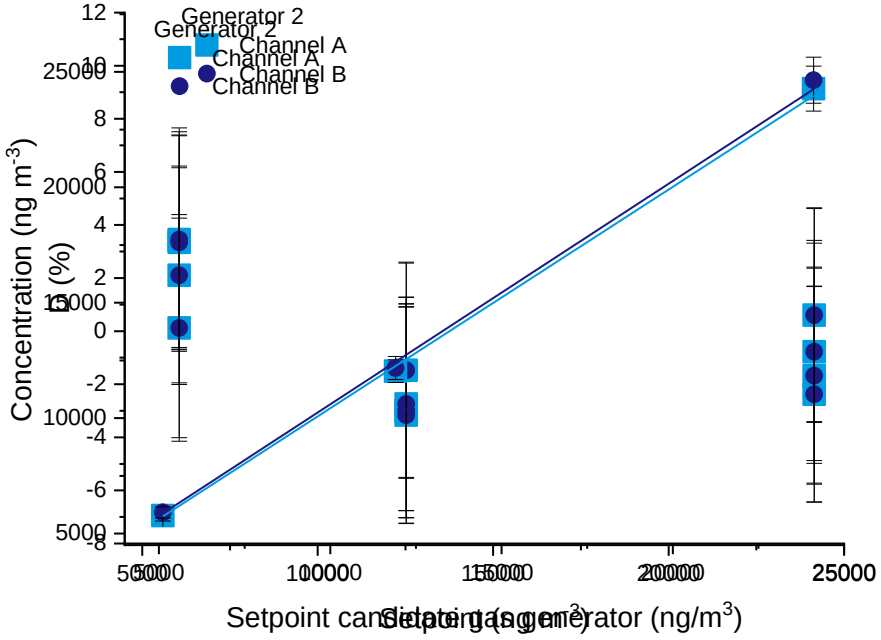
- Characteristics
  - stabilisation period
  - short term drift
  - precision, i.e., reproducibility and repeatability of the concentration generated
  - linearity
  - bias

Elemental mercury

- Stabilisation period: between 10 and 30 minutes
- Short term drift: ≤2%
- Precision: ≤2%
- Bias & linearity:

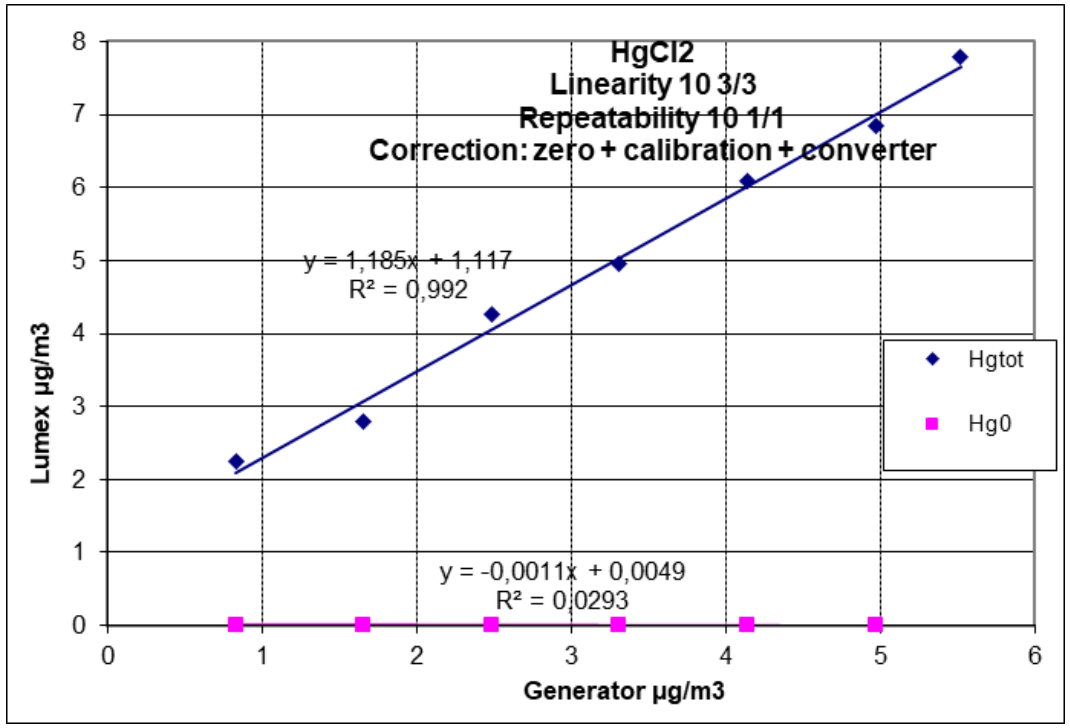






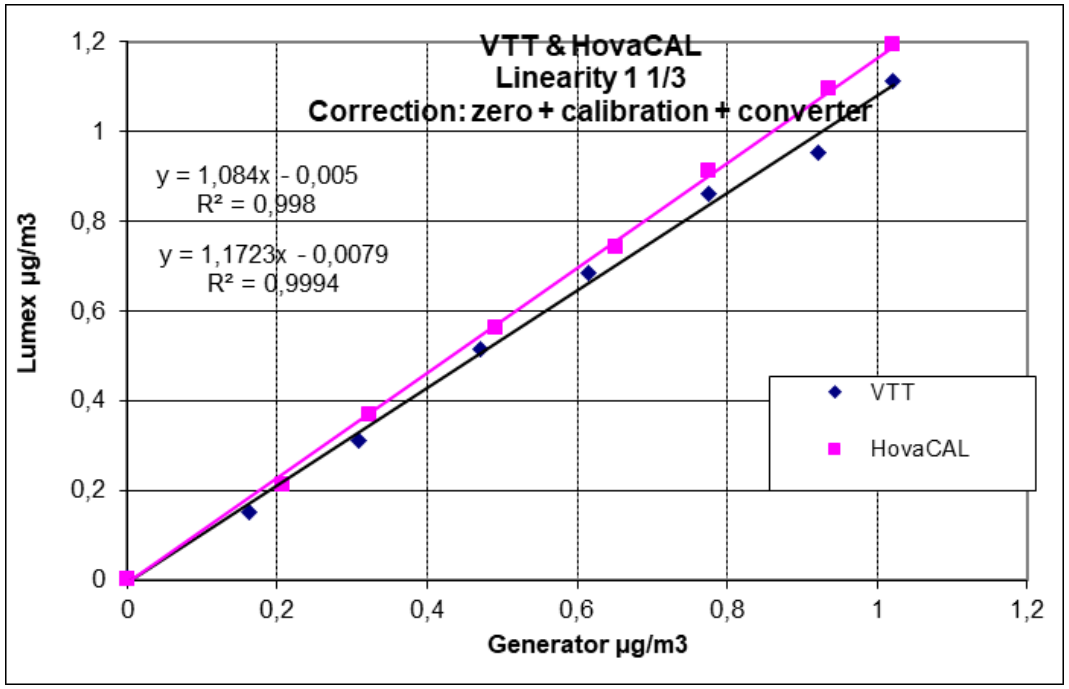
Oxidised mercury

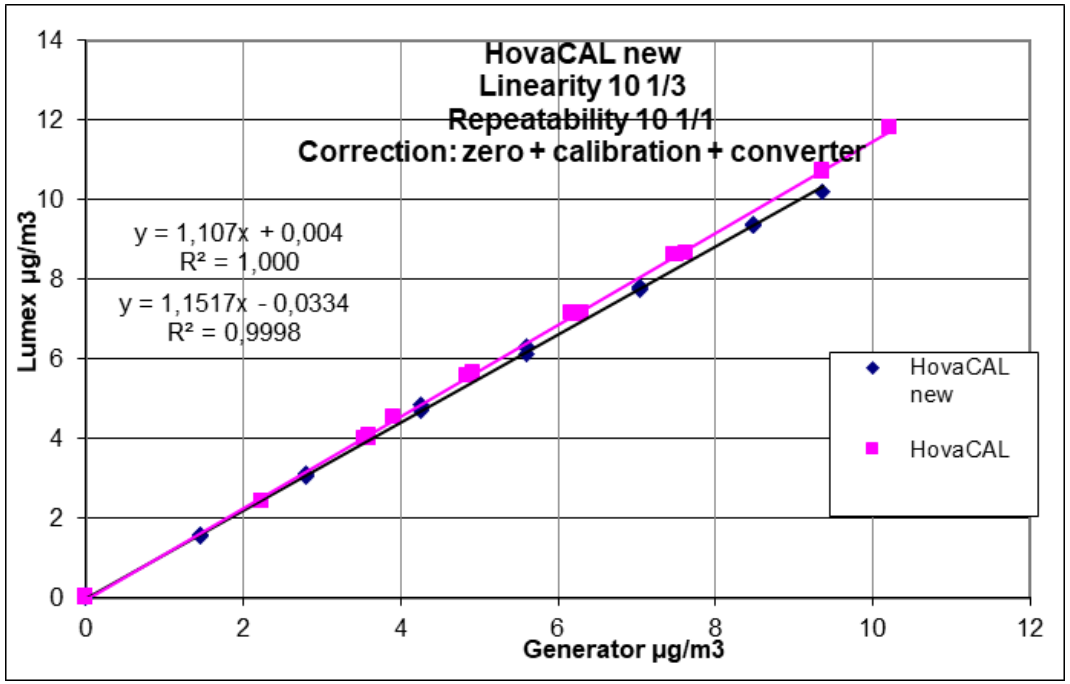
- $HgCl_2$ salt based mercury gas generator



Oxidised mercury

- Liquid evaporative $HgCl_2$ gas generators





$HgCl_2$ solution storage conditions

Temperature:

Fridge

Ambient

Shock heat 60 °C

Matrix:

0.1% v/v HCl

0.024% v/v HNO_3 + 0.0144% v/v HCl

0.125 µg/g HNO_3 + 0.125 µg/g HCl

Bottle:

FEP

FLPE

Borosilicate

Mercury concentration:

50 ng/g

200 ng/g

1000 ng/g

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Conclusion

- SI-traceable calibration protocols for mercury gas generators used in the field
- Validation through performance evaluation of mercury gas generators on the market

- **Reports available online www.SI-Hg.eu**

- Calibration and measurement capabilities (CMCs) and ISO/IEC 17025 accreditation
  - Calibration of mercury analysers and mercury gas generators
  - Sampling of sorbent tubes

Next steps

- NWIP in CEN/TC 264 “Air quality” WG8 “Measurement of total mercury emissions” (*2024*)
- Protocol converted into written documentary standard (*2025*)
- SI-traceable mercury measurement results for emission sources

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