VSL

National Metrology Institute

Workshop SI-Hg

SI-traceable calibration methods for mercury gas generators

Iris de Krom

19th September 2023

Barcelona – Spain

SI-Hg

Introduction

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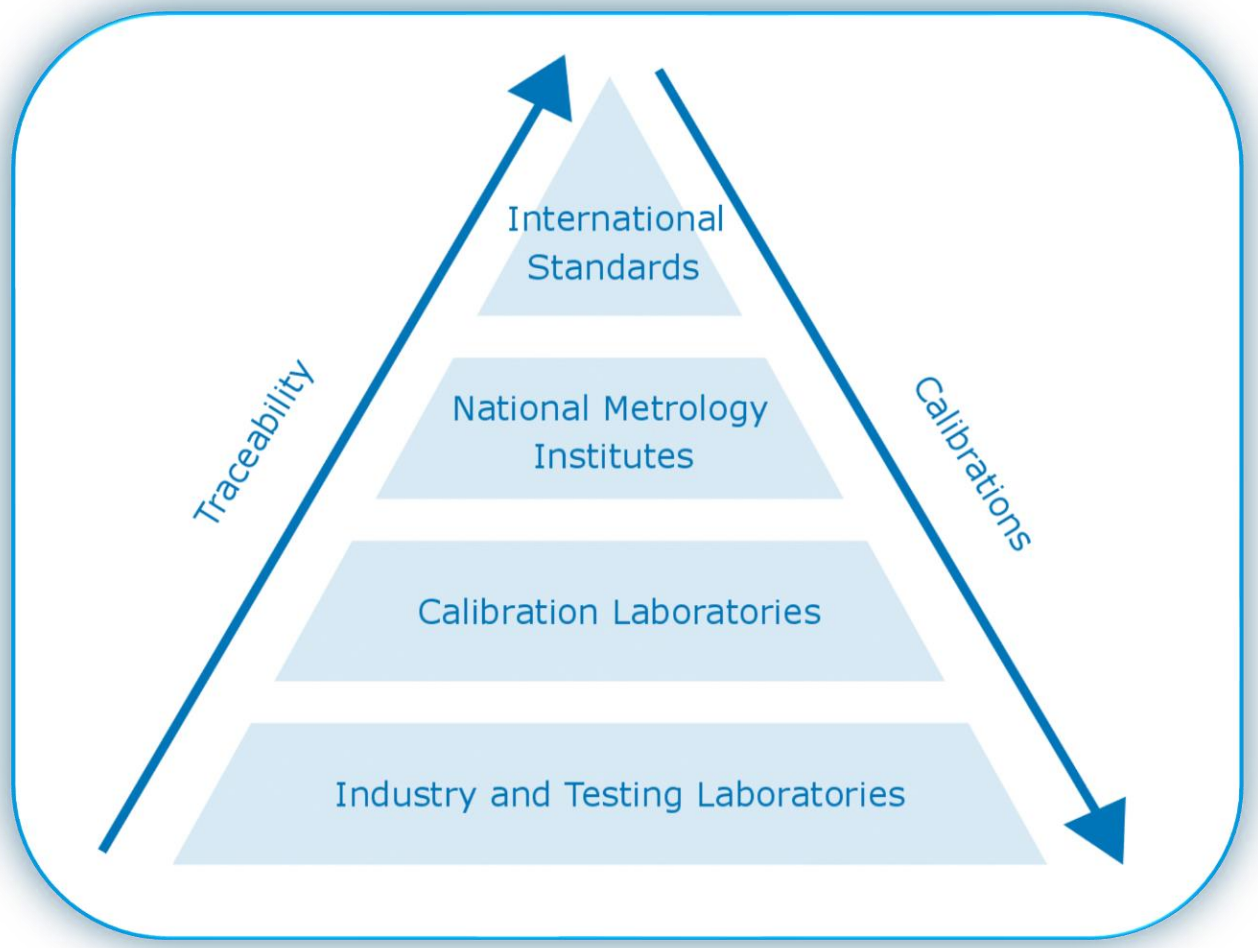
Metrology


kg
m
s
A
K
mol
cd
SI


International Standards
National Metrology Institutes
Calibration Laboratories
Industry and Testing Laboratories
Traceability
Calibrations

Metrology for mercury measurements related projects

- EMRP ENV02 PartEmission (2010 – 2013)
- EMRP ENV51 MeTra http://projects.lne.eu/metra/ (2013 – 2016)
  - Development of traceable calibration methods for mercury
- EMPIR 16ENV01 MercOx http://www.mercox.si/ (2017 – 2020)
  - Development of traceable calibration methods for oxidised mercury
- EMPIR 19NRM03 SI-Hg http://si-hg.eu/ (2020 – 2023)
  - Metrology for traceable protocols for elemental and oxidised mercury concentrations

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SI-Hg partners

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

SI-Hg Objectives

The overall goal of this project is to develop **protocols** for **SI-traceable calibration, evaluation and calibration** of **elemental mercury** (Hg^0) and **oxidised mercury** (Hg^{II}) **gas generators** used in the field. This research will feed into the **standardisation technical committee CEN/TC264/WG8**.

1. To **develop and validate** a **protocol** for the **SI-traceable calibration of elemental mercury** (Hg^0) **gas generators** used in the.
2. To **validate** a **calibration protocol** for the calibration of **oxidised mercury** (Hg^{II}) **gas generators** used in the field.
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.
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**.
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**.

Agenda

- SI-traceable measurement results and standardisation for mercury emission monitoring

  Iris de Krom, VSL

- Development of low-level elemental and oxidized mercury calibrators for atmospheric mercury measurements

  Warren Corns, PSA

- Calibration methods for atmospheric mercury concentrations

  Igor Živković, JSI

- Determining converter efficiency for oxidized mercury measurements

  Sophie Page, LGC

- Validation results of the calibration of mercury gas generators

  Timo Rajamäki, VTT

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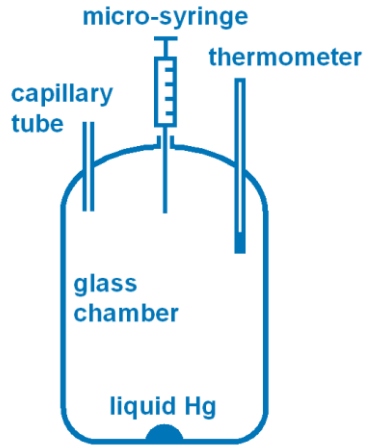
Standardisation

- **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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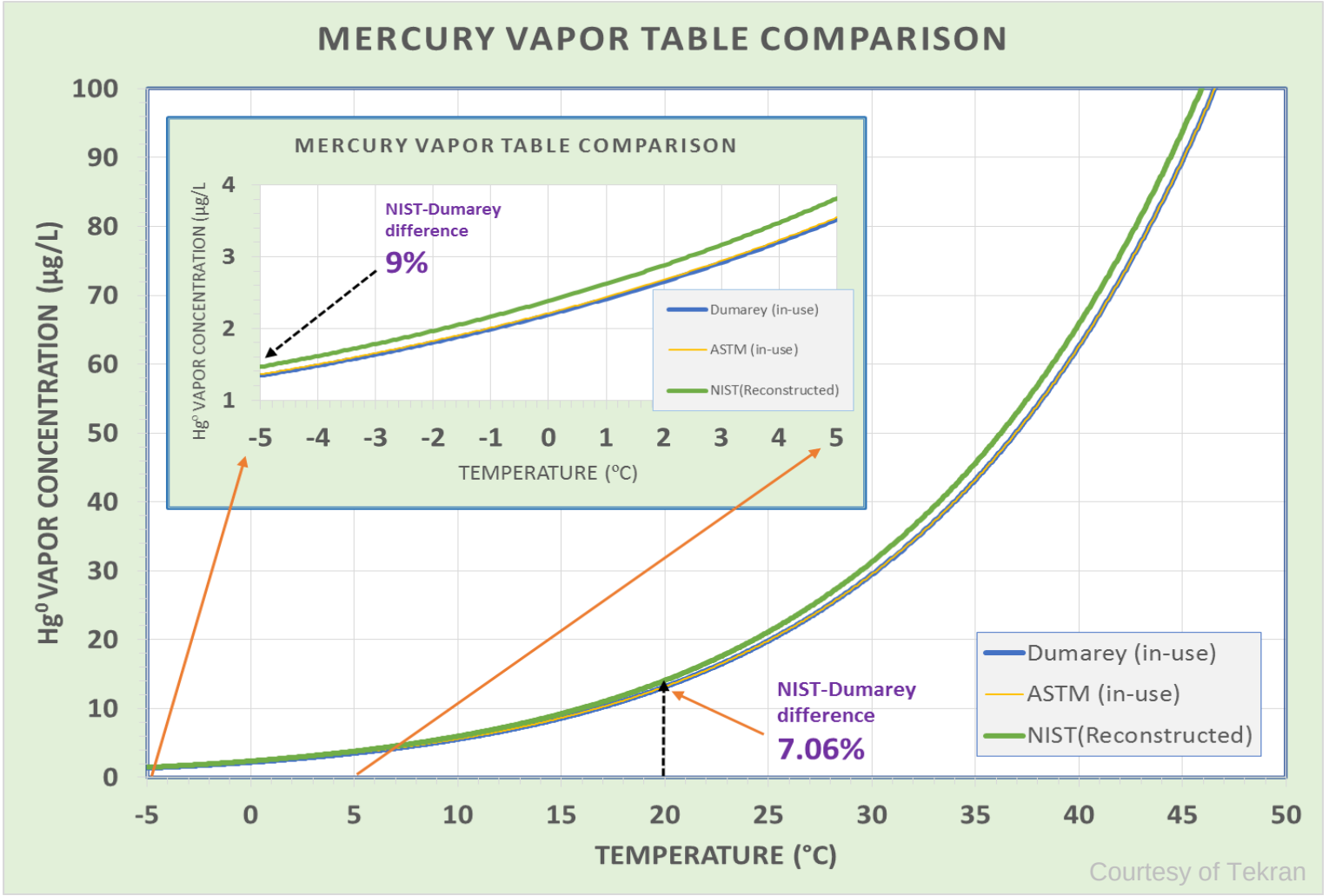
Vapour pressure equations

- Mercury concentration dependent upon vapour pressure equation used



Courtesy of Tekran

Primary Mercury Gas Standards

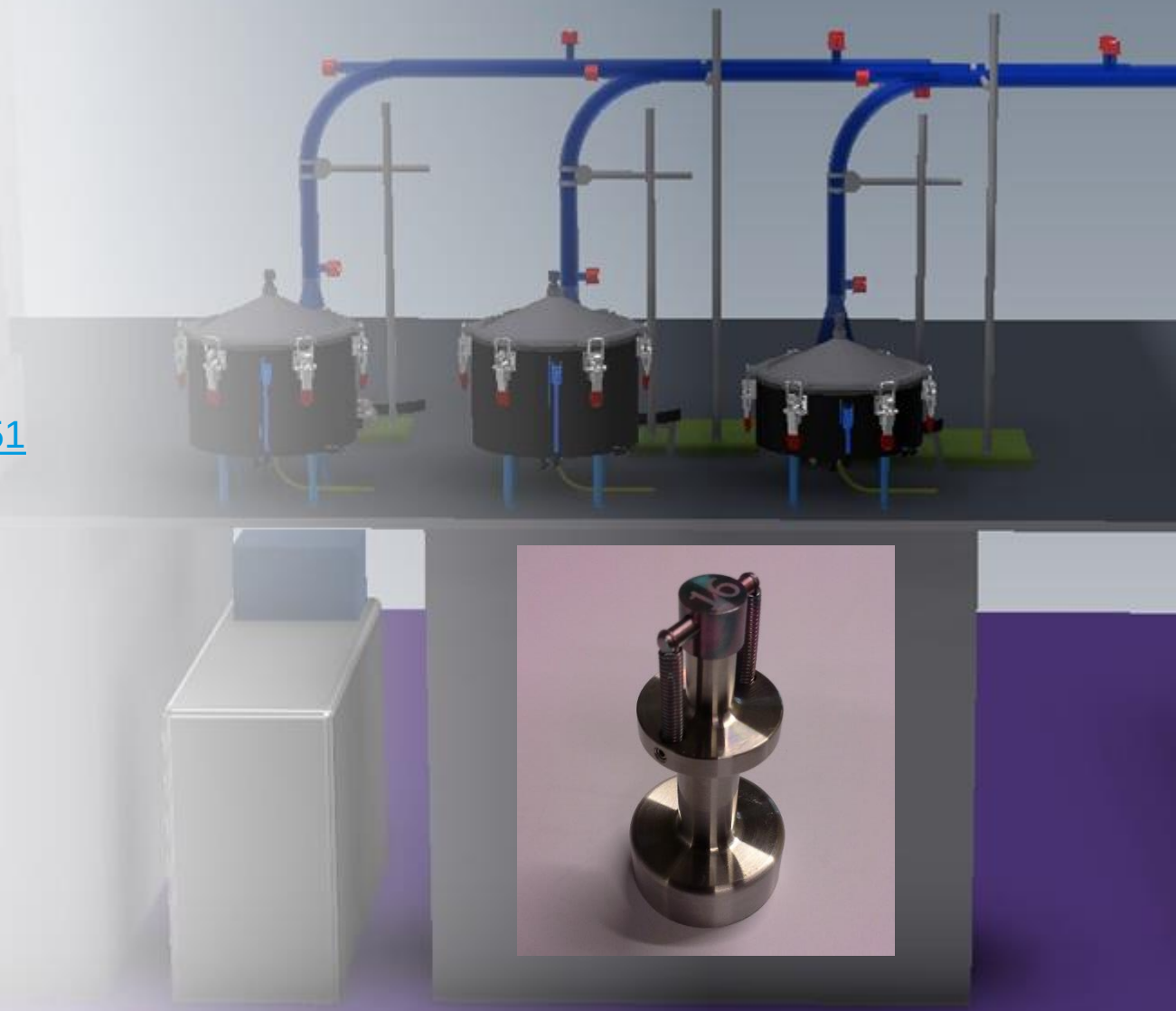
- Gaseous Elemental Mercury
- Traceable to SI-units
- Uncertainty

- VSL – diffusion method

de Krom et al. Measurement 169 (2021) 108351
Doi: https://doi.org/10.1016/j.measurement.2020.108351
de Krom et al. Atmos. Meas. Tech., 14 (2021) 2317
Doi: https://doi.org/10.5194/amt-14-2317-2021

- NIST – spectroscopy

Srivastava et al. Anal. Chem. 90 (2018) 6781
Doi: https://doi.org/10.1021/acs.analchem.8b00757
Srivastava et al. Anal. Chem. 93 (2020) 1050
Doi: https://doi.org/10.1021/acs.analchem.0c04002



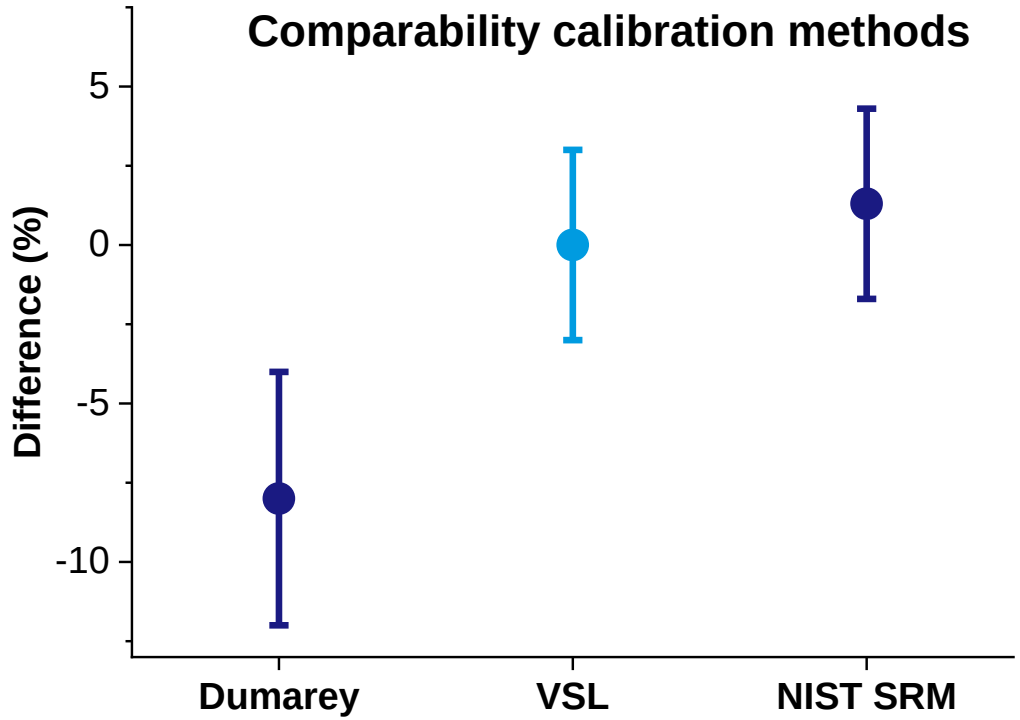
Comparability of the measurement results for gaseous elemental mercury

SI traceable reference materials

VSL gas generator & NIST SRM (3133)

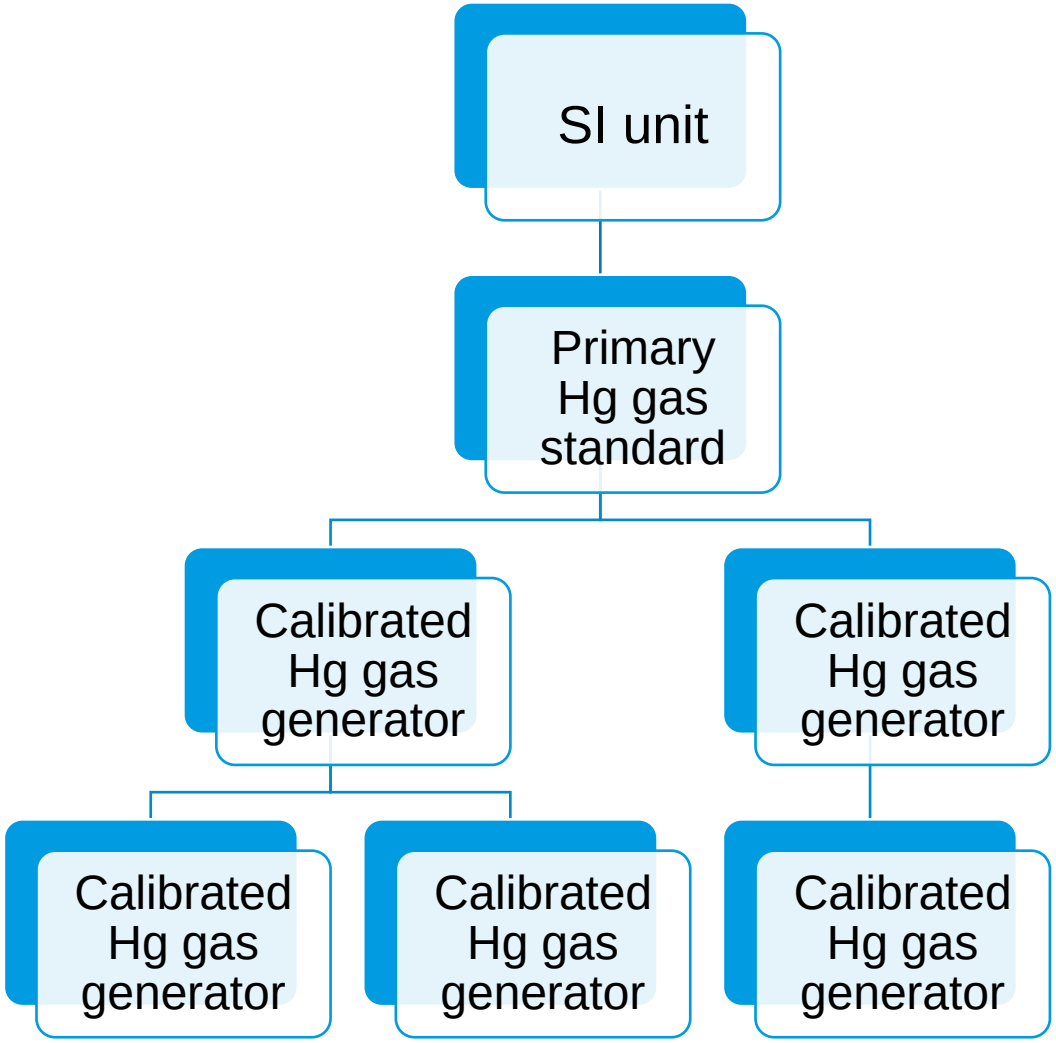
Field method

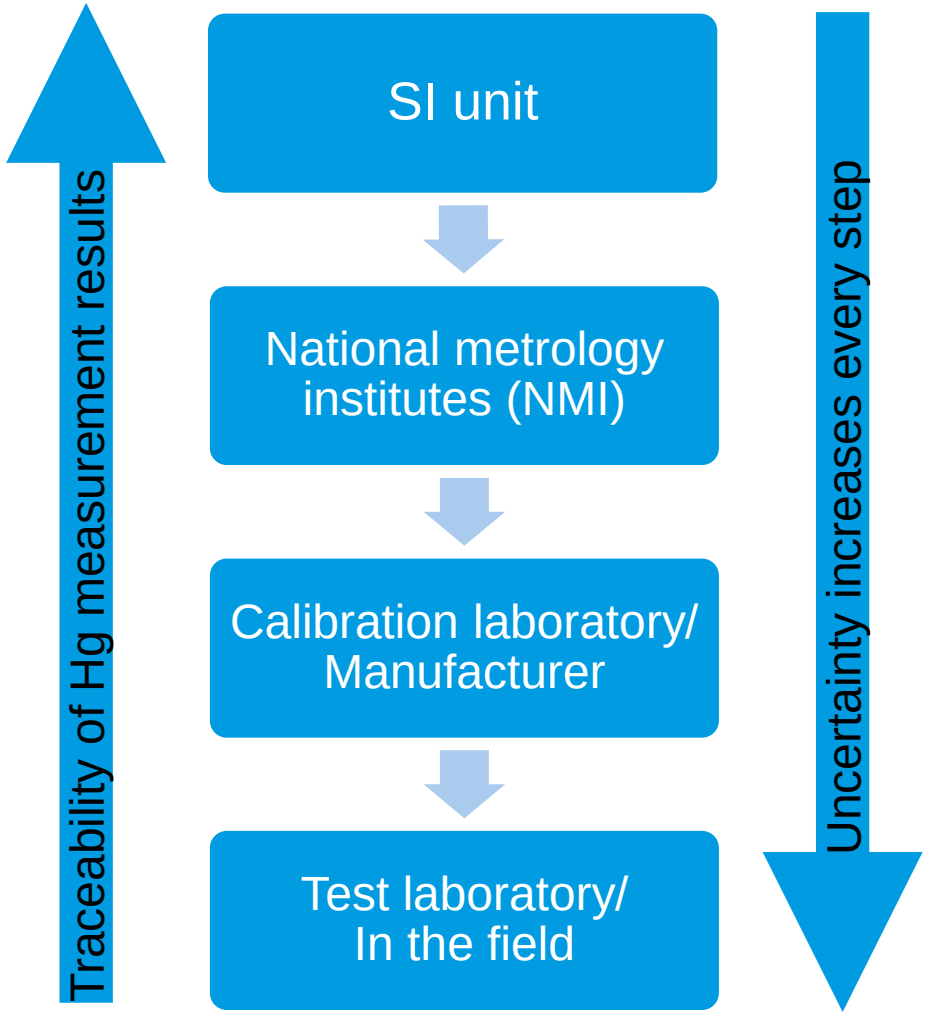
Dumarey equation



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

Traceability chain





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Scope calibration protocol

- This protocol specifies the procedures for establishing **traceability to the SI** for the **quantitative output of elemental 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.

Principle calibration 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	Ref_1
Candidate	$Cand_1$
Reference standard	Ref_2
Candidate	$Cand_2$
Reference standard	Ref_3
Candidate	$Cand_3$
Reference standard	Ref_4

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

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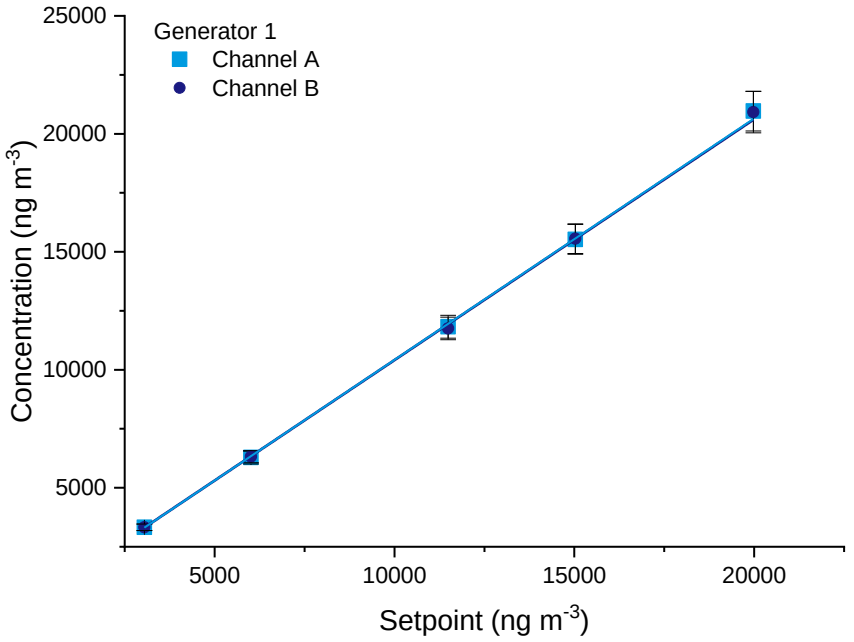
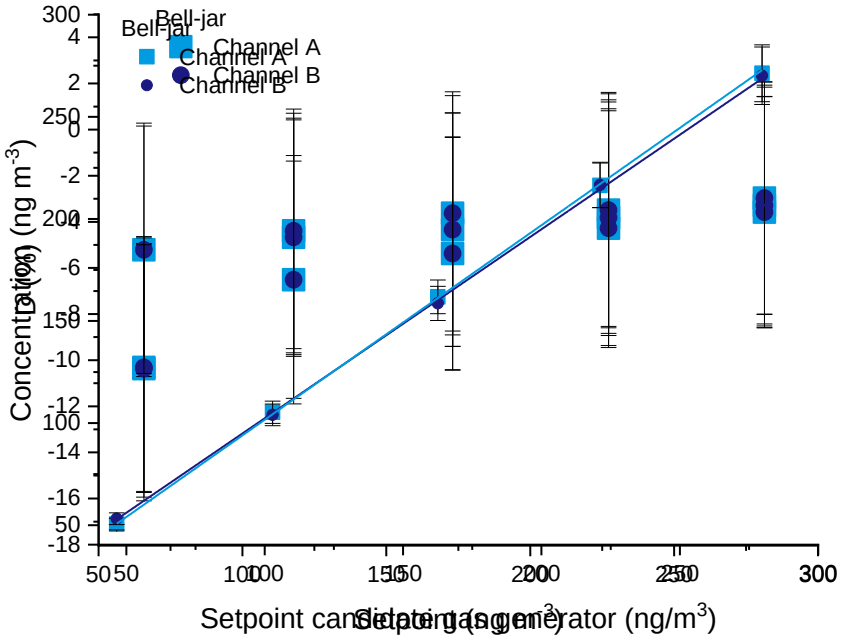
Performance evaluation

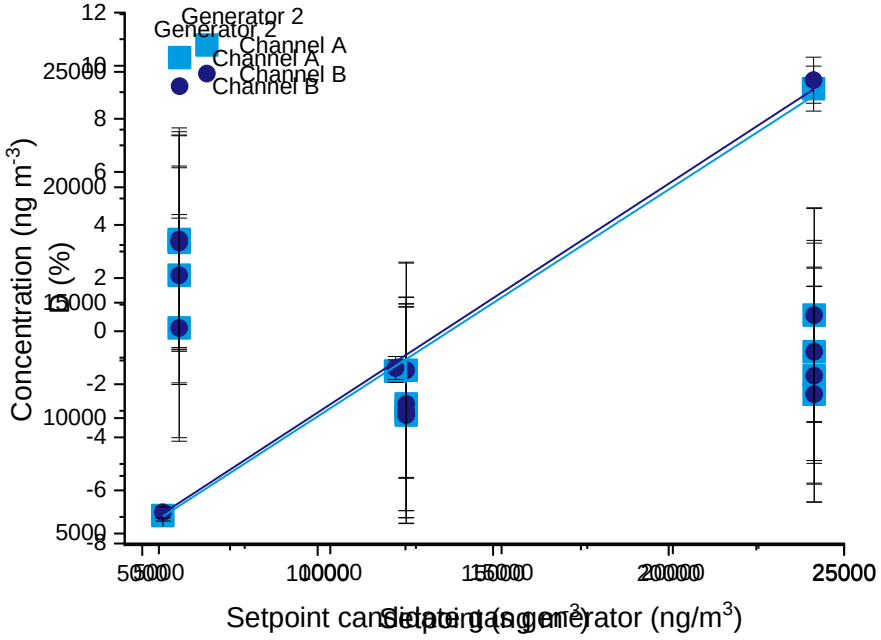
- Goal
  - making sure the developed calibration protocol is fit for purpose
  - establish a benchmark
  - encouraging the use of the best available methods
- Elemental mercury gas generators
  - bell-jar
  - 2 saturation gas generators
- Characteristics
  - stabilisation period
  - short term drift
  - 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:







Conclusion

- SI-traceable calibration protocol for elemental 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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