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Protocol for SI-traceable measurement results of elemental mercury concentrations in air

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ICMGP 2022 – 27 July 2022 – Virtual

Special Session – Metrological Traceability for mercury analysis and speciation

VSL

Introduction

MAKE MERCURY HISTORY

SI kg m s A K mol cd

SI-Hg

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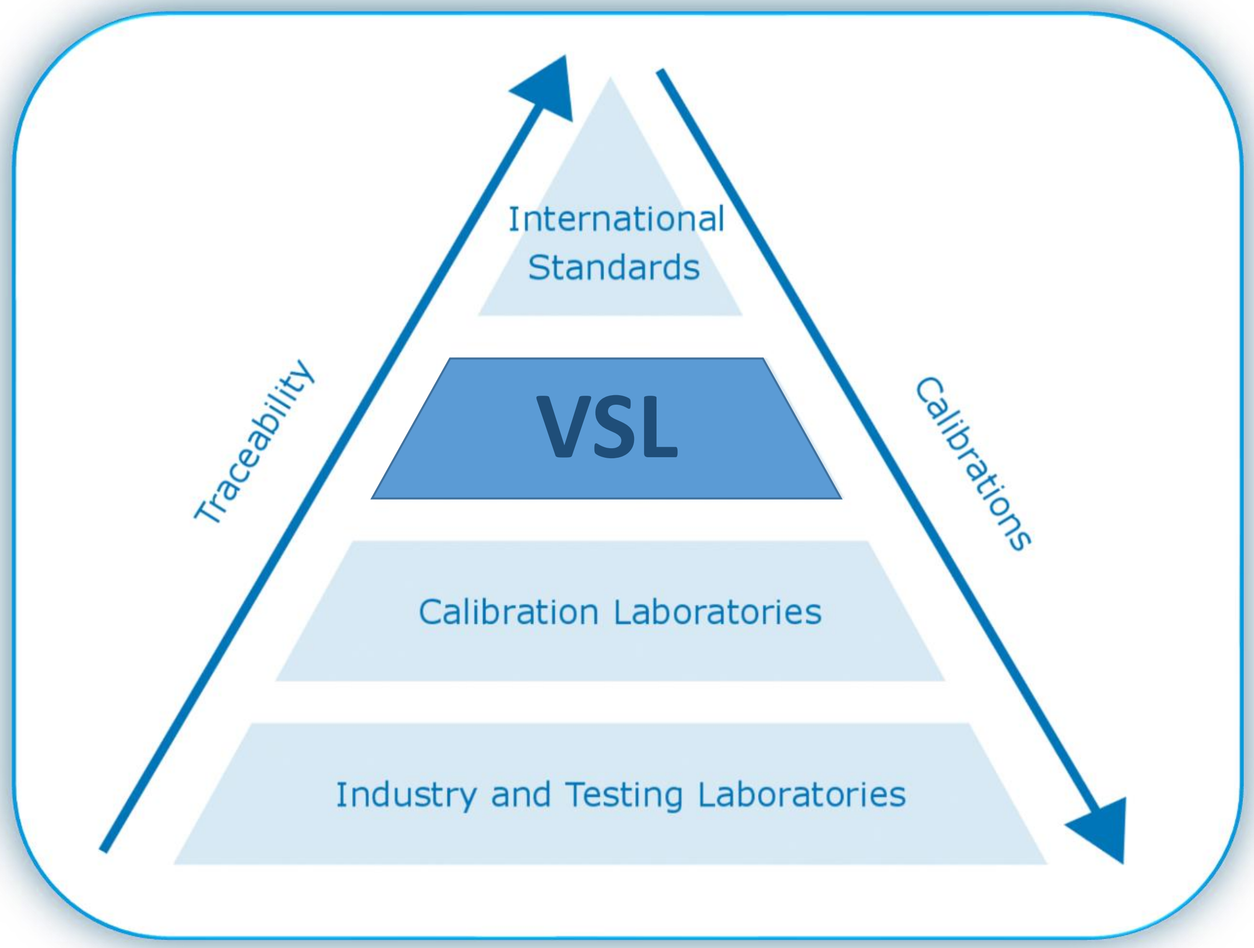
SI-traceability



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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

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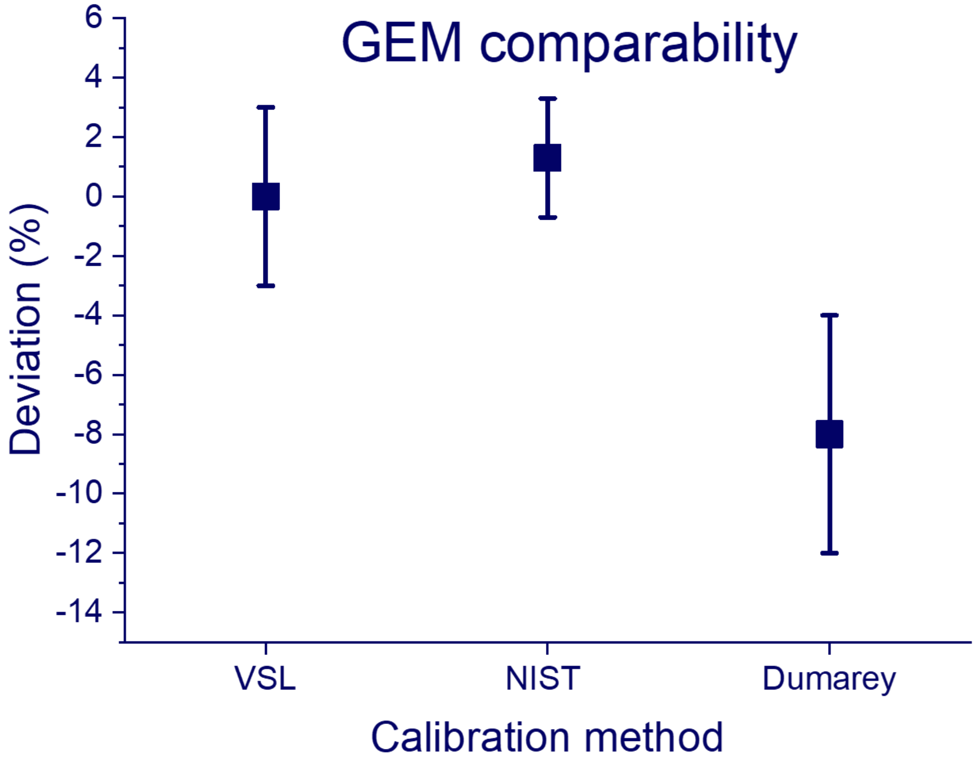
Traceability for mercury measurement results

- Traceability for elemental mercury concentration
  - In emission sources and the atmosphere
  - Comparisons between current calibration facilities
    - NIST SRM
    - Dumarey equation

- Next steps
  - Unbroken chain of calibrations from primary standards to industry and monitoring programmes
  - SI traceability in written standards
    - EMPIR 19NRM03 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

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1. Development and validation of a SI-traceable calibration protocol for **elemental mercury** gas generators
2. Development and validation of a SI-traceable calibration protocol for **oxidised mercury** gas generators
3. Performance evaluation of mercury gas generators on the market

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VTT

PSA

TÜVRheinland®

LGC

Jožef Stefan Institute

National Research Council of Italy

LUMEX

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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.

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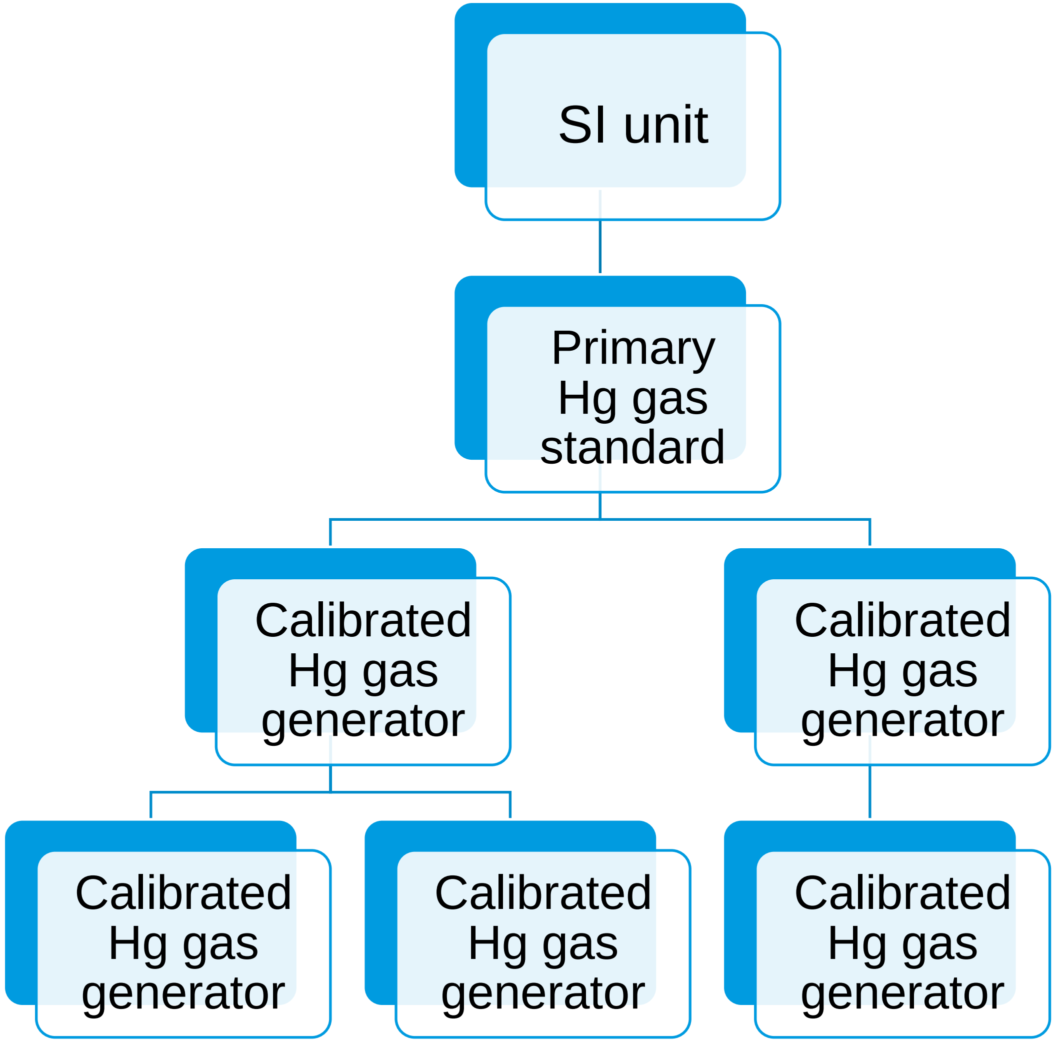
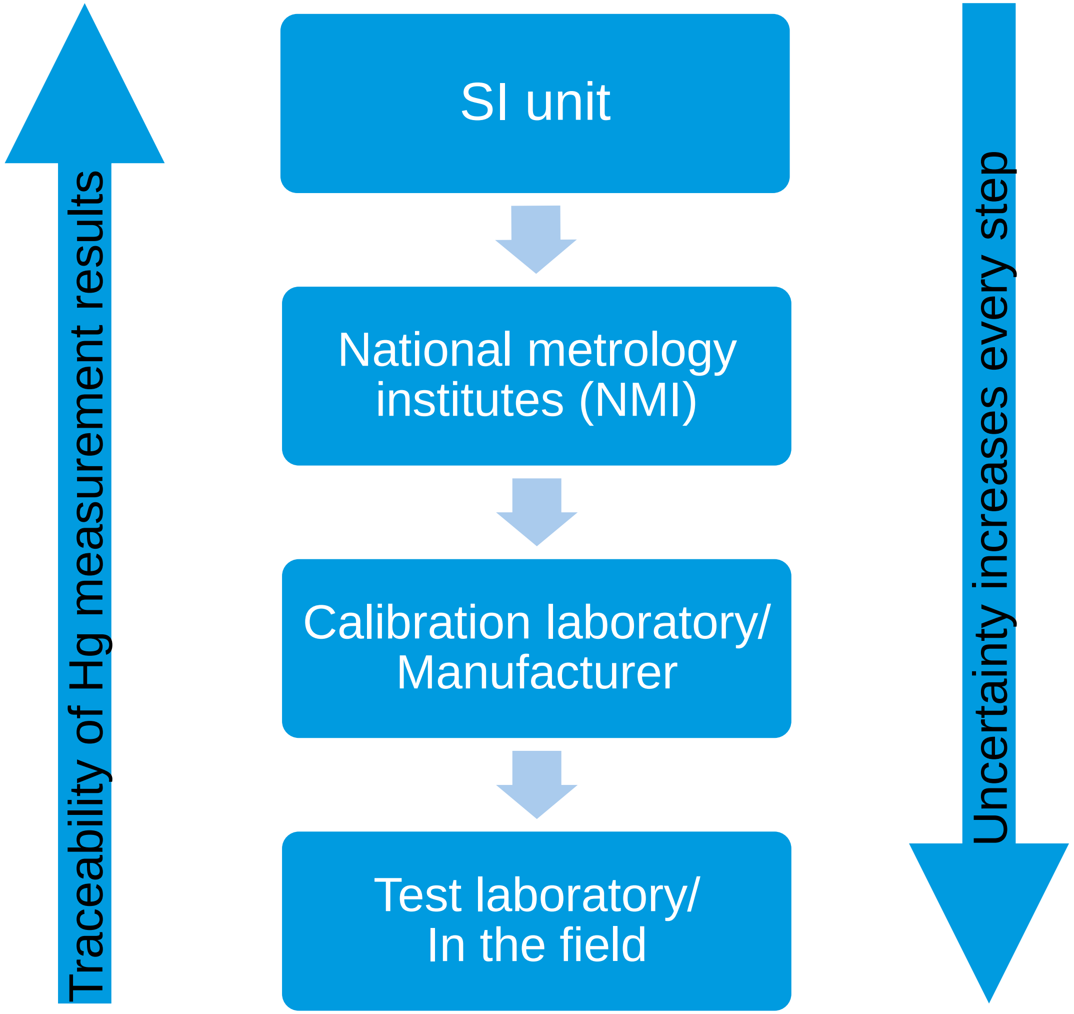
Traceability chain





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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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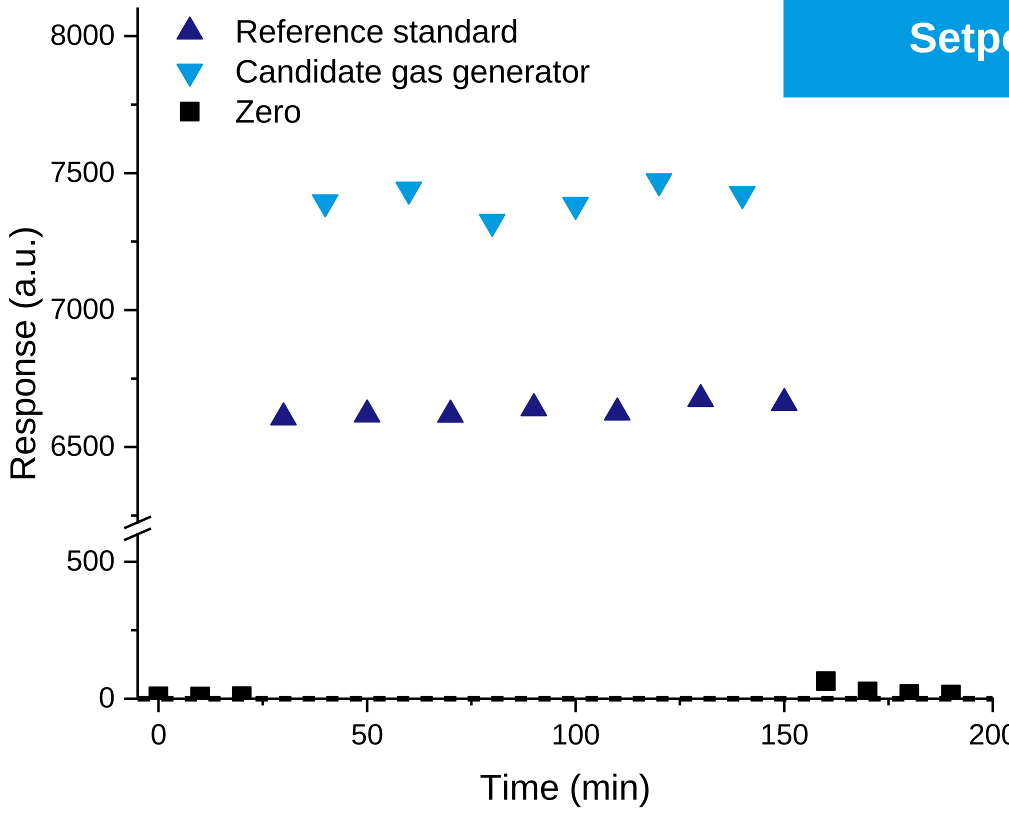
Validation measurements – Single point calibration

Reference Hg conc. ± U (µg m^{-3}, *k* = 2)	2.17 ± 0.07
Setpoint candidate (µg m^{-3})	2.57



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Data processing - Single point calibration

r_{ref}	r_{cand}	Output ratio (R)
6598.0		
	7383.2	1.118
6608.0		
	7429.1	1.124
6606.9		
	7310.5	1.105
6629.7		
	7372.4	1.113
6613.4		
	7457.9	1.124
6661.7		
	7410.2	1.114
6646.6		

Reference Hg conc. ± U (µg m^{-3}, *k* = 2)	2.17 ± 0.07
Setpoint candidate (µg m^{-3})	2.57

Y_{cand_i} (µg m^{-3})	2.43
U (%) (*k* = 2)	3.2

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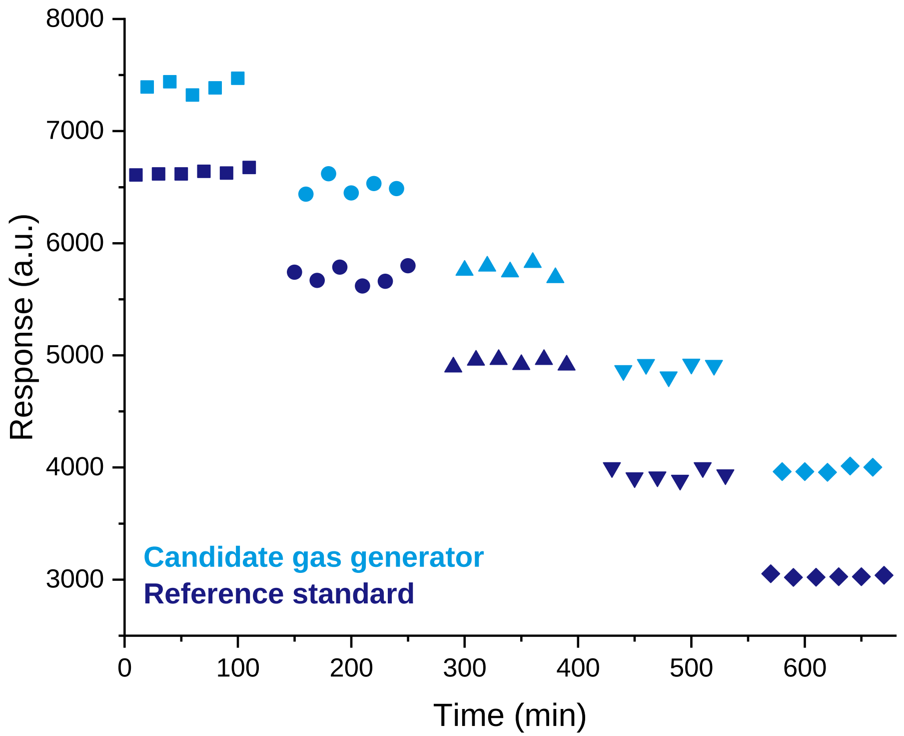
Validation measurements – Multipoint calibration



Setpoint		Reference Hg conc. (µg m^{-3})	Setpoint candidate (µg m^{-3})
1	■	2.17	2.57
2	●	1.87	2.27
3	▲	1.58	1.97
4	▼	1.27	1.68
5	♦	0.98	1.37

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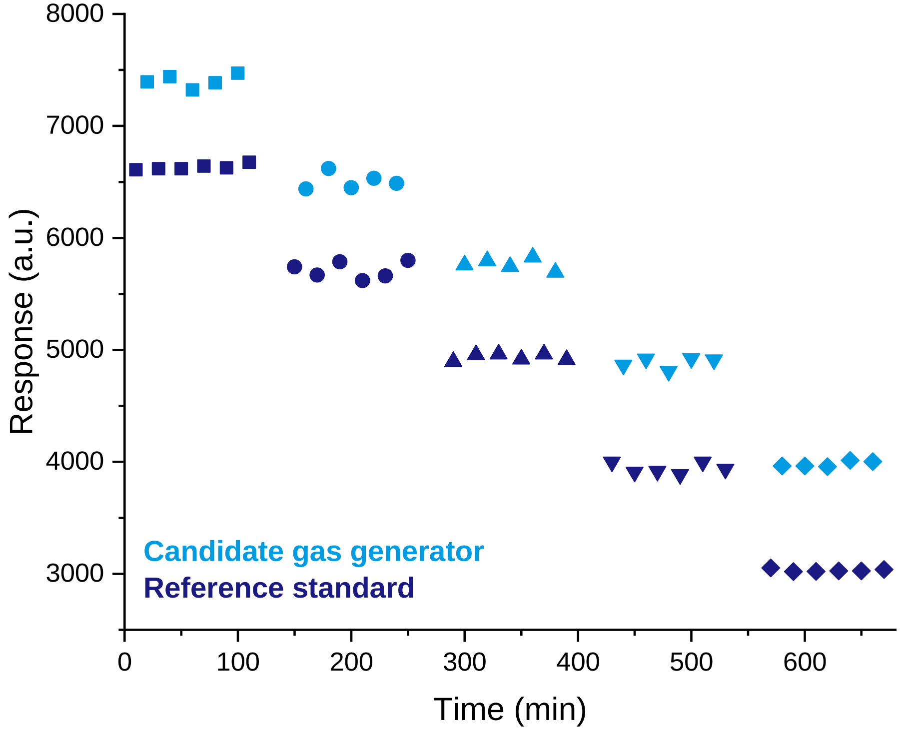
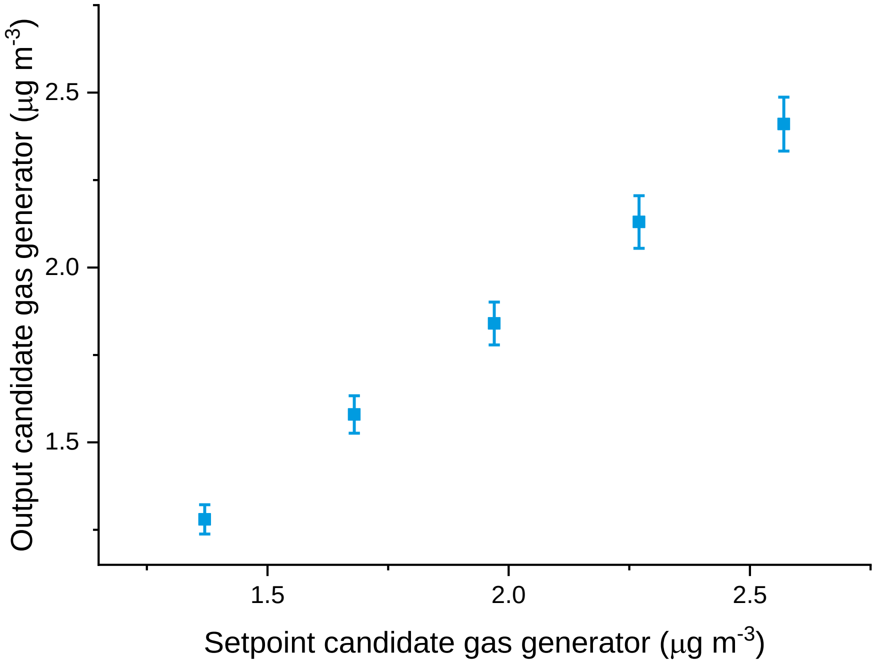
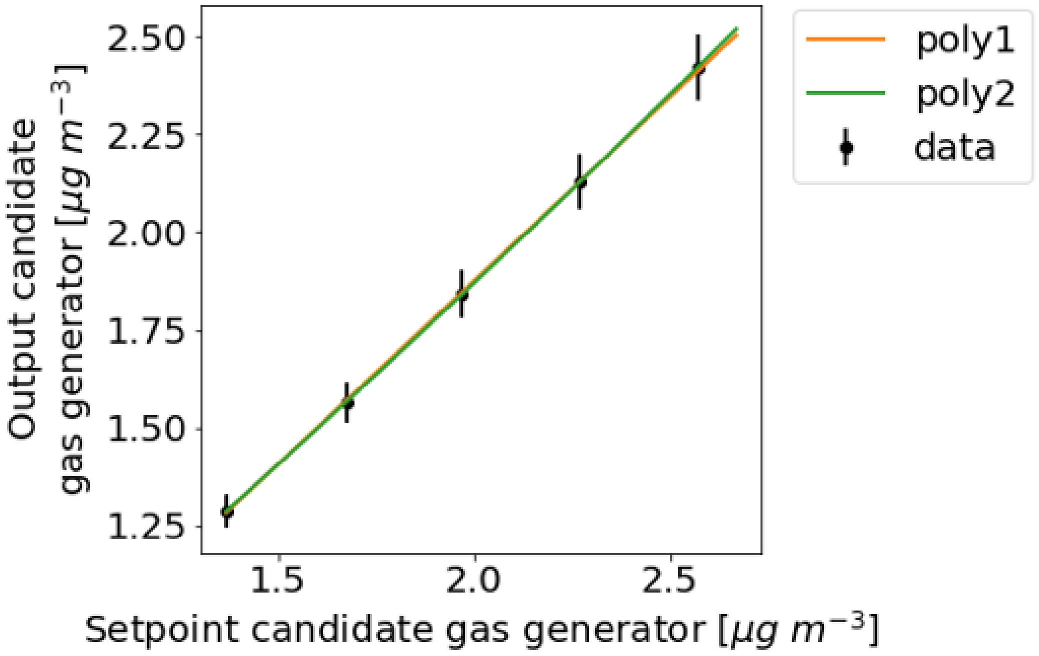
Validation measurements – Multipoint calibration





Data processing - Multipoint calibration interpolation model

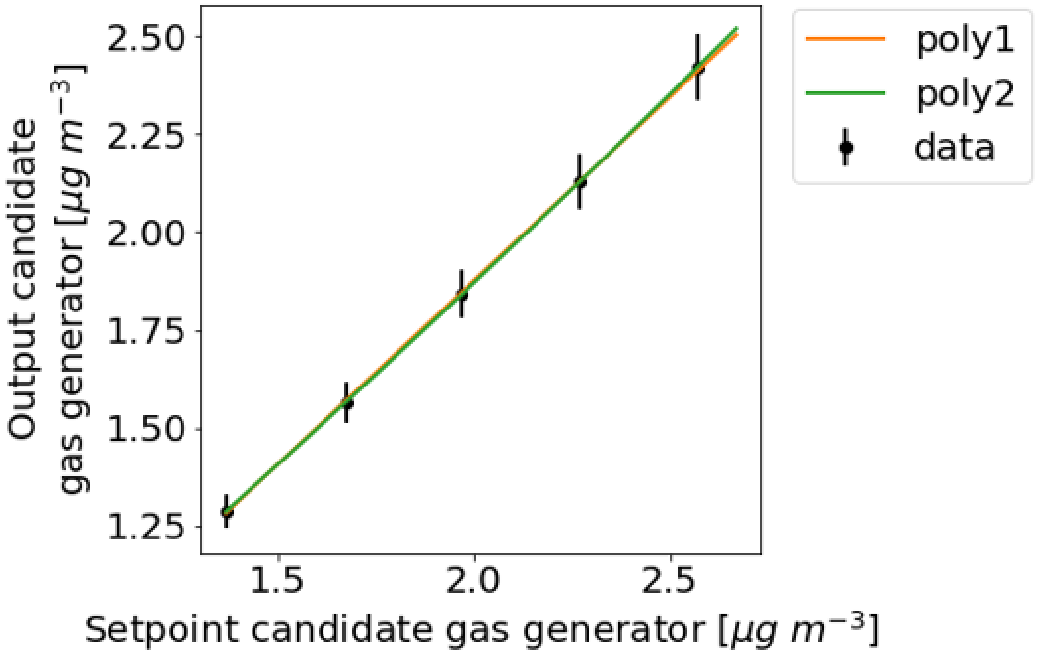
Interpolation functions:



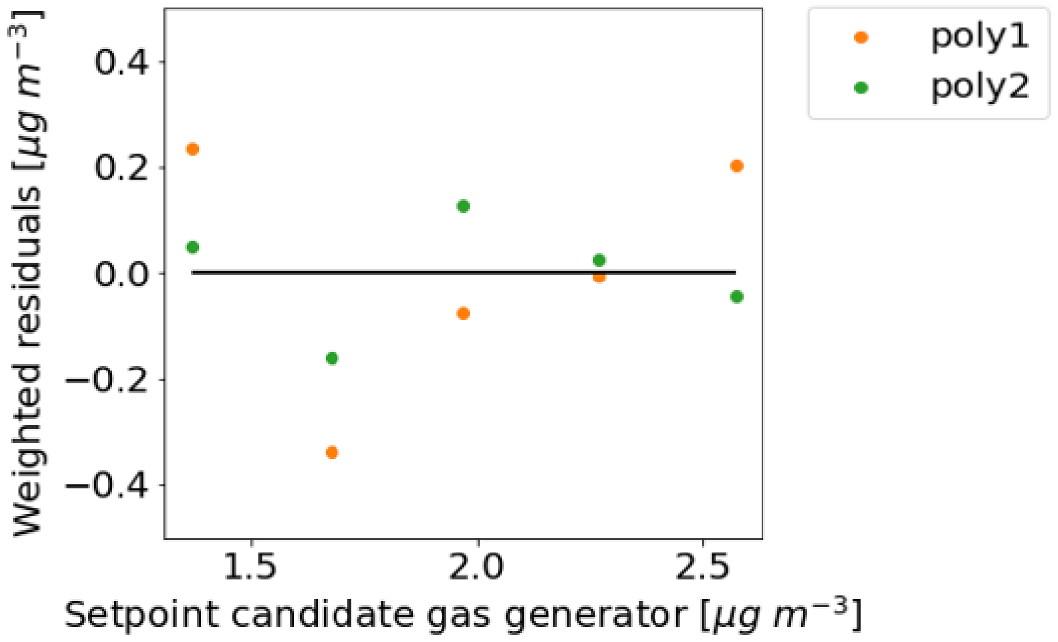
Poly	AICc	Formula
1	-32.95	$y = a + bx$
2	-12.96	$y = a + bx + cx^2$

Data processing - Multipoint calibration interpolation model

Interpolation functions:



Residuals:



poly1: $y = -0.00138 + 0.938471\ x$

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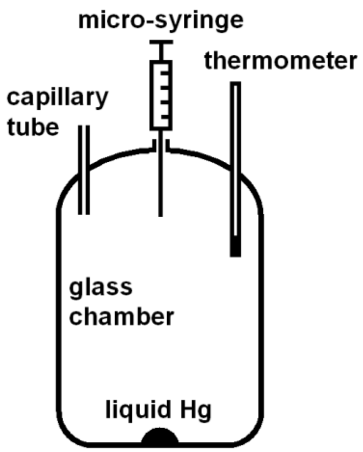
Gas generators used in the field

- Saturation gas generators (ISO 6145-9)
  - Manually with syringe injection (bell-jar)
  - Automatically

- Mercury amount fraction in cylinders (ISO 6142-1)

- Continuous injection (ISO 6145-4)
  - Based on vaporization of a mercury chloride solution followed by reduction



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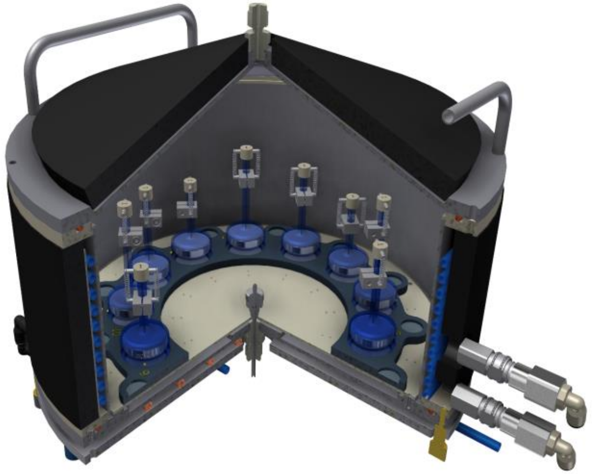
Conclusion

- SI-traceable calibration protocol for mercury gas generators used in the field
  - With and without zero correction
  - Single point and multipoint calibration
  - Uncertainty propagation
- SI-traceable mercury measurement results in the field



Next steps

- Performance evaluation of mercury gas generators on the market (*2022/2023*)
- Validated protocol for the calibration of mercury gas generators (*2023*)
- Protocol converted into a written documentary standard (*2025*)

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