19NRM03 SI-Hg Webinar

Metrology for traceable protocols for elemental and oxidised mercury concentrations

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

4th March 2022 Panayot Petrov

Summary of goals within the SI-Hg project

- 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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Evaluation of Hg analysers and generators

- Hg species, like Hg^0 and Hg(II), are reactive and preparing accurate gas **standards** with traceable Hg concentration and sufficient stability over time, especially and ng m^{-3} fractions, is **currently difficult / not possible**.
- The analysers performance evaluation must be **preceded** by Hg gas standards characterisation.
- Metrology classes of Hg gas standards:
  - **Primary standard:** Dynamic gas standard calibration based on diffusion (ISO 6145-8) – available for elemental Hg at VSL, not available for Hg(II) species
  - **Secondary Standards:** Variety of gas generators exist (based on saturated vapours dilution, liquid evaporation of Hg(II) standard, gas-permeation and others, but achieving **traceability to SI-units** and estimating the **uncertainty** of the generated Hg mass fraction is needed.

- Hg analysers must be calibrated either directly by using the primary gas standard, or by using a standard traceable to it or to SI by a chain of measurements and comparison, each with associated measurement uncertainty

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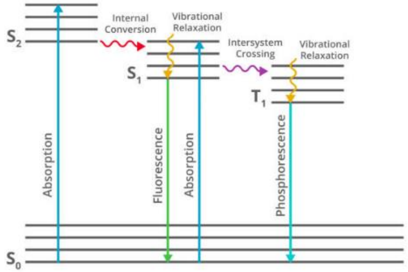
Hg analysers (1/2)

- Analyser types
  - Analysers based on **atomic** spectrometry determinations → most often applied for field measurements at emission- and environmental- Hg levels
  - Analysers based on “other” analytical determinations → less popular; research based applications; Metrology Institutes



- Atomic spectrometry based analysers
  - Detectors sensitive only to elemental mercury (Hg^0)
  - ➢ Do not provide total mercury concentration
  - ➢ Blind to Hg(II) and other species
  - ➢ Cannot provide speciation information
    - ➢ reactivity, mobility and toxicity of Hg is species dependent

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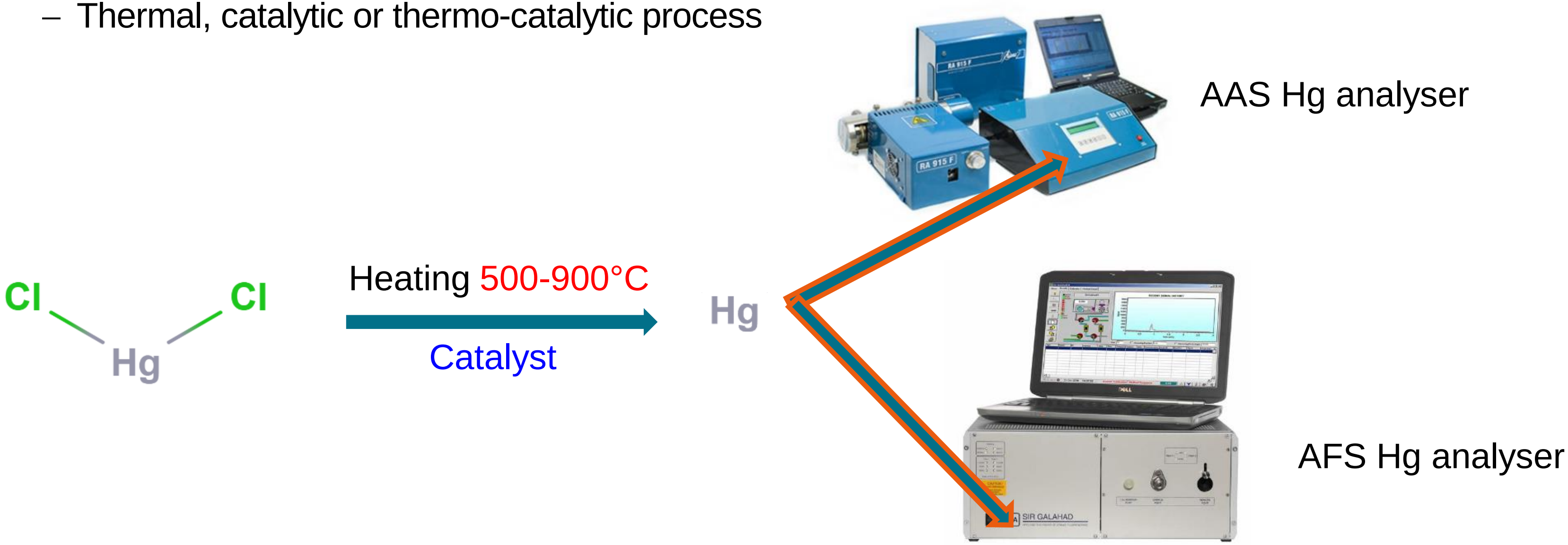
Hg analysers (2/2)

- Application of atomic spectrometry analysers for the determination of oxidised Hg
  - Thermal, catalytic or thermo-catalytic process



N.B. It is critical to achieve complete (100%) conversion to avoid bias!

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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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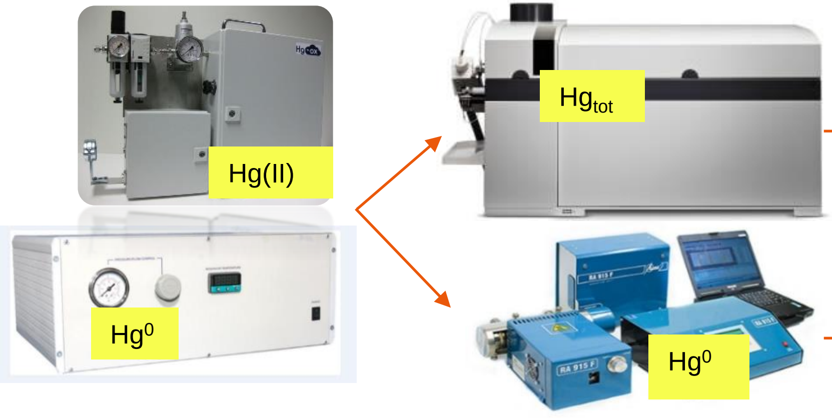
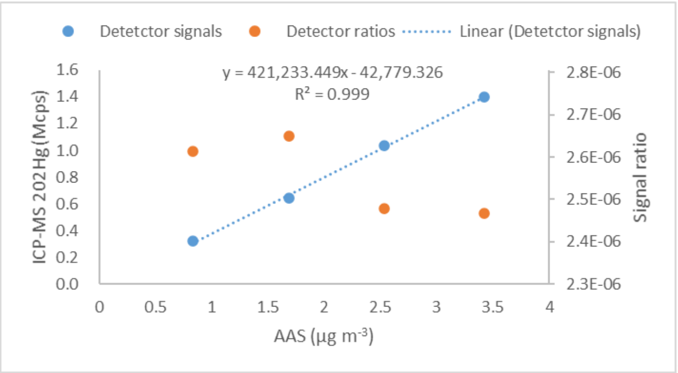
Schematic diagram of instrumental setup for converters efficiencies estimation

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 $\boldsymbol{R_1}$ 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, $\boldsymbol{R_2}$

4. The converter efficiency is calculated as:



$$E_C = \frac{R_2}{R_1}$$



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Other considerations for performance evaluation of Hg generators and analysers (1/2)

- Mercury species sorption effect
  - Inside the generators
  - Inside the analysers
  - Gas transfer lines
  - Affect all type of generators
  - Sorption effect is species dependent, more pronounced with Hg(II)
  - Sorption effect is temperature dependent
  - Other

- Hg source purity effect on generators Hg output
  - Elemental / compound purity analysis is needed – e.g. with 98% $HgCl_2$ purity, if not corrected, contributes to 2% bias!
  - Hg^0 surface oxidation – generator output concentration variability with time. Reproducibility studies are needed.
  - Hg liquid standard concentration and compound purity → relevant to LEGs; e.g. $HgCl_2$ forms Hg(II) vapours, HgO is lost in the evaporation chamber

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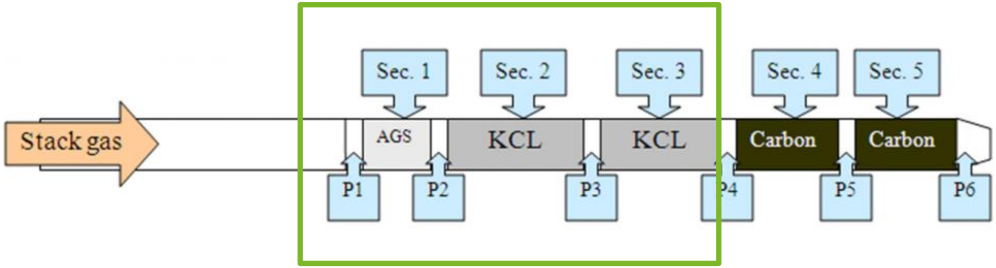
Other considerations for performance evaluation of Hg generators and analysers (2/2)

- Mercury liquid standards stability
  - Relevant to LEGs
  - Container material
  - Temperature
  - Hg concentration – lower concentration Hg more effected. Acidification and/or oxidant stabilisation needed.

- Hg redox reactions at the interfaces
  - Relevant to all type generators
  - Inside generator redox reactions
  - Inside analyser redox reactions



- Analysers limits of quantification
  - Environmental levels of Hg(II) would require preconcentrating (ng/m³ to pg/m³), e.g. by speciation traps
  - Trapping efficiency
  - Selectivity
  - Chemisorption → Hg speciation of the traps sections is required.

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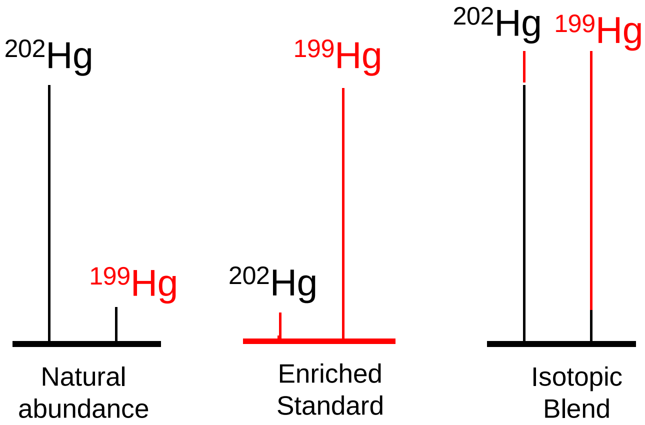
Novel approaches for Hg generators evaluation

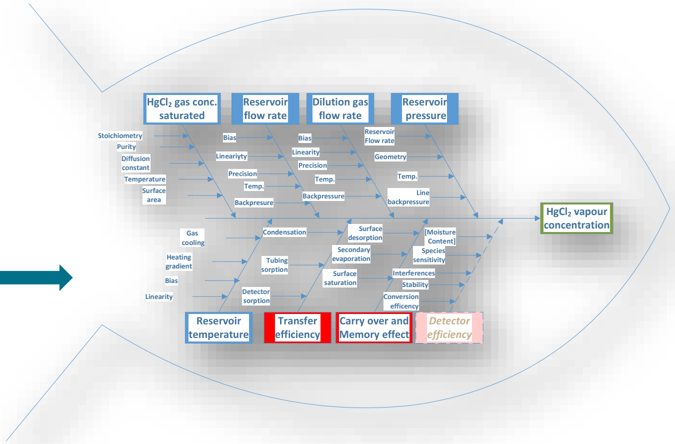
- Method currently under validation
- Applicable to elemental and oxidised gas generators
- Based on Isotope Dilution Mass Spectrometry (IDMS)
- Provides direct traceability to SI
- Species independent detector used (ICP-MS) – can be used with Hg^0 and Hg(II) standards
- Validation range – low ng/m^3 to µg/m^3
- Provides acceptable uncertainty – **target U(k=1) < 3%**



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

Next steps

- Complete converter efficiency studies - report (*2022*)
- Determine Hg standards stability and purity – best practice guide (*2022*)
- Improve the generators evaluation method; decrease uncertainty (*2022/2023*)
- Adjust the certification protocol to determine the output of Hg(II) generators considering the additional sources of uncertainty (*2022*)
- 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*)



Thank you!

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