

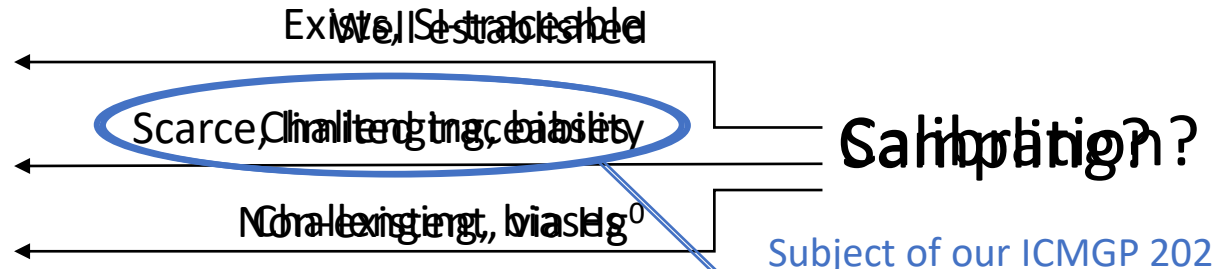
Validation of Sampling Methods for Gaseous Oxidized Mercury Using Traceable Calibration Procedure

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Atmospheric mercury speciation problematic

- Gaseous elemental Hg (GEM)
- Gaseous oxidized Hg (GOM)
- Particulate-bound Hg (PBM)



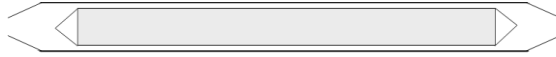
Subject of our ICMGP 2022

Focus of this work
Development of a
Traceable Calibration for Gaseous
Oxidized Mercury Species Based on
Non-Thermal Plasma Approach”

- Majority of analytical challenges – GOM and PBM – why?
 - Low ambient concentrations
 - High reactivity (chemical and redox processes)
 - High adsorption – “stickiness”

GOM sampling methods

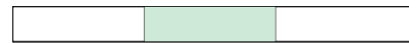
Denuders



Ambient air GOM measurements

- + Automated
- + Good time resolution (approx. 2 h)
- Biased low, GOM losses
- Losses dependent on humidity, ozone

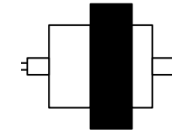
Sorbent traps



Flue gas GOM measurements

- + No GOM losses
- + Good time resolution (depending on airflow, but similar to denuders)
- Currently used only for high (flue gas) GOM concentrations

Membrane traps



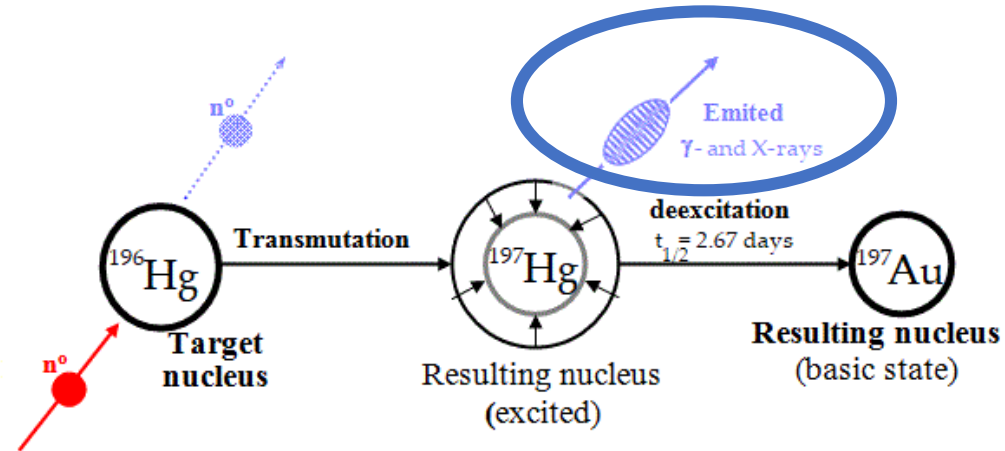
Ambient air GOM measurements

- + No GOM losses
- + No big meteorological influences
- No automation so far, time-consuming digestion
- Low time resolution (1-2 weeks continuous sampling)

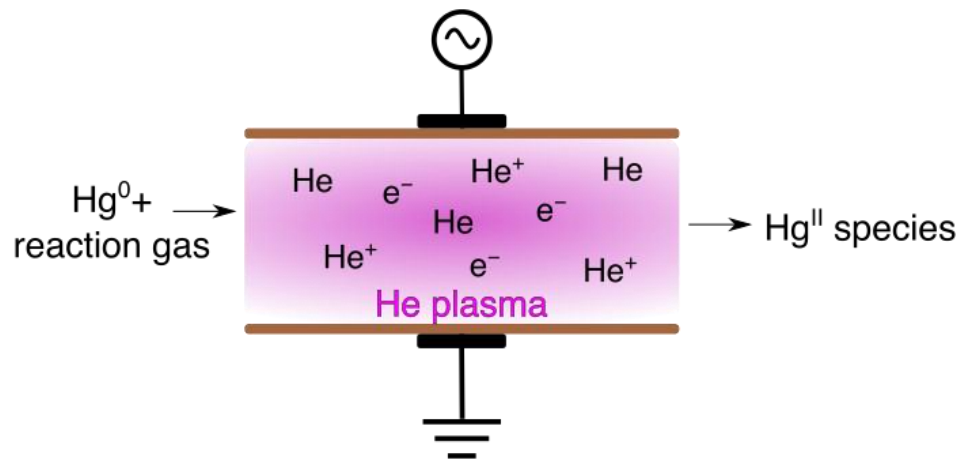
gamma/x-rays with characteristic energy – measurement using gamma HPGe detectors

Methodology

- Validation work done using ^{197}Hg radiotracer
 - Sensitive and selective, no blank issues



- Validation work done using traceable GOM calibration approach – nonthermal plasma oxidation approach
 - Generation of a traceable amount of Hg^0 and subsequent oxidation to Hg^{II} species (HgO , HgCl_2 and HgBr_2) in the presence of traces of a reaction gas



More information in our ICMGP 2022 presentation “Development of a Traceable Calibration for Gaseous Oxidized Mercury Species Based on Non-Thermal Plasma Approach”

Results

Denuders

- Specificity (% of retained Hg^0)?
 - 100 pg of Hg^0 passed through denuders
 - <0.1 % (below LOD) ✓ specific
- Stability: sampling losses (2h total airflow exposure)?
 - Up to 79 % in ambient air and daylight (in darkness 5-7 %) ✗ Not stable, biased low measurements
 - More info available in ICMGP 2022 presentation “Gas-phase Photoreduction and Losses of Hg^{II} from KCl-coated Denuders Used for Sampling Gaseous Oxidised Mercury Species”
- Compatibility of SI-traceable GOM calibration (plasma) and denuders?
 - Mass balance of Hg^{II} loadings: >92 % ✓ compatible

Results

Sorbent traps

Tested types of sorbents: i) KCl crystal and ii) quartz wool impregnated with KCl

- Specificity (% of retained Hg^0)?

- i) <0.23 % ii) <0.20 % ✓ specific

- Stability: sampling losses (2h total airflow exposure)?

Many variations of sampling conditions tested: high/low Hg^{II} conc, type of Hg^{II} loading (spike or evaporative calibrator), HgCl_2 or HgBr_2 species, high/low airflow

- i) max. loss 5.54 % ii) max. loss 3.89 % ✓ stable,
- Mostly losses < 1 %, higher relative losses for low Hg^{II} concentrations acceptable losses

- Compatibility of SI-traceable GOM calibration (plasma) and sorbent traps?

- Mass balance of Hg^{II} loadings: >95 % ✓ compatible

Preliminary results

Sorbent membranes

So far, initial tests with cation-exchange membranes

- Specificity (% of retained Hg⁰)?
 - <0.1 % (below LOD) ✓ specific
- Capture efficiency (% of retained Hg^{II})?
 - 98.6 % ✓ no breakthrough of Hg^{II}
- Specificity (% of retained Hg⁰)?
 - ? To be determined, future work*
- Compatibility of SI-traceable GOM calibration (plasma) and sorbent membranes?
 - ? To be determined, future work*

Implications and future work

- Denuders once again shown to be biased low
- Sorbent traps as a sampling method for ambient atmospheric Hg
 - Shows promise, why? In theory combines the benefits of denuders and membrane traps
- Future work
 - Sorbent membranes evaluation
 - Real-time measurements comparing the three major sampling methods (denuders, membranes and sorbent traps)

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