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

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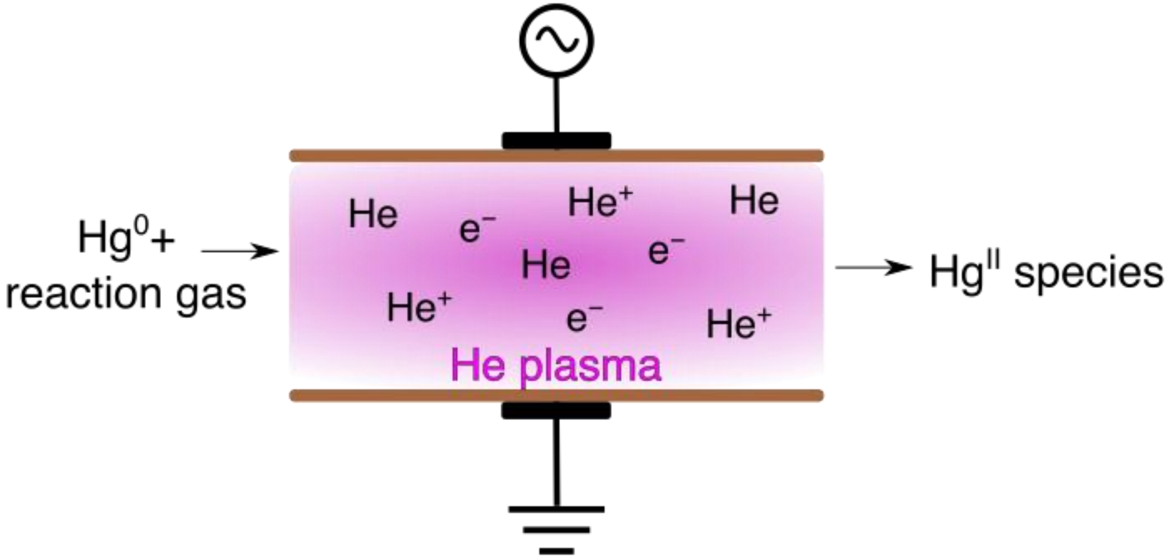
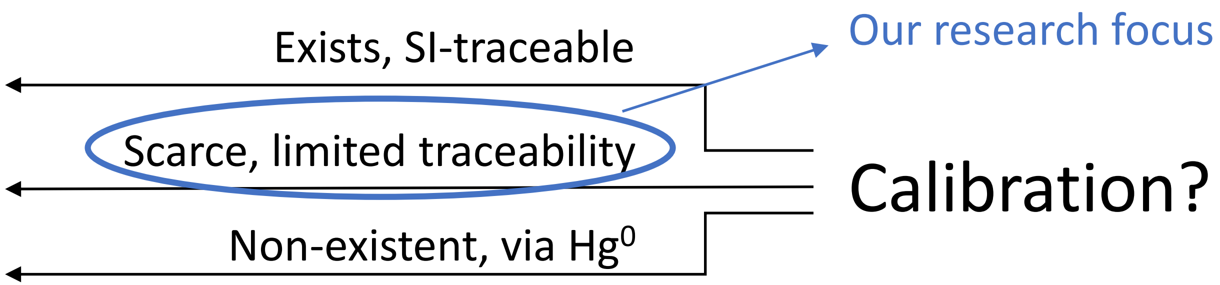


ICMGP conference, 27th July 2022

Atmospheric mercury speciation problematic

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



Our research focus

Exists, SI-traceable

Scarce, limited traceability

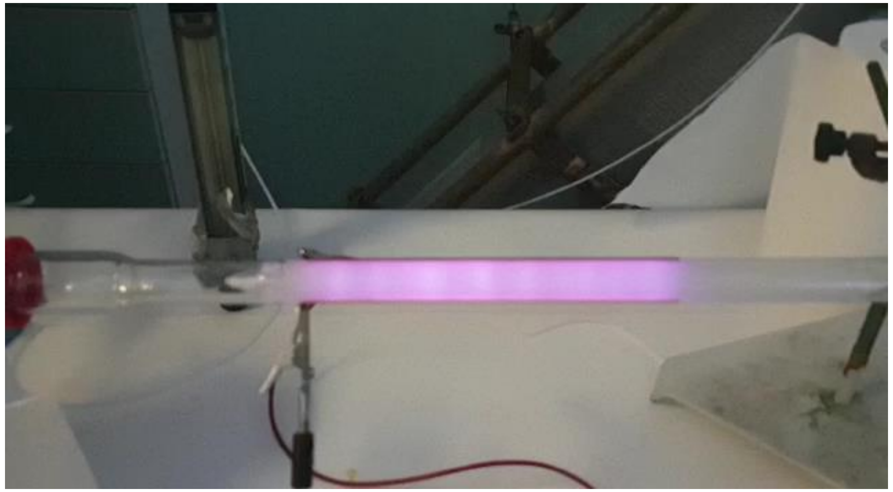
Non-existent, via Hg^0

Calibration?

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

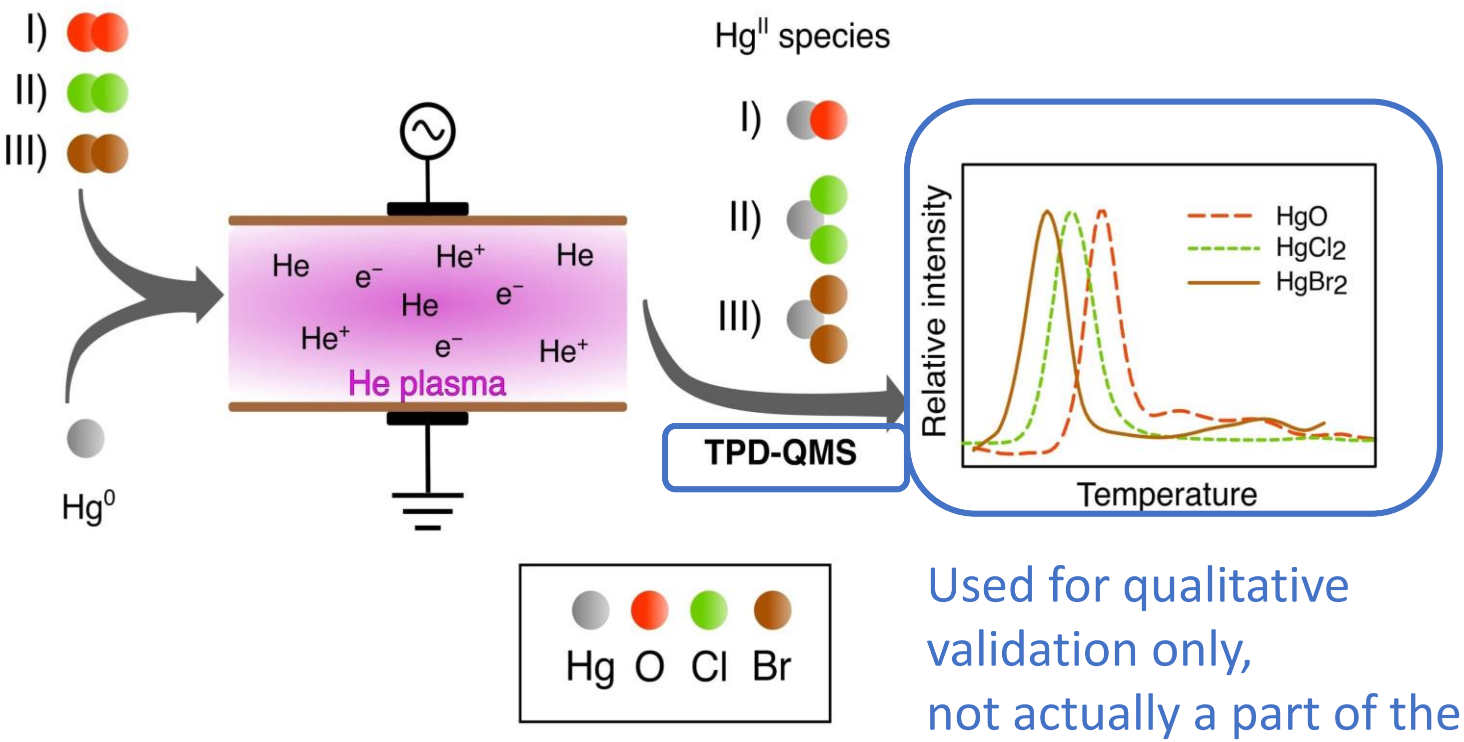
Non-thermal plasma use for GOM calibration

- Non-thermal ("cold") plasma (NTP)
  - Energy is mostly converted into energetic electrons and not into thermal energy – hence "cold"
  - NTP used in Hg research for removal of Hg^0 (via oxidation) in flue gas

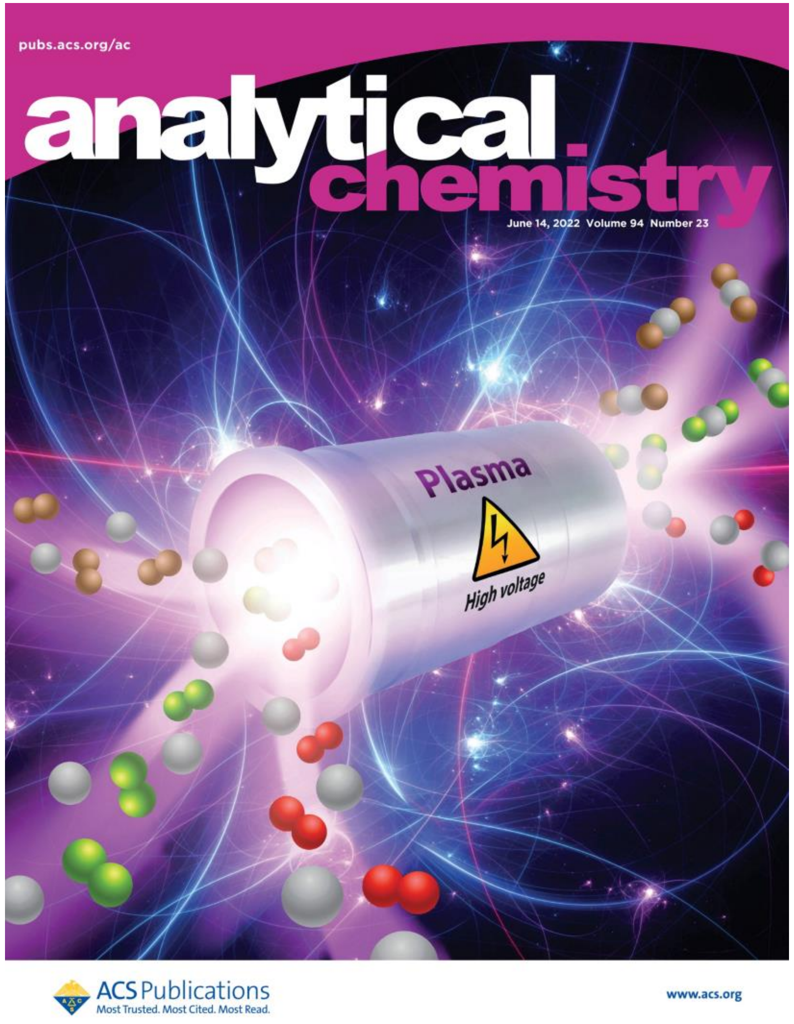


- NTP use for GOM calibration
  - Known quantity of Hg^0
  - Hg^0 into Hg^{II} species by NTP oxidation
  - Calibration of GOM measurement by NTP-produced Hg^{II} species

Principle of operation



Used for qualitative validation only,
not actually a part of the calibration



Cover art

Gačnik et al., *Analytical Chemistry*, 2022

Development and validation via ^{197}Hg radiotracer

1) Generation of known amount of Hg^0
   - Well established, via $Hg^{2+}(aq)$ reduction and purging
2) Oxidation of Hg^0 to HgO, $HgCl_2$ and $HgBr_2$
   - Oxidation efficiency experiments
3) How will instruments be calibrated with the generated Hg^{II} species? –thermal reduction to Hg^0 and (most commonly) AFS/AAS detection
   - Thermal reduction efficiency experiments

Near to 100 % efficiency needed

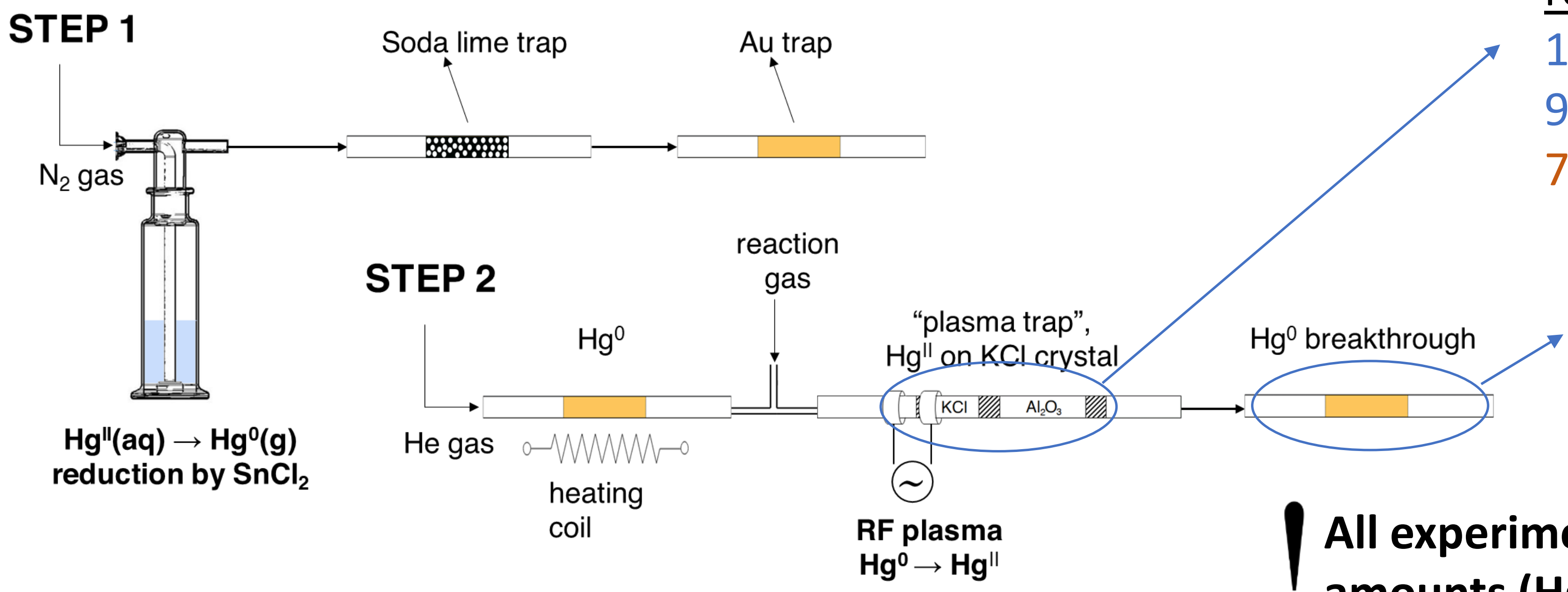
Validation experiments - ^{197}Hg radiotracer

+ high specificity
+ high sensitivity
+ simple and straightforward detection

– reactor needed for ^{197}Hg production

Development and validation via ^{197}Hg radiotracer

A NTP Hg^{II} loading - oxidation



goal: 100 % of Hg^{II}

results:

100.5 % ± 4.7 % (k=2) for HgO

96.8 % ± 7.3 (k=2) for HgCl$_2$

77.3 % ± 9.4 (k=2) for HgBr$_2$

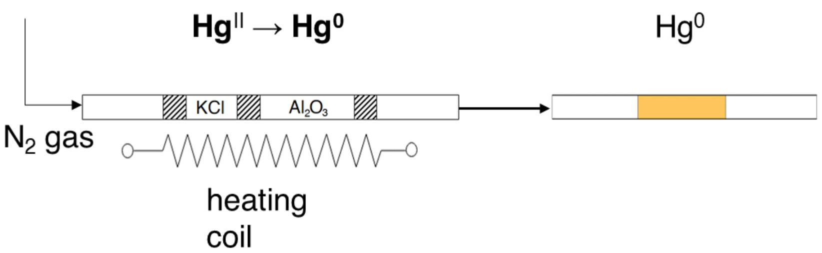
goal: 0 % of Hg^0 breakthrough

results:

< 1 % of Hg^0 breakthrough

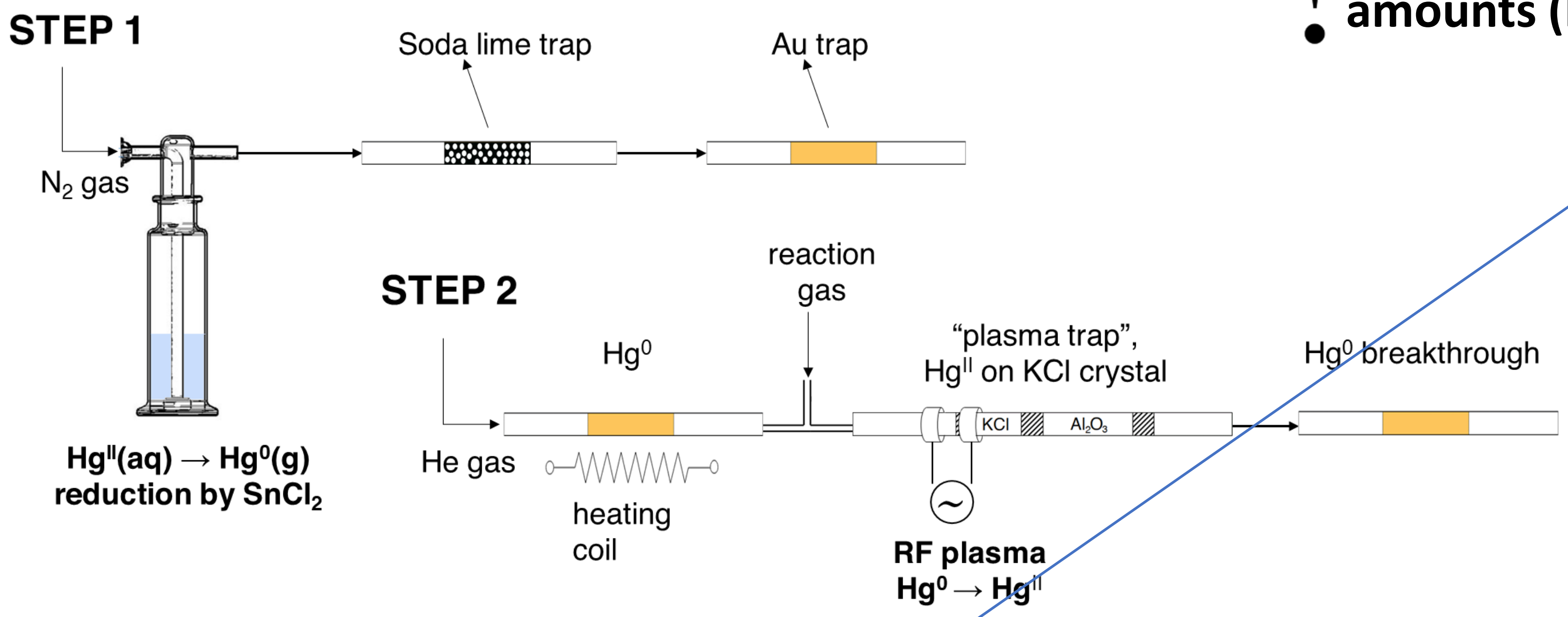
! All experiments done with ambient GOM amounts (HgO 100 pg, HgCl$_2$/HgBr$_2$ 250 pg !

B Hg^{II} thermal reduction

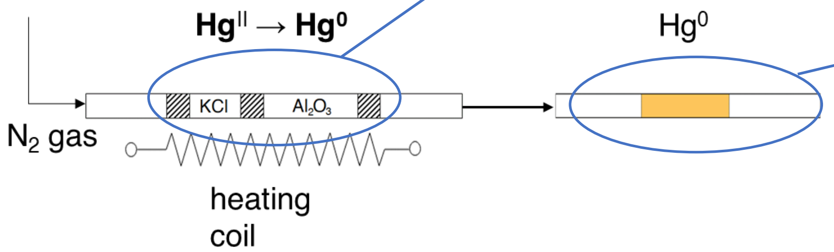


Development and validation via ^{197}Hg radiotracer

A NTP Hg^{II} loading - oxidation



B Hg^{II} thermal reduction



! All experiments done with ambient GOM amounts (HgO 100 pg, $HgCl_2$/$HgBr_2$ 250 pg !

goal: 0 % of unconverted Hg^{II}

results:

→ 0 % - with Al_2O_3 catalyst and >650 °C heating

→ unrepeatable and bad results with catalysts: Pt wire, Au coated corundum, quartz wool

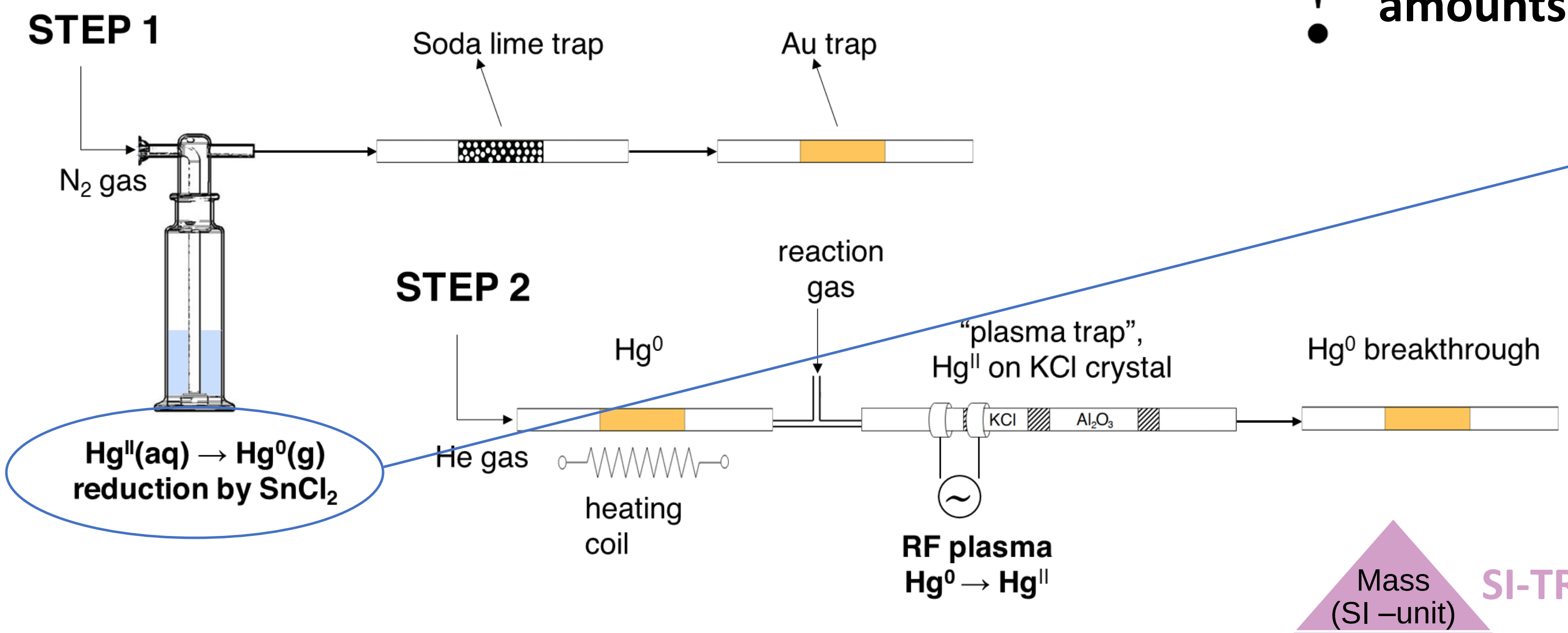
goal: 100 % of Hg^0

results:

→ 100 % of Hg^0 - with Al_2O_3 catalyst and >650 °C heating

Establishment of SI-traceability via NIST 3133

A NTP Hg^{II} loading - oxidation



! All experiments done with ambient GOM amounts (100 pg of HgO, $HgCl_2$, $HgBr_2$) !

Instead of $^{197}Hg^{II}$ radiotracer, NIST 3133 Hg^{II} solution

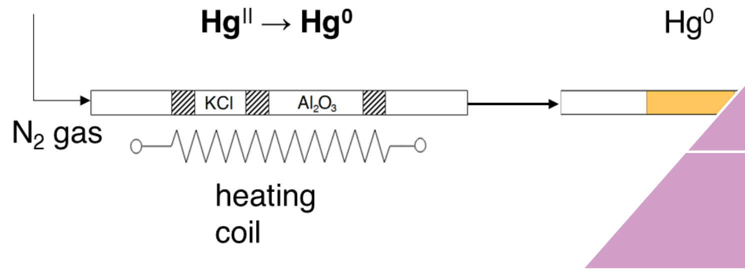
Results (uncertainty estimation undergoing):

98.5 % ± 2.0 (1 SD) for HgO

96.8 % ± 4.3 (1 SD) for $HgCl_2$

98.2 % ± 3.3 (1 SD) for $HgBr_2$

B Hg^{II} thermal reduction



SI-TRACEABILITY CHAIN

Mass (SI –unit)

NIST 3133 Mercury standard solution

Plasma oxidation approach to GOM calibration

Traceable and comparable GOM determinations (FUTURE PLAN)

Conclusions

- NTP successfully applied for generation of HgO, $HgCl_2$ and $HgBr_2$
- Presence of HgO, $HgCl_2$ and $HgBr_2$ confirmed by TPD-QMS
- All Hg^{II} species produced quantitatively
- Ambient amounts of Hg^{II} species were used
- SI-traceability Hg^{II} calibration achieved via NIST 3133

Future (undergoing/planned work)

- Real time calibration using NTP for ambient air analysis
- Comparison with other GOM calibration units
    - Permeation generators
    - Evaporative generators
    - Tekran speciation unit and its internal calibration source
    - Application for continuous emission calibration

Some of the presented material is in publication, do not replicate.

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