Converter Efficiency & Hg^{II} Solution Storage for Oxidised Hg Measurements

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Determining Converter Efficiency

Why do we care about converter efficiency?

- The most commonly used Hg analysers by field testing laboratories for gaseous Hg monitoring are atomic detectors such as AAS or AFS
- Atomic analysers can only detect Hg^0
- Volatile Hg^{II} compounds are also prominent species in anthropogenic Hg emissions
- Without the conversion of Hg^{II} species to Hg^0 they will not be detected which causes negative bias for total Hg measurements

Lumex RA-915F

- Lumex developed it's RA-915F Hg analyser that combines a thermal converter and an AAS detector
- However, the efficiency of the conversion was uncertain
- As part of the SI-Hg project, LGC developed a method for determining converter efficiency and determined it under the typical operating conditions

Considerations for Developing a Converter Efficiency Method

- Need to monitor both Hg^0 and Hg^{II} gases either selectively or independently
  - PSA 10.534 Hg^0 gas generator
  - PSA 10.536 Hg^{II} gas generator

- Species need to be monitored either online & continuously or intermittently
  - Used independent but parallel AAS & ICP-MS/MS
  - AAS detects Hg^0
  - ICP-MS/MS detects species independent total Hg

Underlying Principle

Hg^0 Generator ICP/AAS Ratio

$$\boldsymbol{R_{Ref}} = \frac{C_{AAS}^{Hg^0}}{{}^{i}Hg_{ICPMS}}$$

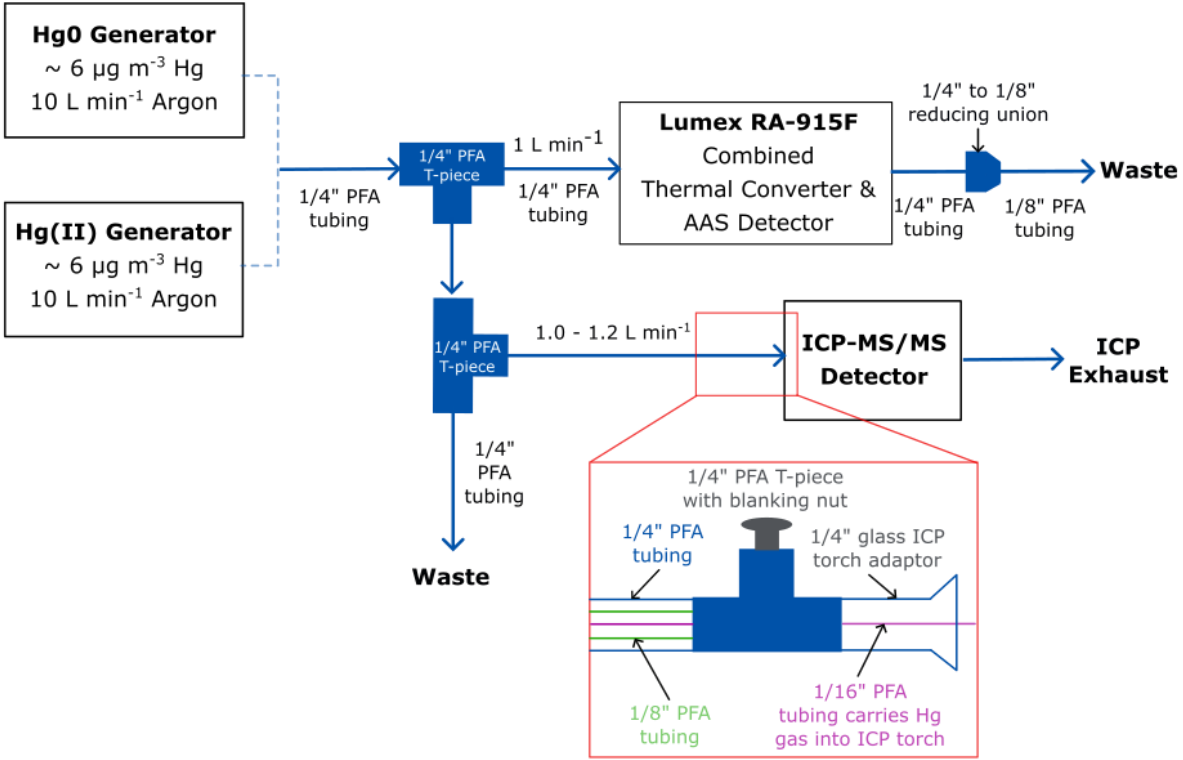
$HgCl_2$ Generator ICP/AAS Ratio

$$\boldsymbol{R_C} = \frac{C_{AAS}^{\boldsymbol{Hg^{II}}}}{{}^{i}Hg_{ICPMS}}$$

Converter Efficiency

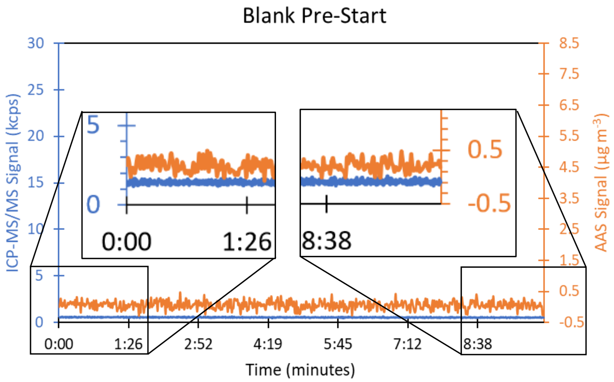
$$E_C = \frac{\boldsymbol{R_C}}{\boldsymbol{R_{Ref}}}$$

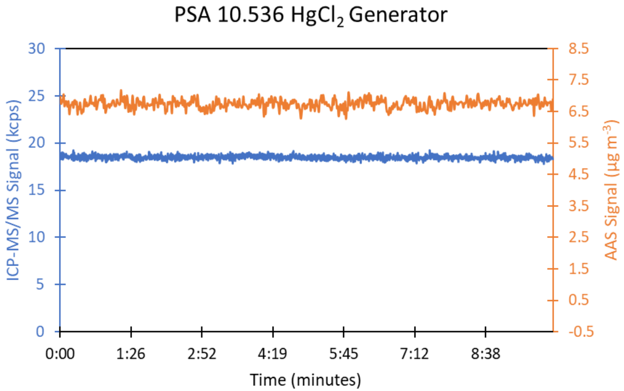
Converter Efficiency Determination Method

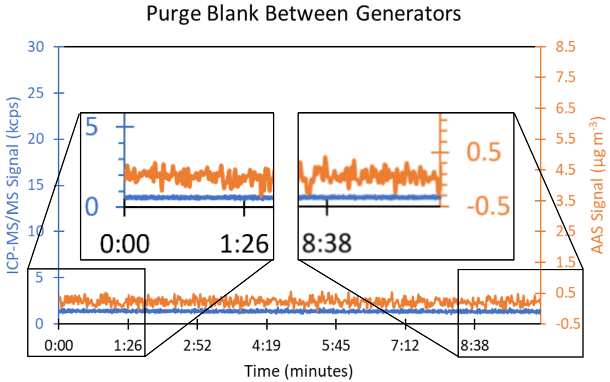


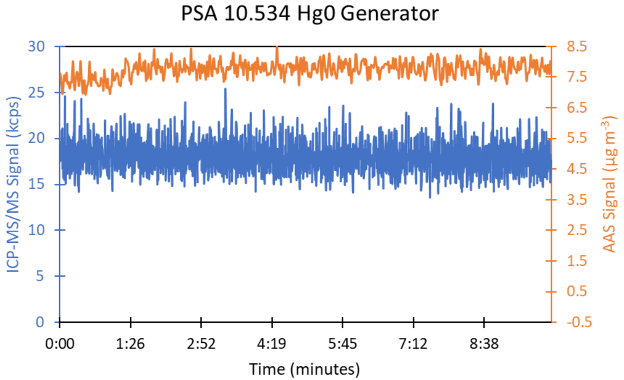
Converter Efficiency Measurement

1. Blank
2. Hg^{II} Generator
3. Blank
4. Hg^{0} Generator









Results

Date	Generator	Lumex/ICP Ratio (R_{Ref} & R_C)	Converter Efficiency	U_C (k=2)
27/10/2022	PSA 10.534 Hg^0	0.000392 (3)	88 %	0.02
	PSA 10.536 $HgCl_2$	0.000343 (2)		
28/10/2022	PSA 10.534 Hg^0	0.000435 (4)	84 %	0.02
	PSA 10.536 $HgCl_2$	0.000365 (2)		
01/11/2022	PSA 10.534 Hg^0	0.000724 (12)	85 %	0.03
	PSA 10.536 $HgCl_2$	0.000617 (4)		

Average Converter Efficiency	**86 %**
Standard Deviation	0.01
Overall Expanded Uncertainty (k=2)	0.04

Storage of $HgCl_2$ Solutions

Use of $HgCl_2$ Solutions

- $HgCl_2$ solutions prepared from salts are used with liquid evaporative Hg gas generators
- The stability of these salts and solutions over time are a critical uncertainty parameter for liquid evaporative generators
- In the SI-Hg project, the elemental and chromatographic stability of $HgCl_2$ solutions and salts was examined
- SI-Hg industry and research partners including VDZ, TÜV Rheinland, VTT, and CNR were consulted to understand the range of solution storage conditions

$HgCl_2$ Solution Storage Conditions

Temperature:

Ambient

Shock 60°C heat

Fridge

Matrix:

0.1% v/v HCl

0.024% v/v HNO_3 + 0.0144% v/v HCl

0.125 µg/g HCl + 0.125 µg/g HNO_3

Bottle Type:

FEP

FLPE

Borosilicate

Concentration:

0 ng g^{-1}

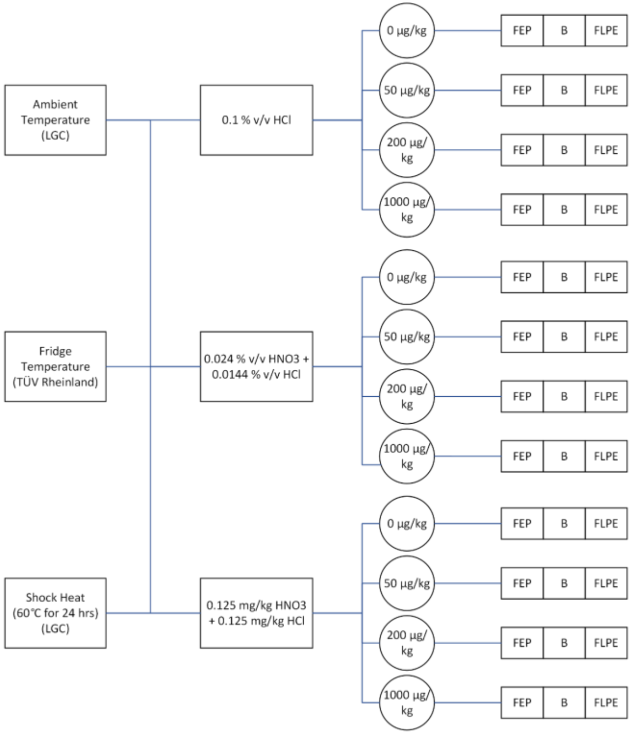
50 ng g^{-1}

200 ng g^{-1}

1000 ng g^{-1}

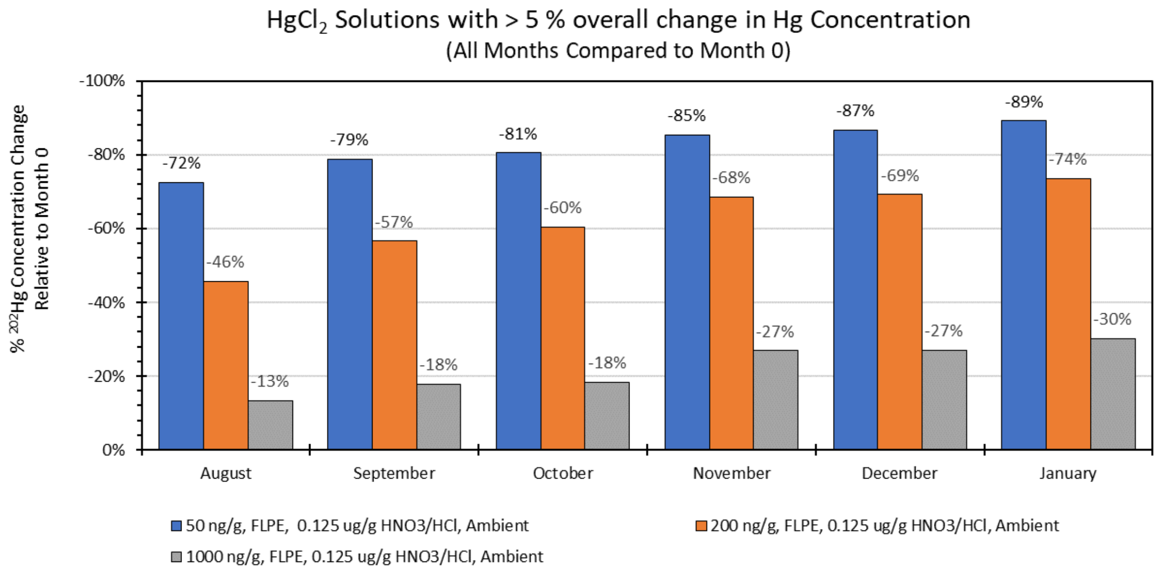
$HgCl_2$ Solution Stability Study

- 36 solutions per temperature
- The total Hg concentration of each solution was measured once a month of six months at ambient and fridge temperatures
- A one-off 24-hour shock heat experiment at 60 °C
- LGC performed the ambient and shock heat experiments and TÜV Rheinland the fridge experiment



Ambient Solution Stability Results – ICP-MS/MS

- All but 3 of the 36 solutions maintained a stable concentration over the 6 months



Unstable solutions were all in:

FLPE bottles

&

0.125 µg/g HNO_3 +

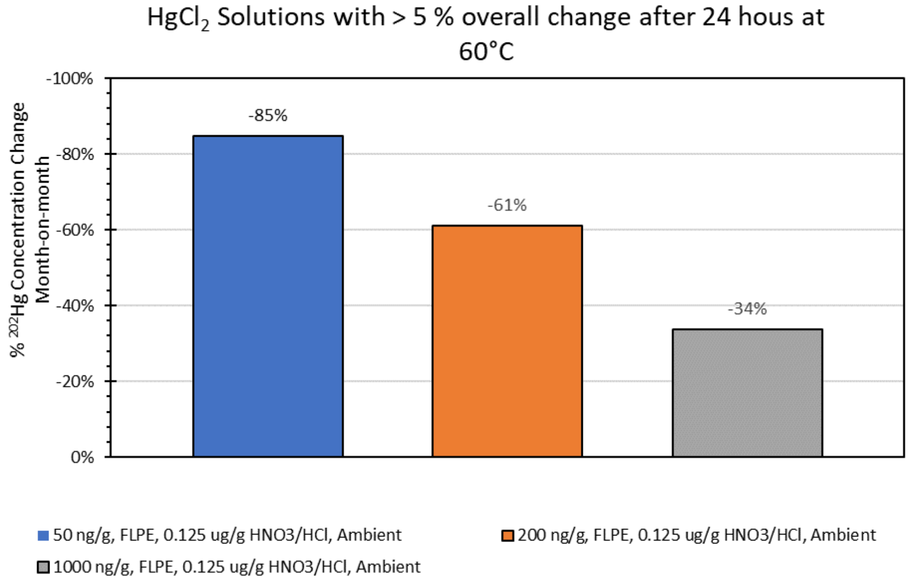
0.125 µg/g HCl

Shock Heat Solution Stability Results – ICP-MS/MS

- All but 3 of the 36 solutions maintained a stable concentration after heating to 60°C for 24 hours

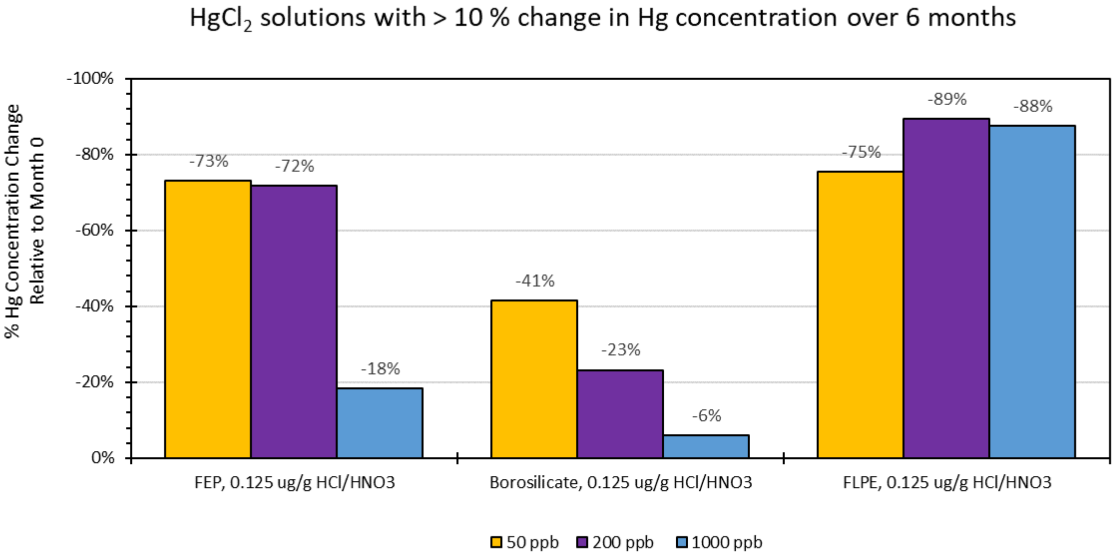
- Storage conditions that performed poorly in the ambient temperature study also performed poorly in the shock heat study

- The percentage change in Hg concentration was of a similar magnitude to 6 months of ambient temperature storage



Fridge Solution Stability Results – CV-AAS

- All solutions stored in 0.1% v/v HCl and 0.024% v/v HNO_3 + 0.0144% v/v HCl were stable over the 6 months



<u>Unstable solutions were all in:</u>

0.125 µg/g HNO_3 +

0.125 µg/g HCl

irrespective of

bottle type

Chromatographic Stability of $HgCl_2$ Solutions

- Analyse the 36 $HgCl_2$ solutions stored for the 6-month stability study (now 1 year old) and compare amongst themselves and to newly prepared solutions
  - Three new blanks, one of each matrix
  - Three new 50 ppb $HgCl_2$ solutions, one of each matrix

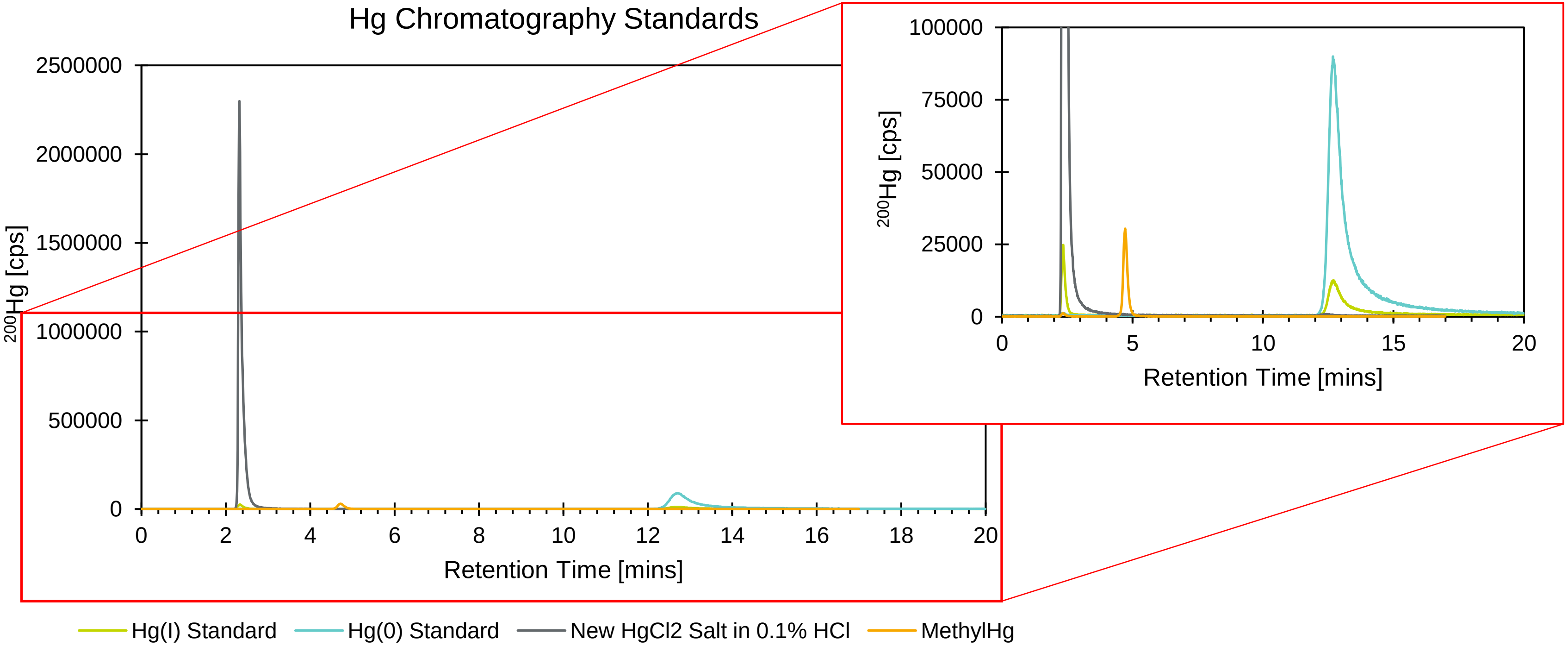
- Semi-quantitative since only a comparative study is needed

- Dilute all samples to 40 ppb and compare peak areas and chromatograms to determine effects of different storage conditions on the speciation of Hg in the $HgCl_2$ solutions

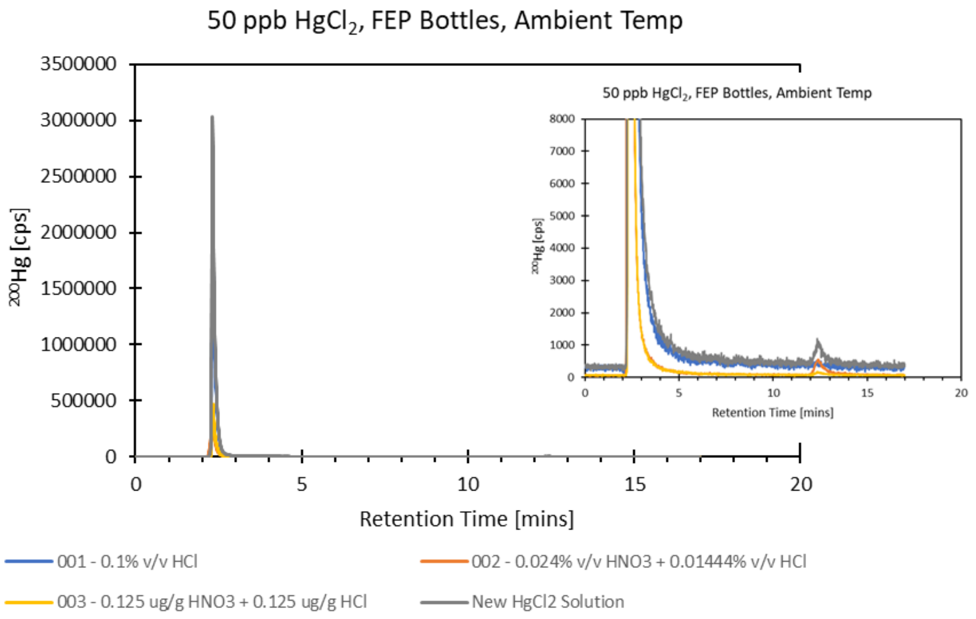
- Mobile phase: 0.1% m/v Cysteine (HCl), 1 mM acetic acid, adjusted to pH 4 with ammonia solution

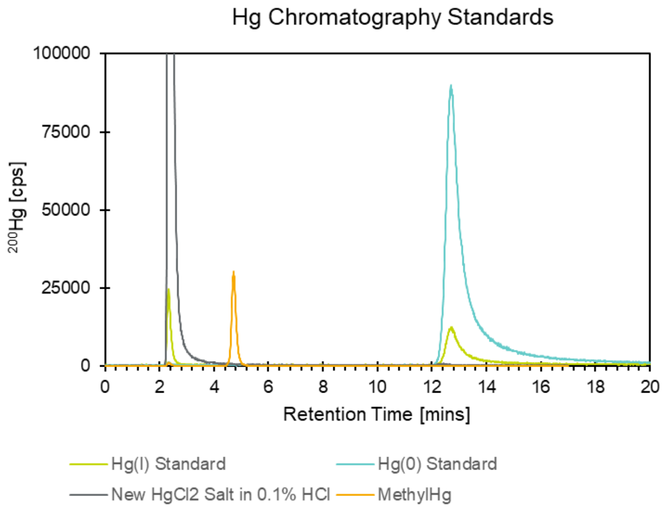
- Column: ProteCol ™ C18G 120Å 3µm particle size, length 150mm 4.6mm id

Hg Chromatography Standards

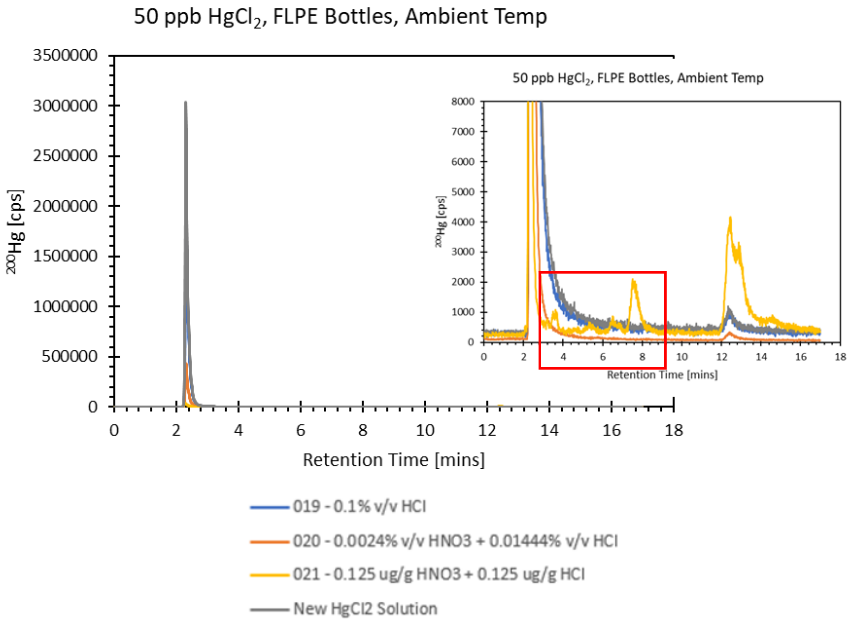


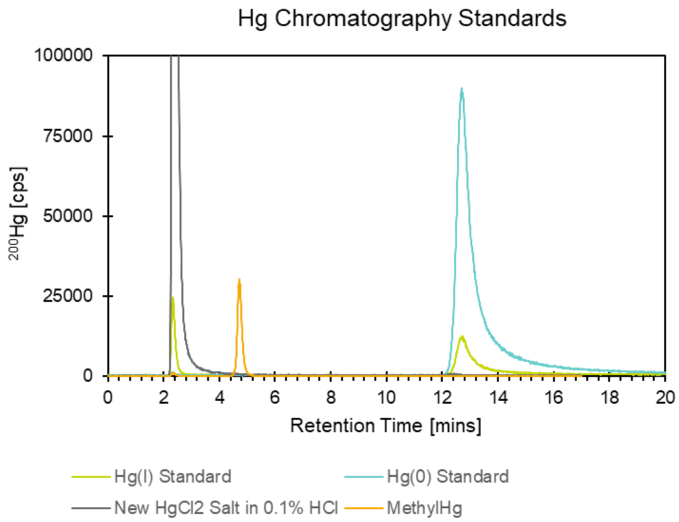
Chromatography Results – FEP & Borosilicate





Chromatography Results - FLPE Bottles





$HgCl_2$ Solution Stability Conclusions

- FLPE bottles and 0.125 µg/g HNO_3/HCl storage solutions should not be used to store $HgCl_2$ solutions at ambient temperatures or up to 60°C for 24 hours
- FEP and borosilicate bottles are suitable for storing $HgCl_2$ solutions with 0.1% HCl, 0.125 µg/g HNO_3/HCl & 0.024% v/v HNO_3 + 0.0144% v/v HCl at ambient temperatures and up to 60°C for 24 hours
- 0.125 ug/g HNO_3/HCl should not be used at all to store $HgCl_2$ solutions at fridge temperatures
- Higher storage concentrations typically result in less Hg loss

Good Practice Guide

The Good Practice Guide will be made available by the end of September

For more information, please visit the SI-Hg project website

Thank you for listening