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Solubility and Fate of Mercury in Gas Processing Solvents

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Objectives of the Project

The main objective of the project was to determine solubility data for elemental mercury in conditions that closely resemble key separation equipment in gas plants.

- Literature search of existing mercury solubility data with relevant water, glycol, methanol and amine systems
- Measurement of elemental mercury solubility in water and selected glycol (MEG, TEG), amine (MEA, MDEA) and MeOH solutions at different temperatures and concentrations



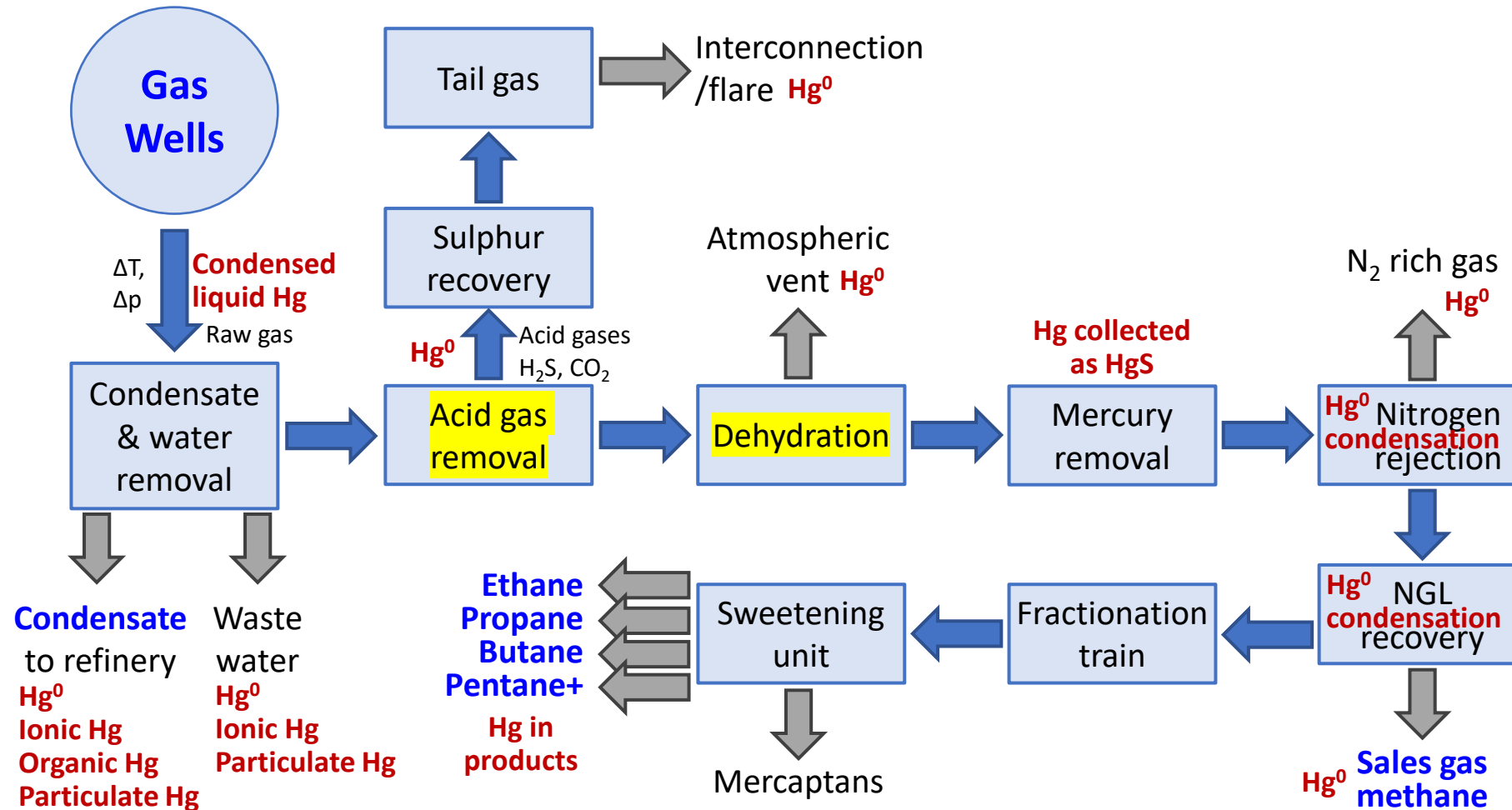
Research Report

RR-246

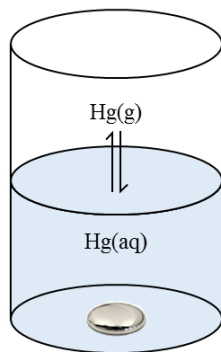
**Solubility of Mercury in Selected
Gas Processing Solvents**



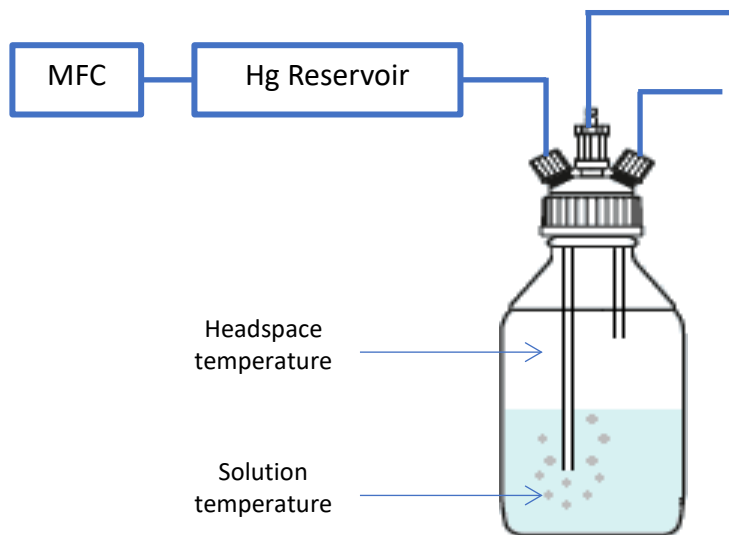
Hg during Gas Purification Processing



Overview of the Initial Approaches used

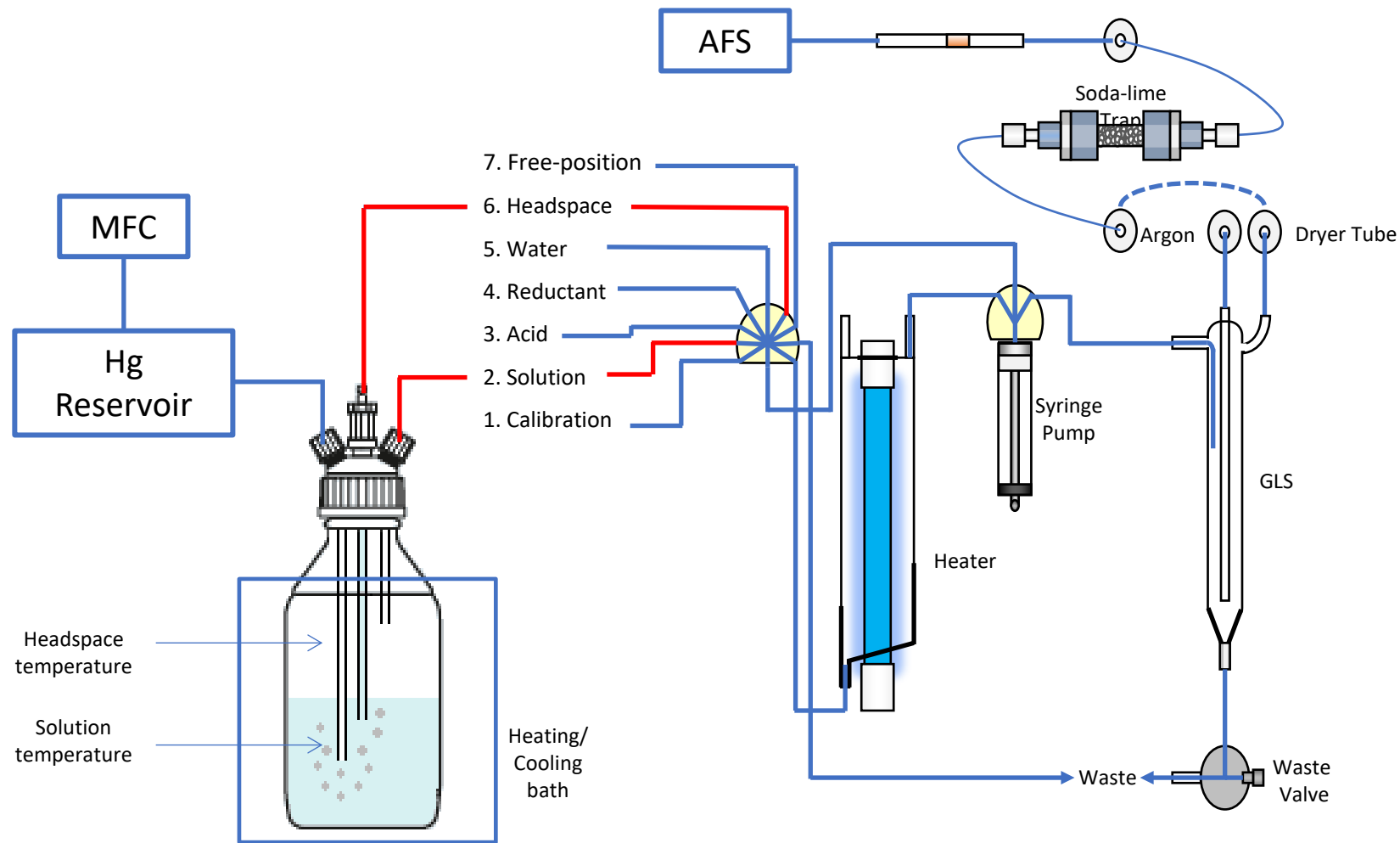


- Saturation and dissolution of elemental Hg was very slow
- Impurities within the solvent cause surface oxidation of elemental Hg droplets. Oxidized Hg has a higher solubility so high bias.
- Addition of a reductant such as tin(II) chloride was required but this was consumed over time and adding more reductant caused discolouration and changes of pH and Eh
- Extraction of the liquid solvent at temperatures above ambient is difficult as Hg condenses and the result goes down.



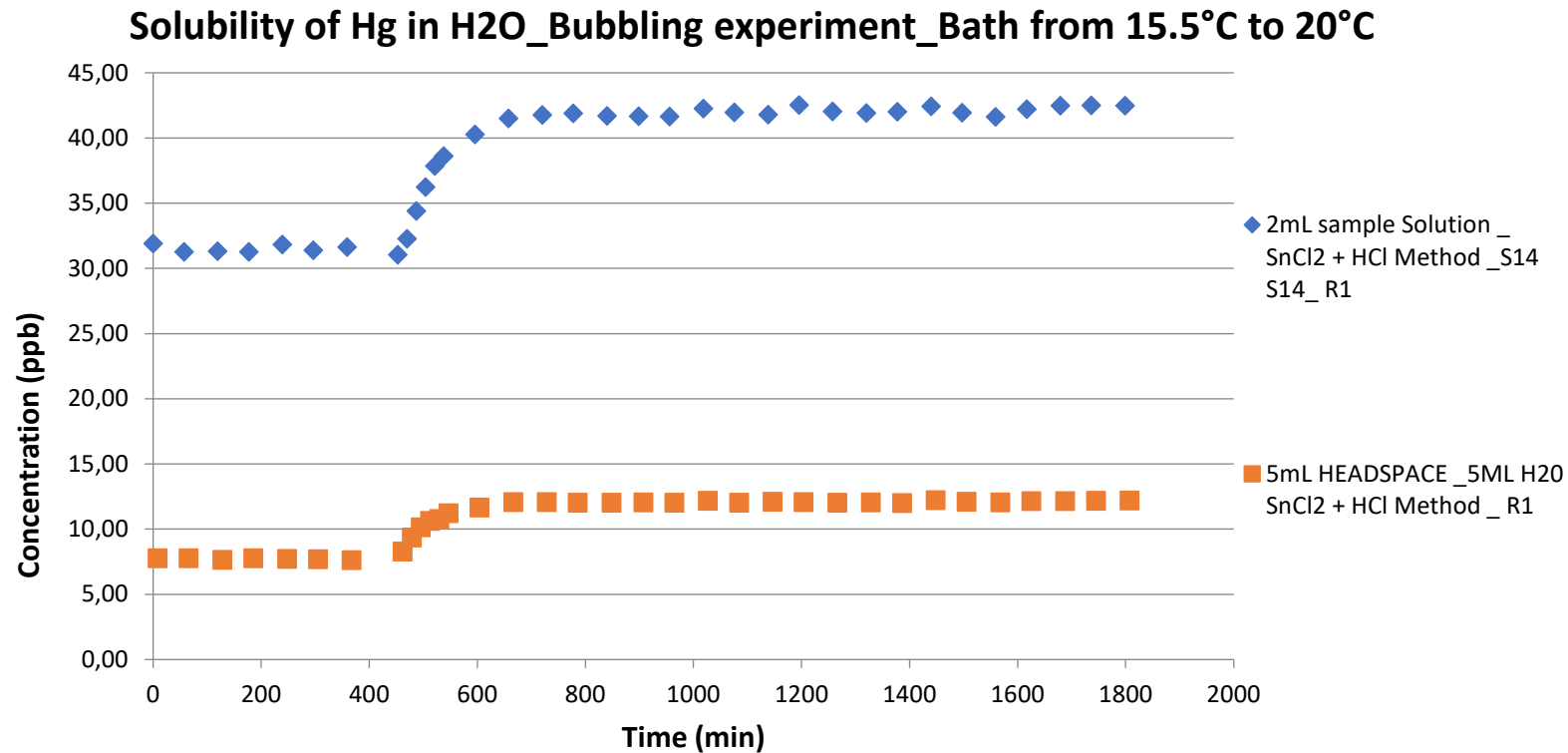
- Better contact between elemental Hg and the solution
- Solution saturation is quicker
- Less degree of oxidation
- Low amount of Hg is used
- Possibility to make the saturation faster increasing reservoir temperature and flow of argon

Schematic Layout of the Automated Mercury Measurement System for Gas and Liquid Phases



Data Acquisition

The following raw data are an example of a dynamic solubility experiment. 600mL de-ionised water solution plus 2g/L of SnCl₂ were purged with gaseous elemental Hg



The developed instrumentation shows stability over the time and high precision



Apparatus for Establishing the Dimensionless Henry's Law Constant.

Photograph of Apparatus

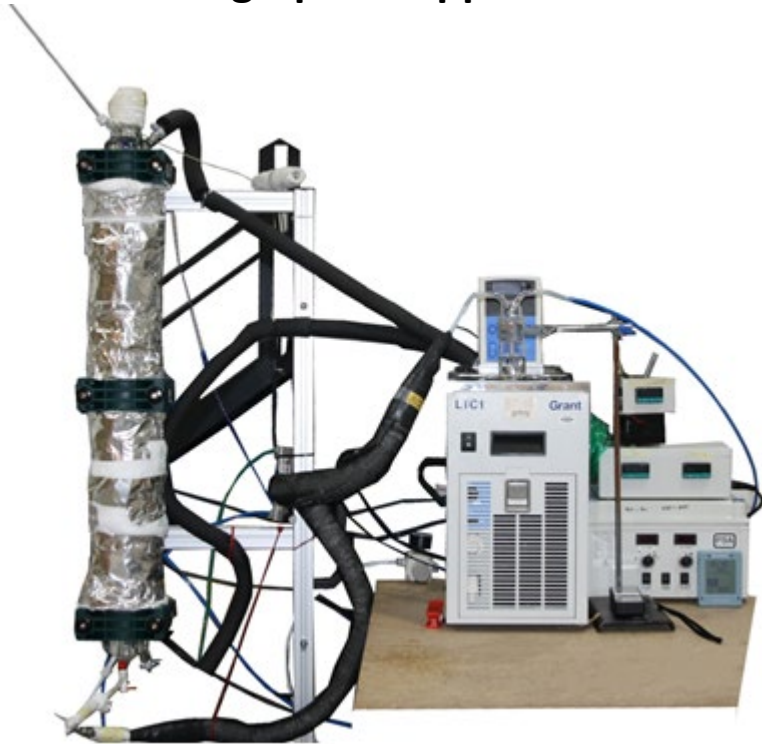
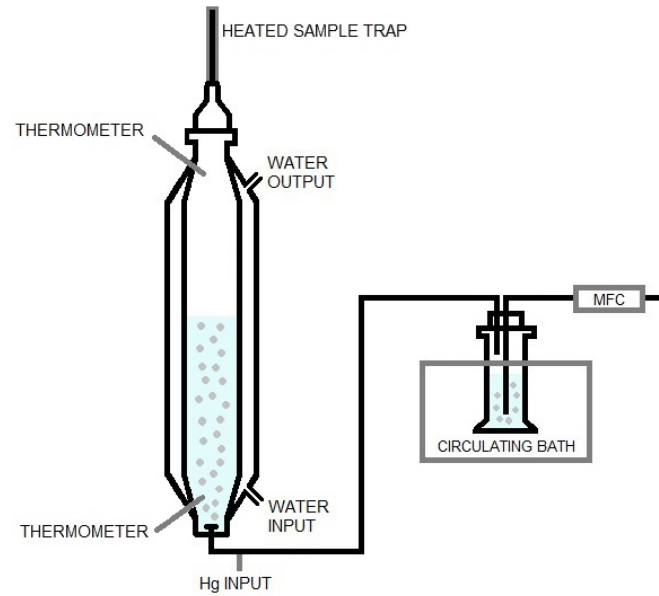
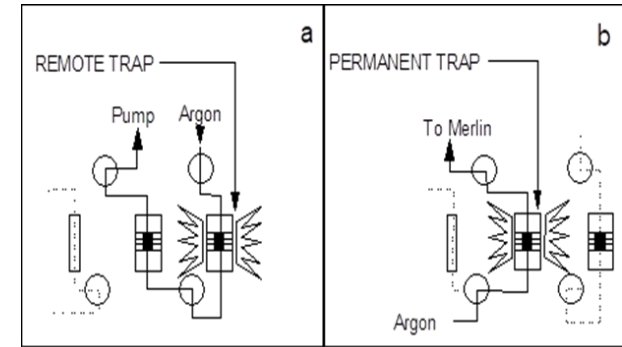


Diagram of Method Set-up



Hg Determination



Analysis of the remote gold sample traps was carried out using thermal desorption with amalgamation AFS

Andersson et al. Chemosphere 73 (2008) 587–592



Dimensionless Henry's Law Constant

$$k_{H'} = \frac{\text{Hg saturated (gas)}}{\text{Hg solubility (solvent)}}$$

Provided that elemental Hg is in equilibrium between the gas and solvent phases it is possible to calculate the solubility of elemental Hg in the solvent by inputting the saturated gas phase concentration of Hg vapour at the temperature of the solvent being tested



The saturated gas phase concentration of Hg is derived using the Dumarey equation



Dimensionless Henry's Law Constant Calculations

$$\frac{dC_{aq}}{dt} = - \frac{Q_{Ar} * k'_H * C_{aq}}{V_{aq}} \quad \rightarrow \quad C_{aq} = C_0 * e^{-\frac{V_g * k'_H}{V_{aq}} t} \quad \alpha = (V_g * K'_H) / V_{aq}$$

The amount of mercury collected every extraction is expressed as

$$m_{Hg}(n) = V_{aq} * C_{aq}(n - 1) - V_{aq} * C_{aq}(n)$$

Knowing the concentration equation

$$\ln[m_{Hg}(n)] = -(n * \alpha) + \ln[V_{aq} * C_{aq} * (e^\alpha - 1)]$$

α is the slope of a linear correlation and from it we can calculate the K'_H and the solubility of Hg

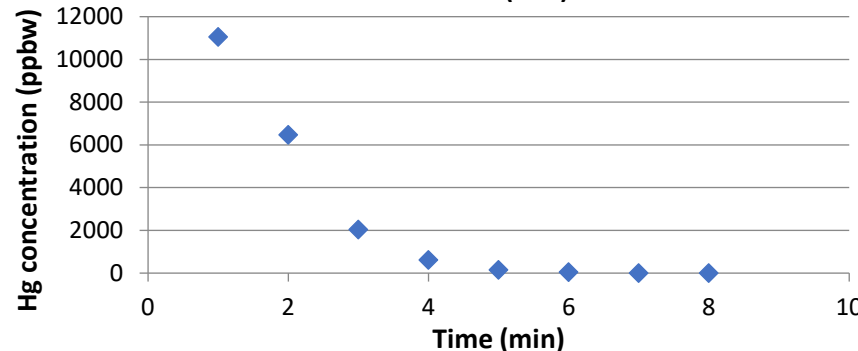
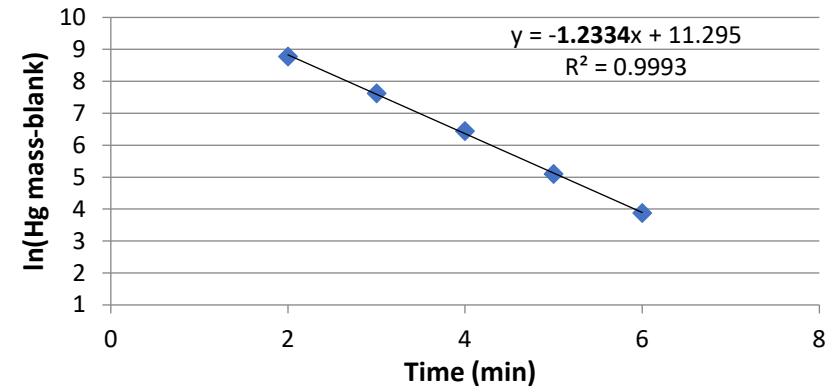


Dimensionless Henry's Law Constant

Example Data for Water

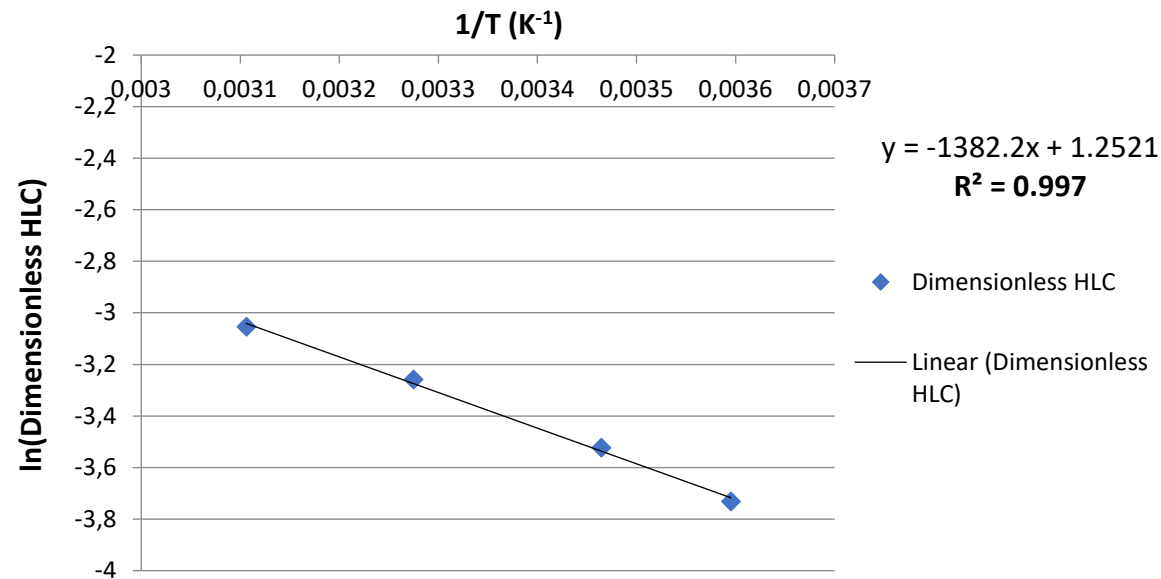
Extraction (n)	ID	Method	Units	Hg Mass	Hg Mass - Blank	ln(Hg mass-blank)	Date/Time
1	GDF	Gain 10.msf	pg	11154.60645	11051.7751	9.310346337	21/11/2018 15:14
2	GDF	Gain 10.msf	pg	6582.48682	6479.65547	8.77642262	21/11/2018 15:24
3	GDF	Gain 10.msf	pg	2152.65894	2049.82759	7.625510966	21/11/2018 15:35
4	GDF	Gain 10.msf	pg	726.67078	623.83943	6.435893012	21/11/2018 15:45
5	GDF	Gain 10.msf	pg	265.88953	163.05818	5.09410707	21/11/2018 15:56
6	GDF	Gain 10.msf	pg	151.01869	48.18734	3.875096331	21/11/2018 16:07
7	GDF	Gain 10.msf	pg	113.7019	10.87055	2.386057298	21/11/2018 16:18
8	GDF	Gain 10.msf	pg	102.83135	0		21/11/2018 16:28

α	T (K)	T_0 (K)	
1.2334	288.65	273.15	
Q (mL/min)	V_{aq} (mL)		P_0 (mbar)
301.5	800		1003.2
t (min)			P_w (mbar)
10			17.5332
		P Trap1	QTrap1
		1078.4	301.2897372
		P Trap2	QTrap2
		1065.6	304.9693773
k_H'			$Q_{average}$
0.325510982			303.1295573
$C_{g,Hg}$ (15.5°C)	Density water (15.5°)		
ng/mL			
8.99835	1.00489		
$C_{aq,Hg}$ (15.5°C)	Solubility (15.5°C)		
ng/mL	ppbw		
27.64	27.51		

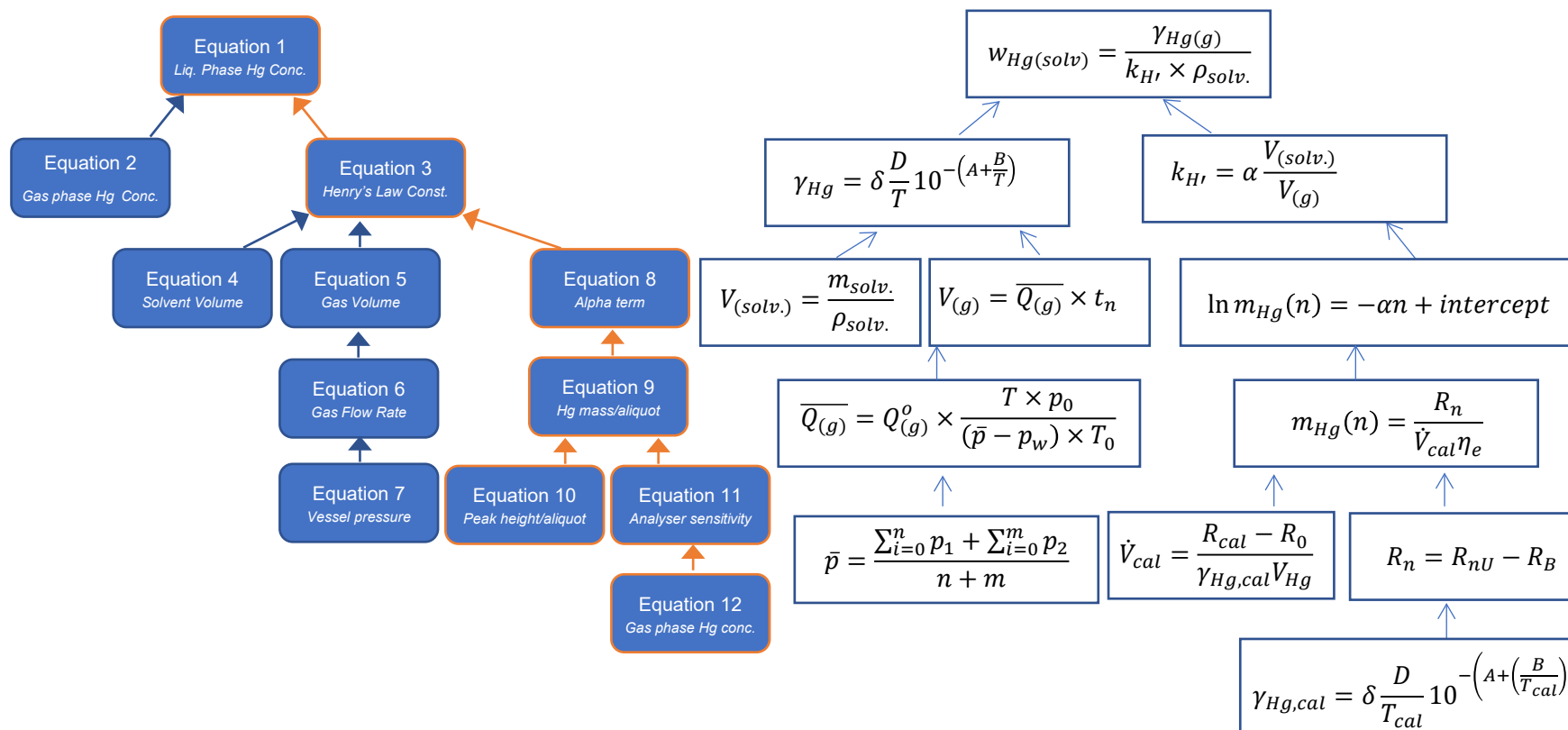


Dimensionless HLC Advantages

- there is no handling and transfer of samples which are Hg saturated which are highly likely to exhibit Hg condensation with small temperature decreases.
- there is good linear correlation for $\ln(\text{HLC})$ against reciprocal temperature. Errors in the higher temperature results would negatively impact R^2 .
- oxidation of Hg in solution can be excluded because in the HLC determination experiment all the mercury injected is recovered from the gas phase (also presence of SnCl_2 and low residence time of Hg in solution)



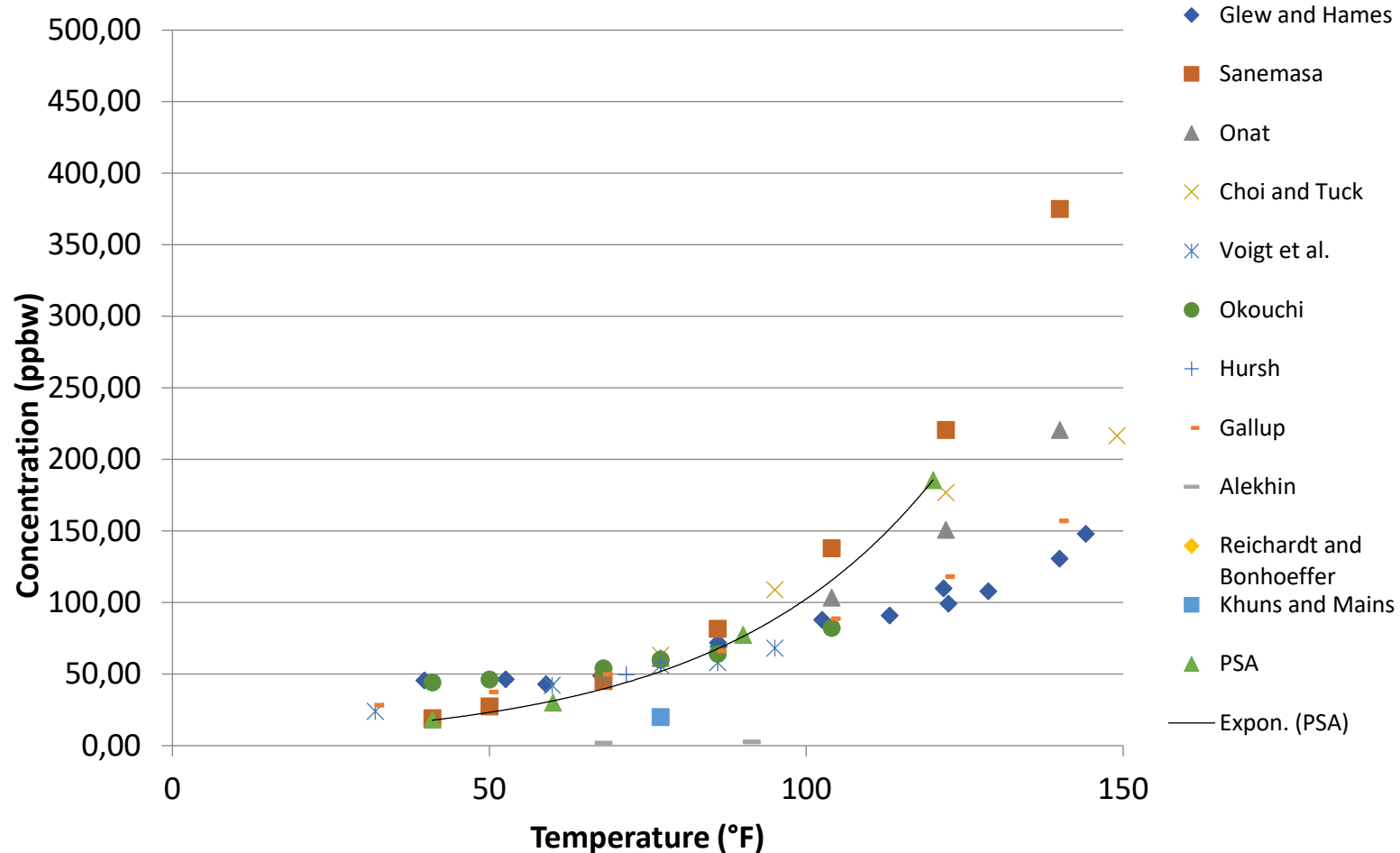
Bottom-up Uncertainty Budget



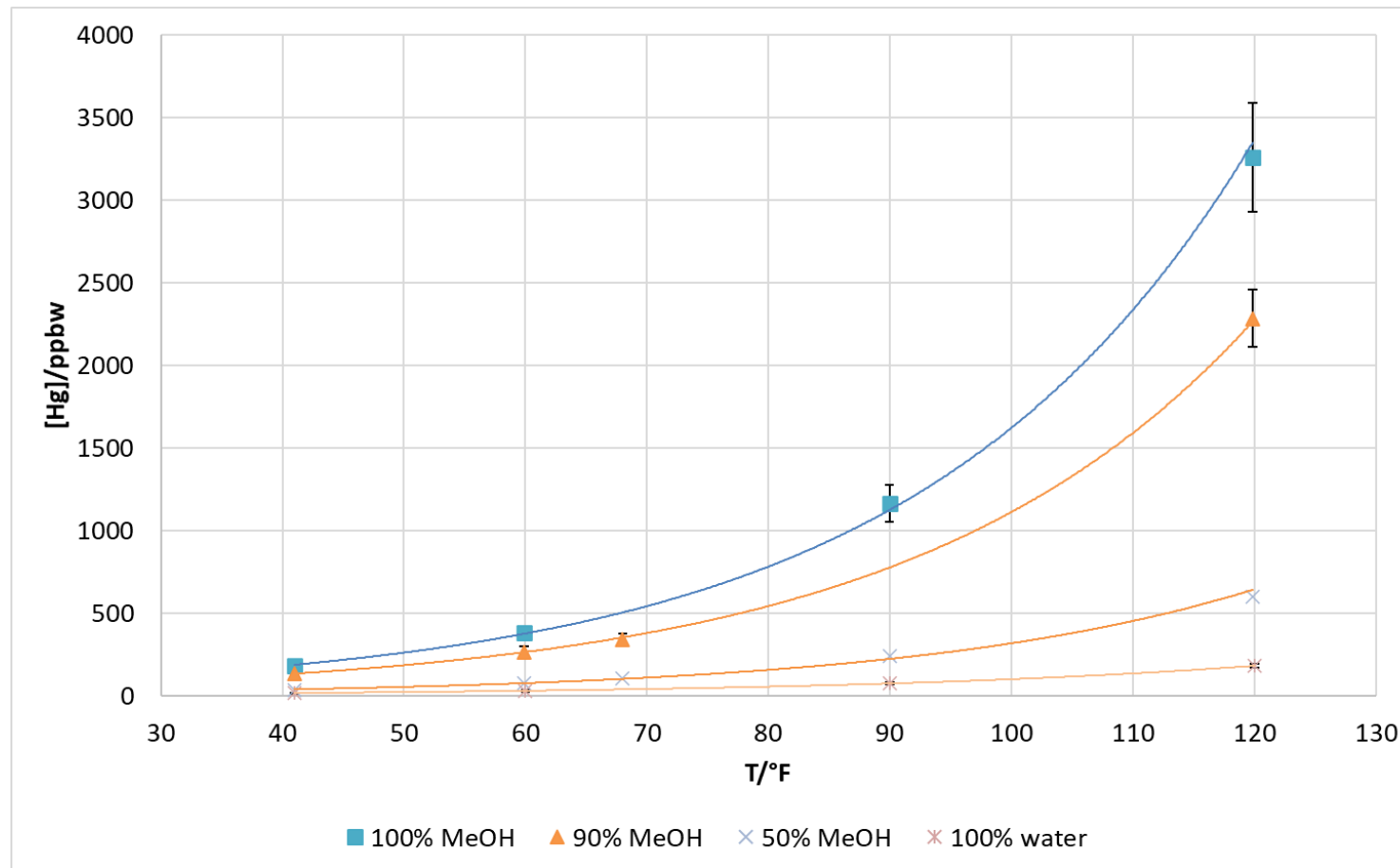
A bottom-up uncertainty budget on the dimensionless Henry's law constant experiment was developed



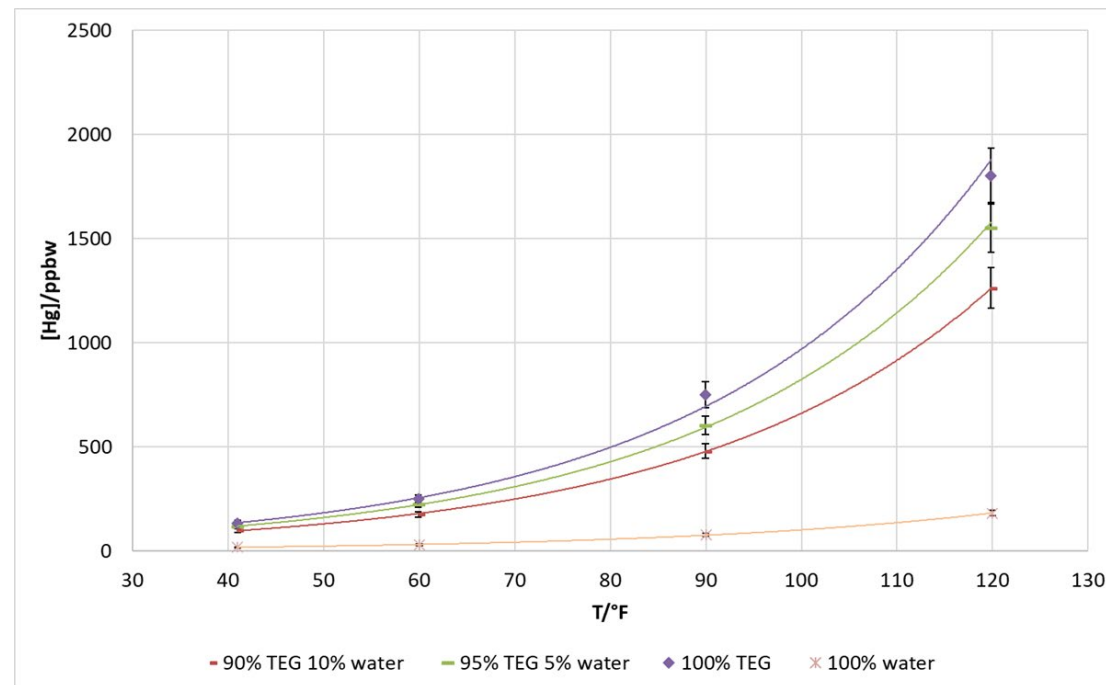
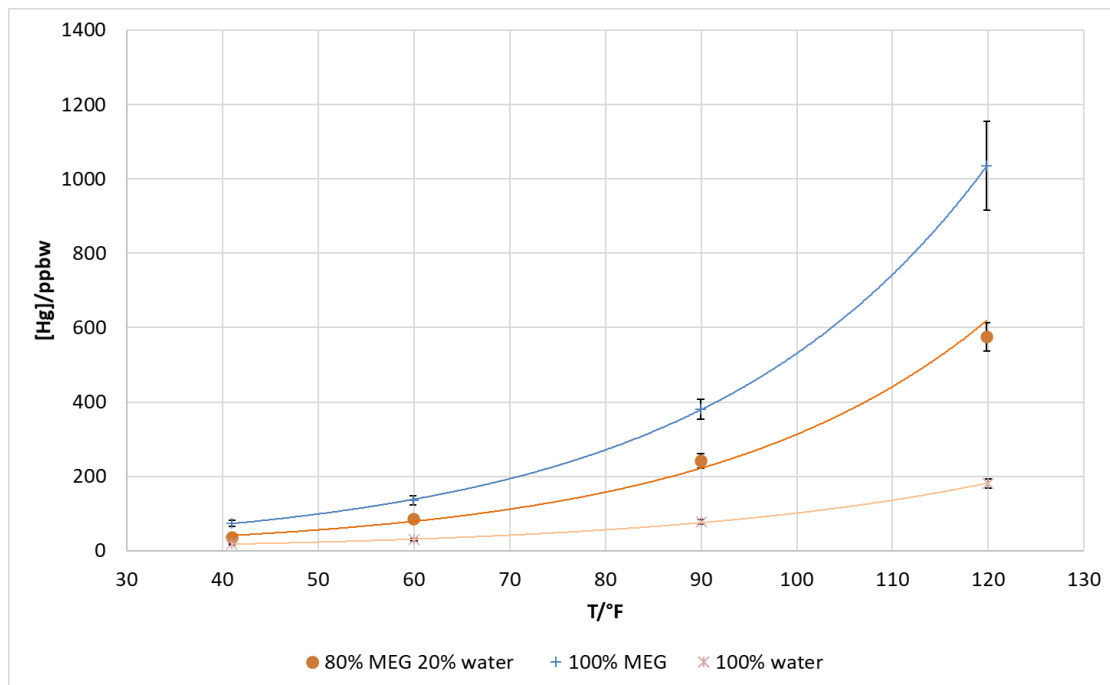
Solubility of Elemental Hg in Water Literature Comparison



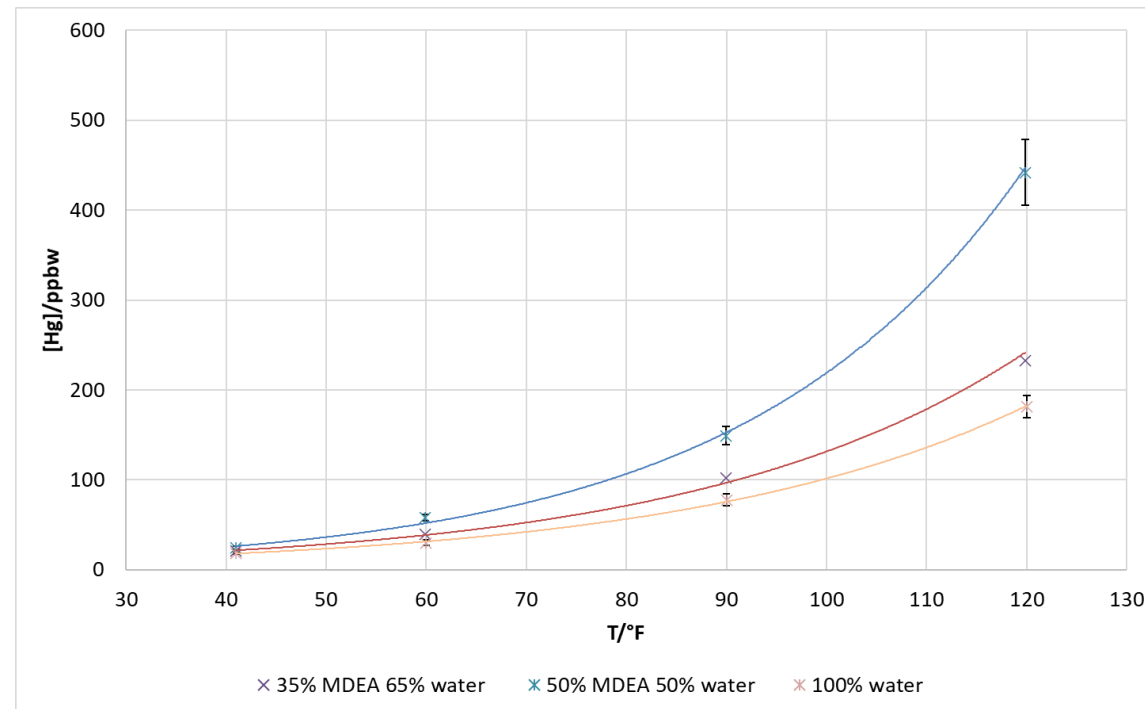
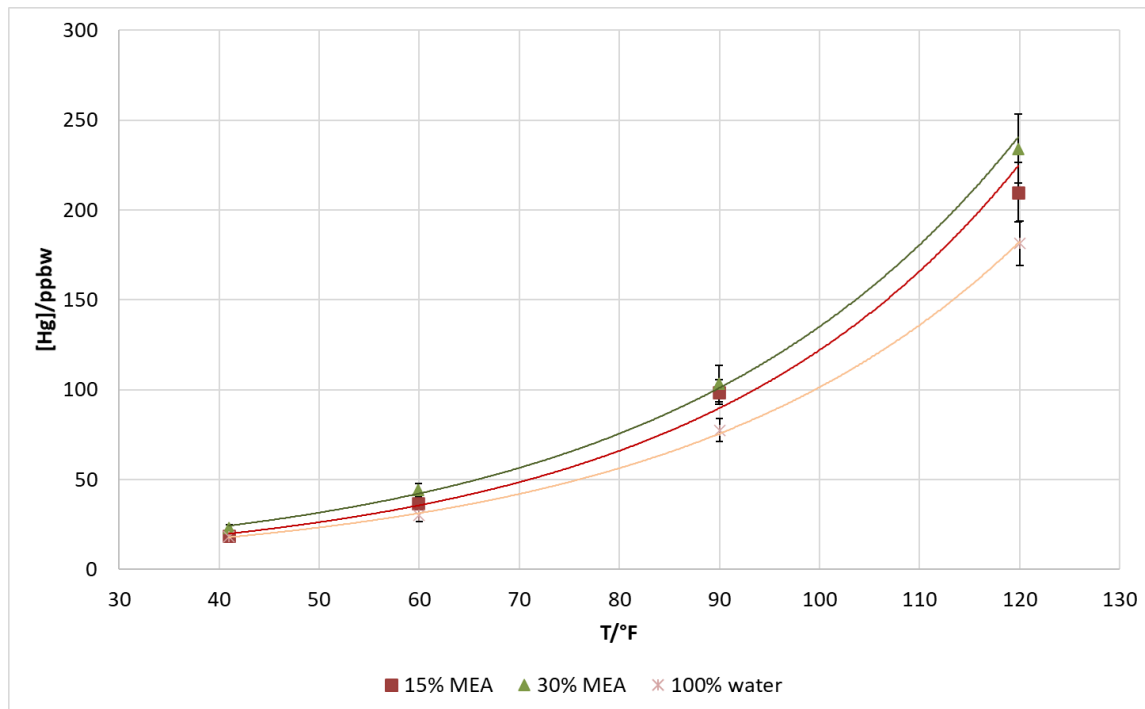
Solubility of Elemental Hg in Methanol



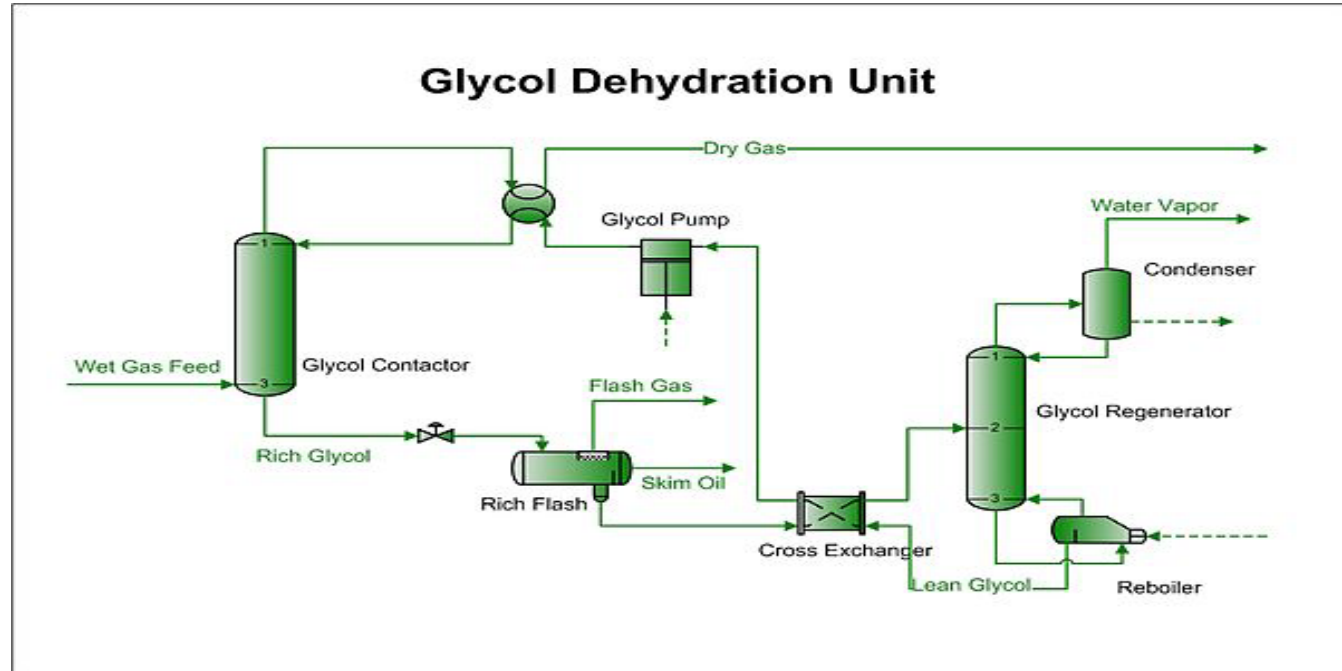
Solubility of Elemental Hg in Glycols



Solubility of Elemental Hg in Amines



Hg found in real samples of Rich and Lean Glycol



Sample Description	T-Hg (ng/g, n=2)	SD (n=2)	Spike Recovery
Lean Glycol Day 1	113.1	0.9	98%
Rich Glycol Day 1	286.8	3.3	102%
Lean Glycol Day 2	165.7	1.2	99%
Rich Glycol Day 2	53736.5	638.0	96%
Lean Glycol Day 3	18.1	4.6	103%
Rich Glycol Day 3	85052.2	70.6	96%



Conclusions

- Measuring the solubility of elemental Hg in using static and dynamic approaches is difficult because of the difficulty of handling of Hg saturated solutions above ambient conditions
- Elemental Hg is easily oxidized even in pure solvents. This has to be avoided and measured because oxidized Hg is more soluble than elemental Hg.
- The most reliable method to measure the solubility of elemental Hg is to establish a relationship between temperature and the Henry's law dimensionless constant. This avoid the use of saturated solutions of Hg and oxidation can be controlled by use of reductants and short experiment times
- The approach offers a low and calculable expanded uncertainties
- Elemental Hg solubilities were measured for water, glycols, methanol and amines at various temperatures and the data generated was compared to the data in the literature
- A classic distillation apparatus showed the fate of elemental Hg during the regeneration process. Elemental Hg was stripped from the solvent and remained in the gas phase
- Real samples may contain oxidized Hg and other species of Hg which behave quite differently to elemental Hg remaining in solvent and accumulating in solvent and associated equipment.

