EMPIR-19NRM03 SI-Hg

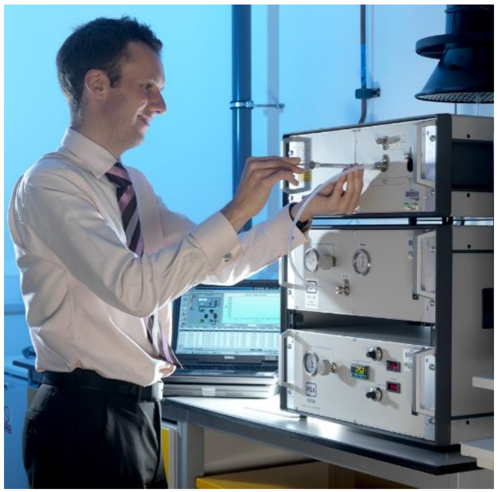
Development of low-level elemental and oxidized mercury calibrators for atmospheric mercury measurements

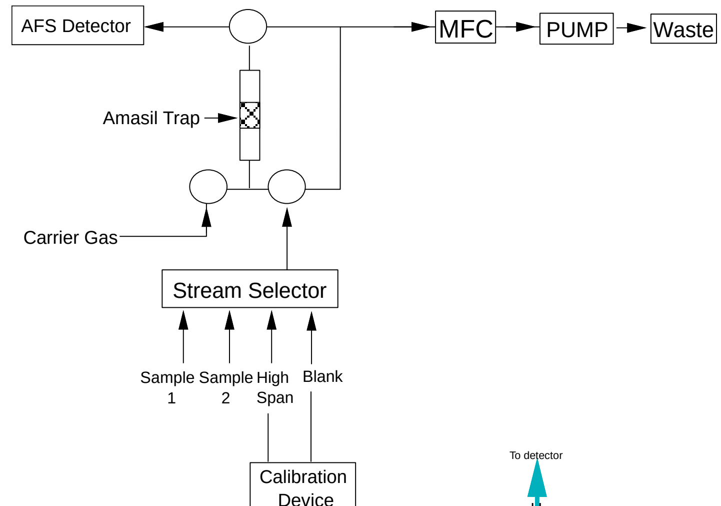
Warren Corns

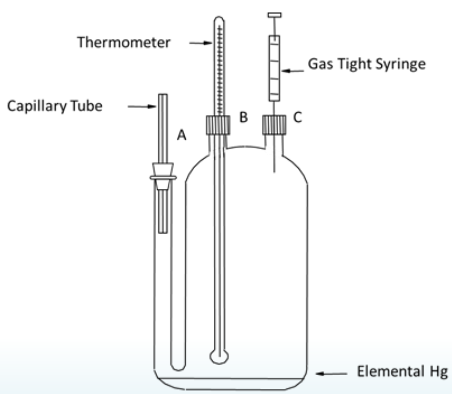
P S Analytical UK Office: Arthur House, Crayfields Industrial Estate, Main Road, Orpington, Kent, BR5 3HP, UK

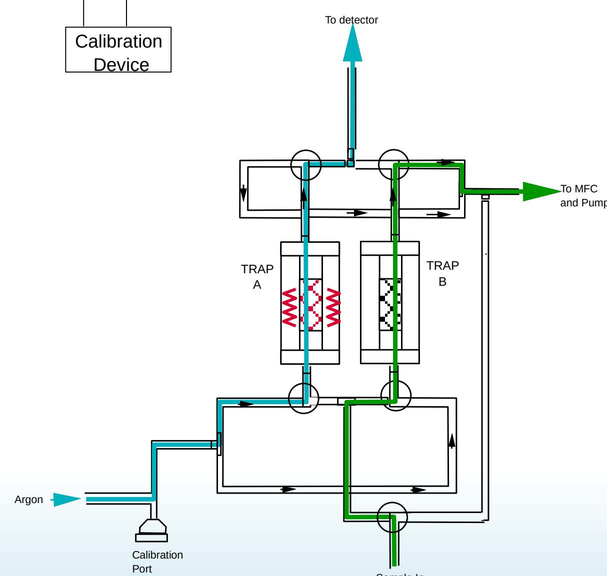
PSA

PSA Hg in Ambient Air System for Remote and Online measurements

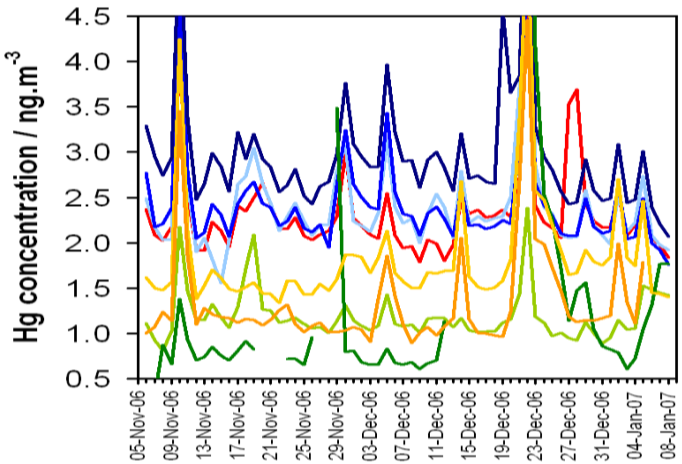


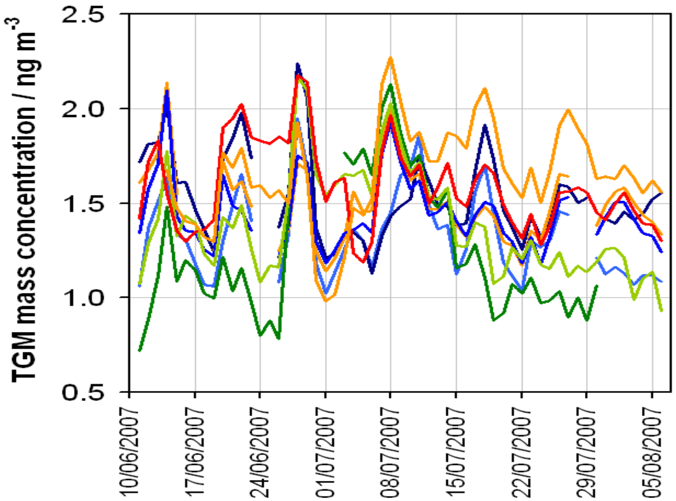






Comparison of 4 different Hg analyser systems operated in parallel. CEN TC 264 WG25. Field Trials for EN 15852 TGM in Ambient Air 2006-2007. Calibration using Bell Jar





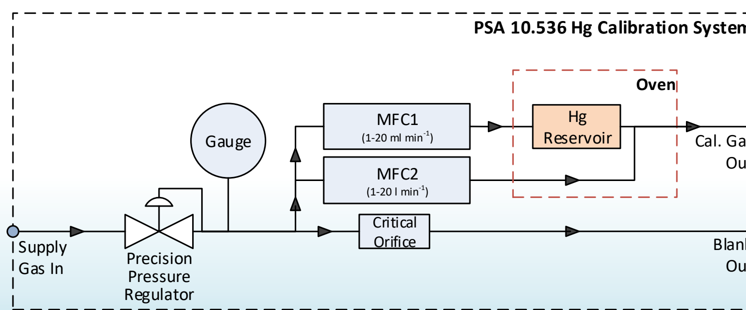
All instruments trended well, with low random uncertainty but the data showed an unacceptable systematic bias caused by the calibration and sampling period. Instruments using small sample volumes, short collection times and higher calibration range gave a higher uncertainty and less accurate results.

The field test was repeated several months later at a different site later with a reduced calibration range and longer sampling periods. All instruments trended well with improved agreement.

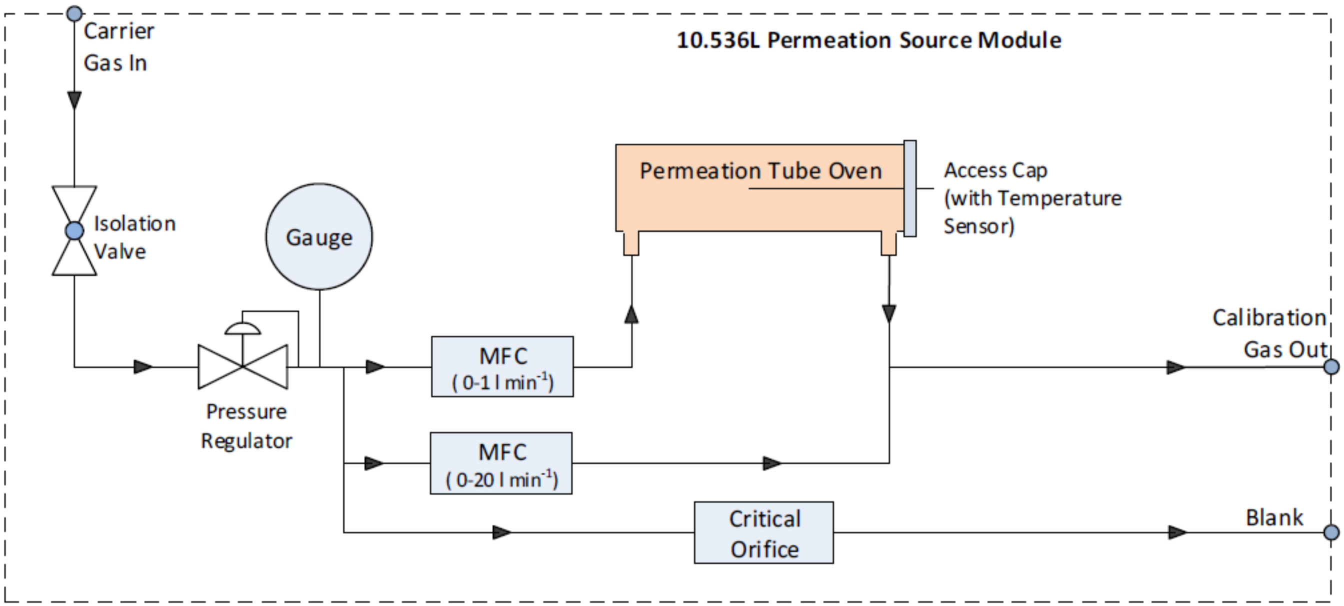
PSA

PSA Elemental Hg Generators

- **PSA 10.532** – Fixed Output Generator – Critical Orifice. Saturated source Temp control 30-60^{o}C - Customer defines output between 1-300µg/m^3
- **PSA 10.536** – Variable Output Generator using 2 thermal mass flow-controllers. Saturated source, Reservoir 1-20ml/min, Dilution 1-20L/min. Temp control 30-60^{o}C, Output range 2-6000µg/m^3
- **PSA 10.536H**-Variable Output Generator using 2 thermal mass flow-controllers. Saturated Source, Reservoir 1-30ml/min, Dilution 1-20L/min. Temp control 30-100^{o}C, Output range 2-90,000µg/m3
- **PSA 10.536L**-Variable Output Generator using 2 thermal mass flow-controllers. Permeation Tube ~0.10ng/min@50^{o}C. Perm tube Oven 0-1 l/min, Dilution 1-20L/min. Temp control 40-60^{o}C- Output range at 50^{o}C 3-60ng/m^3
- ***PSA 10.536Z*** - Variable Output Generator using 2 thermal mass flow controllers. Saturated source. Reservoir 0.1-2.0ml/min, Dil 1-20L/min. Oven control -20-50^{o}C- Output range at -20^{o}C 1-470ng/m^3 . Output range 50^{o}C 0.7-280-µg/m3



10.536L Elemental Hg Permeation System



- Permeation Rate – Not gravimetrically certified as this takes too long
- Permeation Rate is established by measuring output range against Bell Jar calibration using amalgamation – AFS at different conditions. Oven flow is fixed at 0.5L/min.
- Temp sensor position is on perm tube in flow of gas.
- Expanded Uncertainty calculated on accuracy of flow and temperature of components and measured permeation rate variance

Example Permeation Rate ng/min Calculation

		Total Dilution rate L/min			Blank sub Dil. Rates			Average Perm Rate ±		% RSD
Perm Temp	zero	15.5	10.5	5.5	15.5	10.5	5.5			
50°C test_1	0.193	7.636	10.992	20.077	7.443	10.799	19.884			
18/01/2023				Perm rate:	**0.1154**	**0.1134**	**0.1094**	0.113	0.00306	2.72
Perm Temp	zero	15.5	10.5	5.5	15.5	10.5	5.5			
50°C test_2	0.193	7.719	10.709	19.587	7.526	10.516	19.394			
19/01/2023				Perm rate:	**0.1167**	**0.1104**	**0.1067**	0.111	0.00504	4.53

Historical Permeation Rate Data (ng/min) Example at 60°C

10.536L S/N:	2020	2021	2022	2023	mean	SD	RSD %
13	0.2783	0.2700	0.2572	0.2621	0.2669	0.00924	3.46
14	0.1589	0.1756	0.1630	0.1705	0.1670	0.00748	4.48

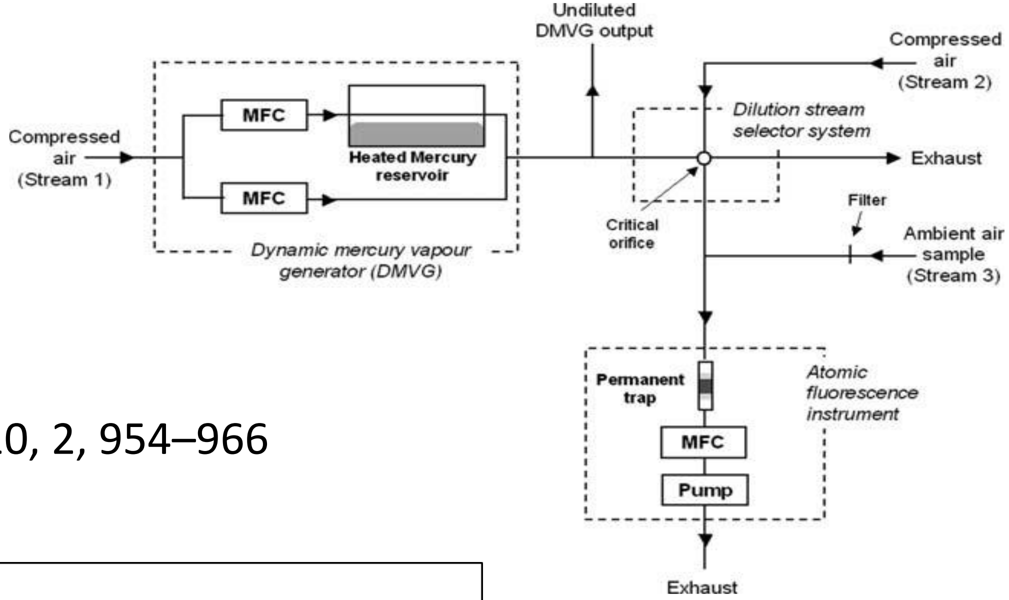
Permeation Tube Uncertainty Calculation

symbol	quantity	units	value	uncertainty	sensitivity coefficient	uncertainty/ µg m^{-3}	type	probability distribution	divisor	contribution to standard uncertainty	Significance check*
PR_{Hg}	permeation rate (Hg)	ng min^{-1}	0.12	0.007	0.095	0.001	B	rectangular	1.732	0.000	96.0%
v_1	MFC1 flow rate (carrier)	ml min^{-1}	500	44	0.000	0.000	B	rectangular	1.732	0.000	0.5%
v_2	MFC 2 flow rate (diluent)	ml min^{-1}	10000	120	0.000	0.000	B	rectangular	1.732	0.000	3.5%
c	concentration output	µg m^{-3}	0.011							0.000	100.0%
(equation 1)						expanded uncertainty (k=2)				0.001	
										7.02%	

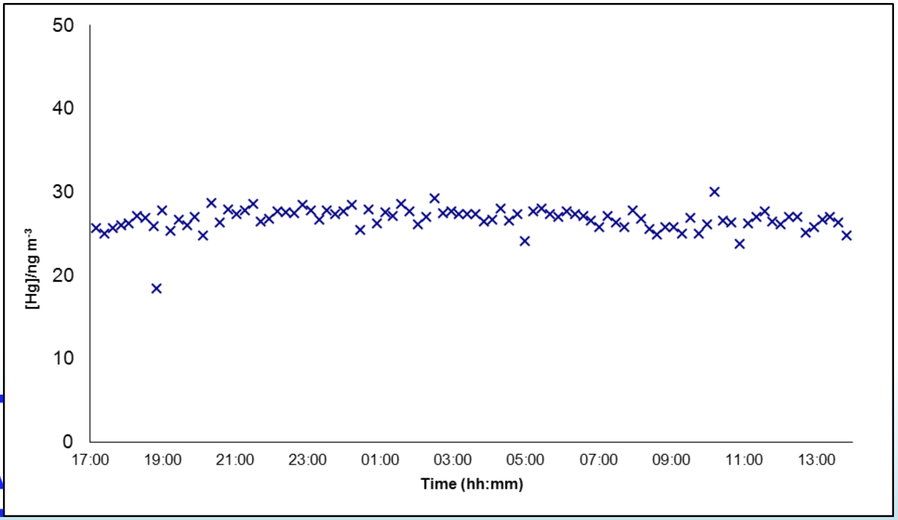
Notes:	
	expanded uncertainty (k=2) = 0.4% on MFC certs. So 0.2% std uncertainty used.
	MFC certs also give "rated accuracy" 0.8% of reading + 0.2% of full scale
	* >5% is a significant contribution

$$c = 1000 \frac{PR}{\nu_{res} + \nu_{dil}}$$

10.536 Generator with 50.119 Critical Orifice Diluter 200:1

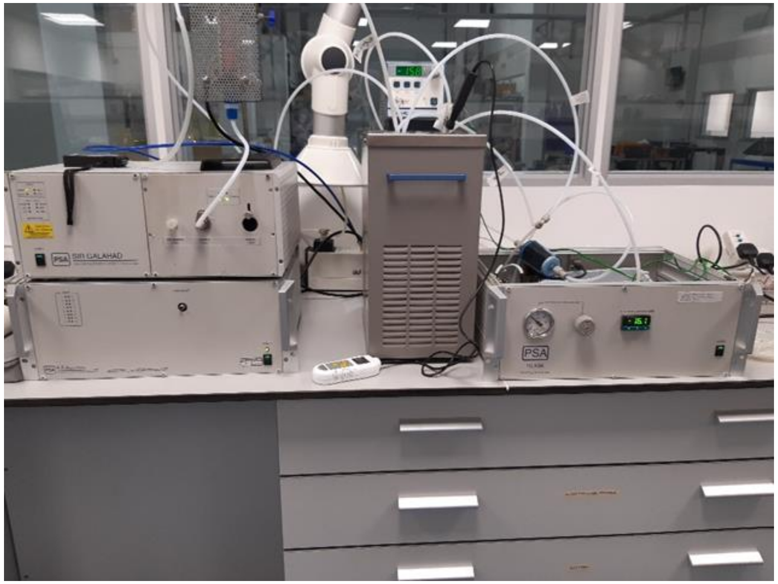


Anal. Methods, 2010, 2, 954–966
Brown et al.



5270 ng/m3 undiluted
26.4 ng/m3 diluted

Low temperature generator Prototype

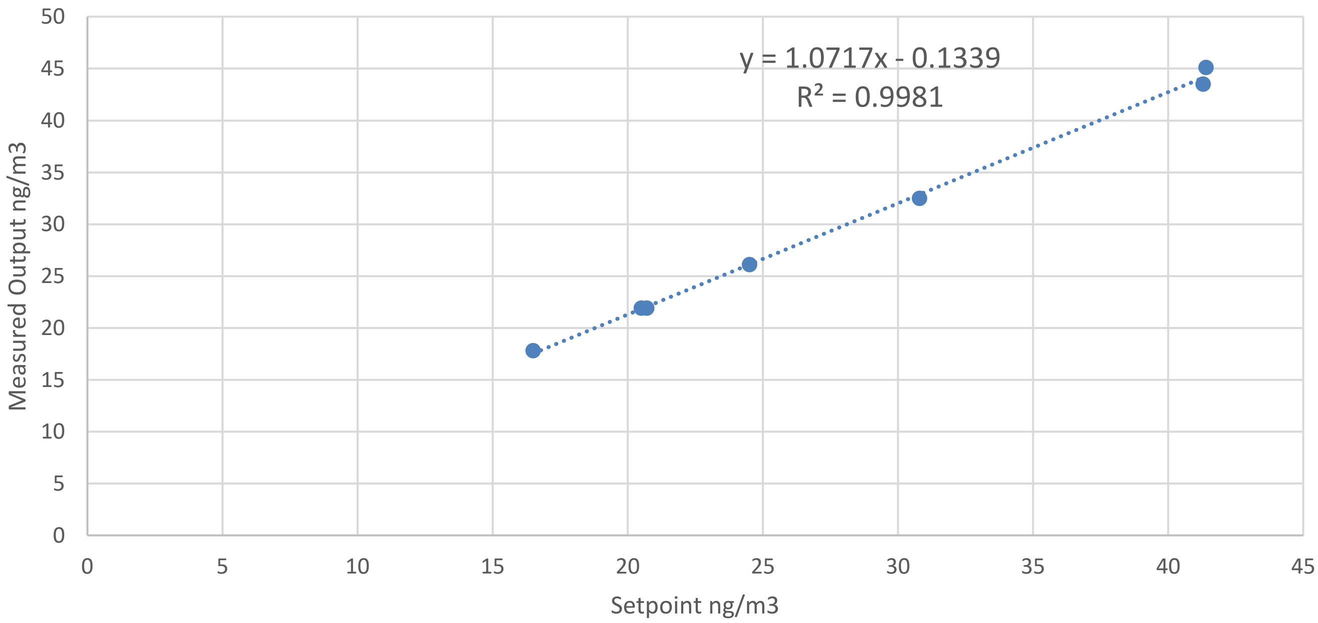


PSA 10.536Z - Variable Output Generator using 2 thermal mass flow controllers. Saturated source. Reservoir 0.1-2.0ml/min, Dilution 1-20L/min. Nominal Output range at -20^{o}C 1-470ng/m^3 .

Theoretical Output based on Dumarey equation but how good is the relationship originally developed for 15 – 25 °C extrapolated for sub zero temperatures?

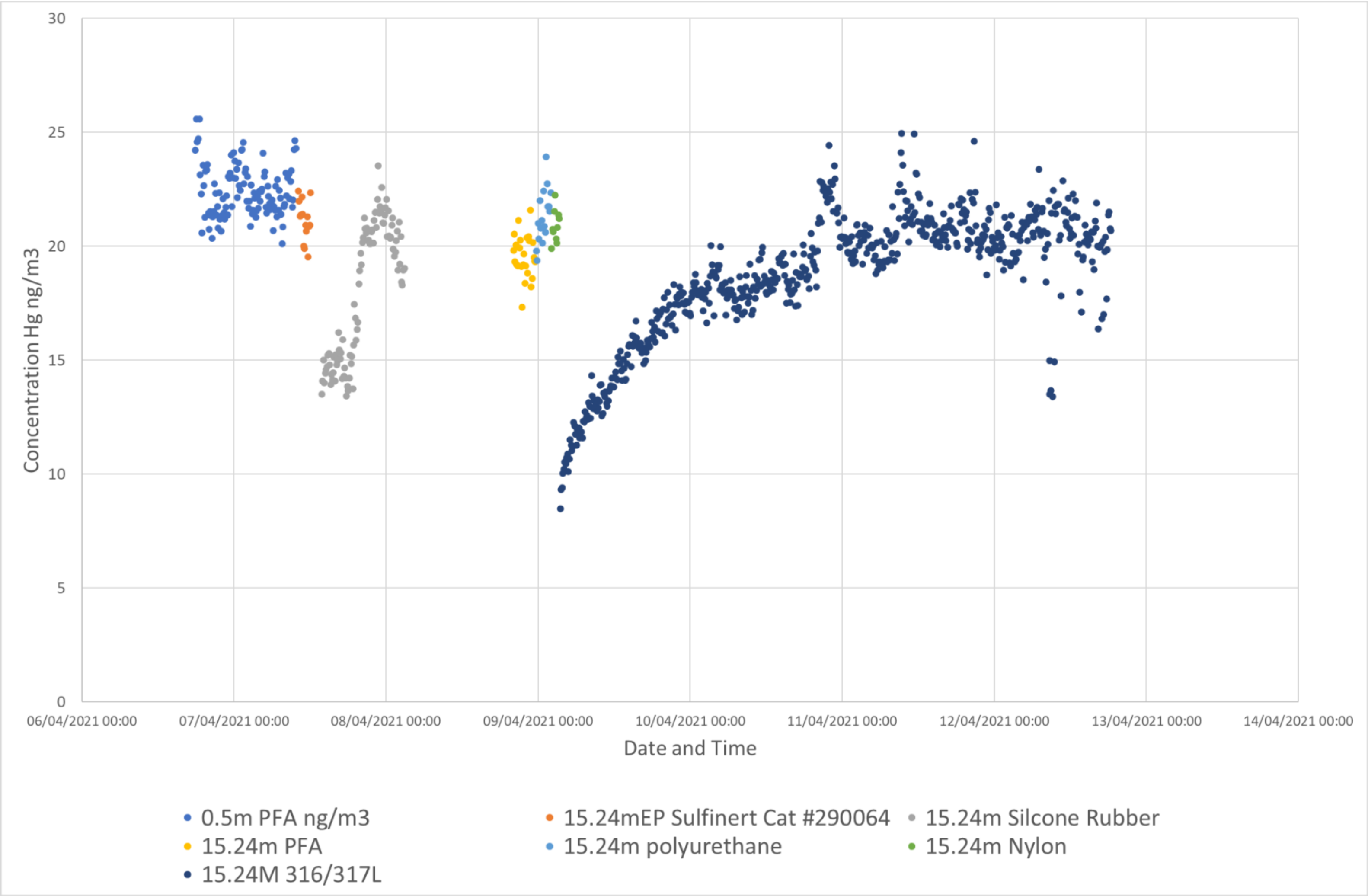
PSA

Measured output against setpoint with Bell Jar Calibration



Res Flow (ml/min)	Dil Flow (L/min)	Res Temp (°C)	Back Press (mbar)	Expected (ng/m3)	Uncertainty (ng/m3)	Measured (ng/m3)	SD (ng/m3)	Recovery (%)
1.0	15.0	-17.54	1032	20.5	0.45	21.9	3.4	106.83
2.0	15.0	-17.49	1032	41.3	0.83	43.5	1.2	105.33
1.5	15.0	-17.54	1036	30.8	0.6	32.5	0.6	105.52
1.2	15.0	-17.54	1037	24.5	0.26	26.1	2.6	106.53
1.0	15.0	-17.44	1037	20.7	0.45	21.9	0.2	105.80
0.8	15.0	-17.42	1037	16.5	0.38	17.8	0.2	107.88
1.0	15.0	-17.42	1037	41.4	0.45	45.1	0.4	108.94

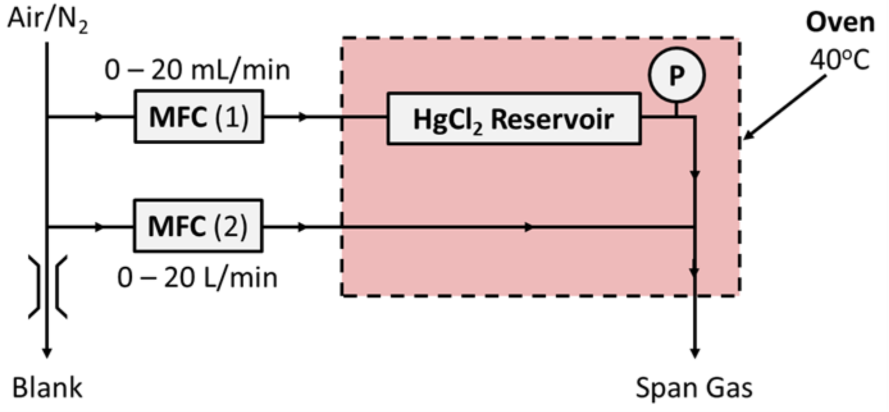
Testing different Tube materials at 0.5 L/min at 21.4 ng/m3



PSA

PSA oxidized Hg Generators, $HgCl_2$ reservoir

- **PSA 10.532ox** – Fixed Output Generator – Critical Orifice. Saturated source Temp control 30-60^{o}C - Customer defines output between 1-300ug/m3
- **PSA 10.536ox** – Variable Output Generator using 2 thermal mass flow-controllers. Saturated source, Reservoir 1-20ml/min, Dilution 1-20L/min. Temp control 30-60^{o}C, Output range 1-900µg/m3
- ***PSA 10.536Z*** - Variable Output Generator using 2 thermal mass flow controllers. Saturated source. Reservoir 0.2-2.0ml/min, Dilution 1-20L/min. Output range at -20^{o}C 0.1-1.0ng/m^3



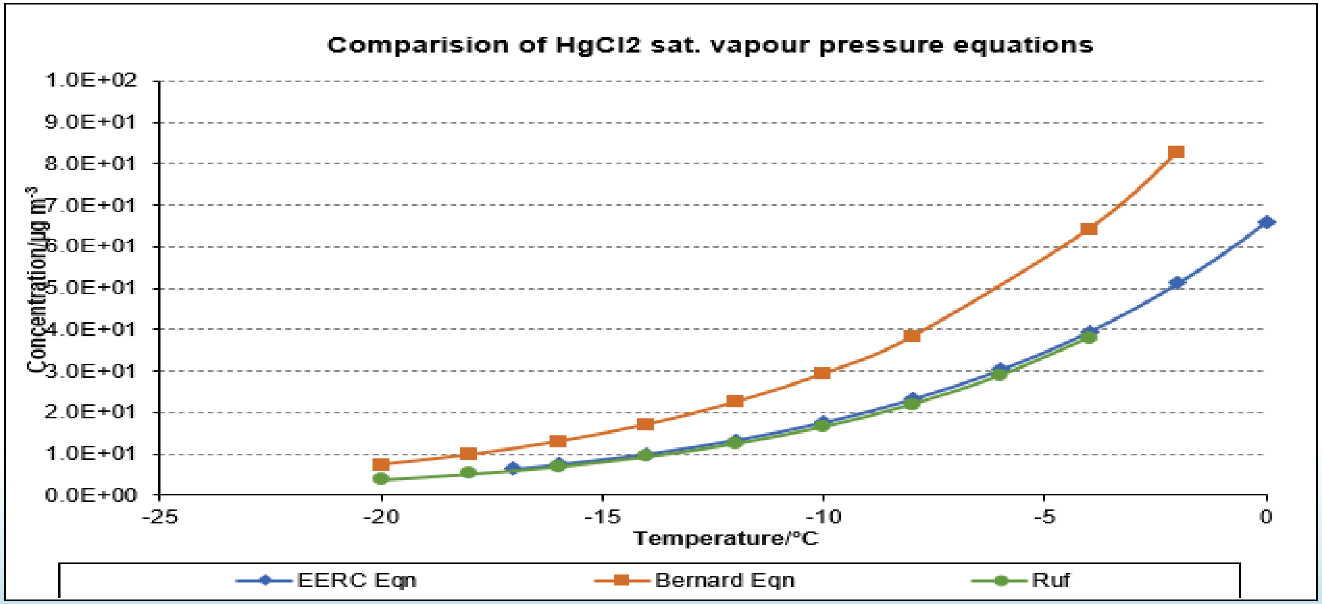
PSA

$HgCl_2$ Vapour Pressure

L. Bernard et al. J Phys, III France, 1997, 7, 311

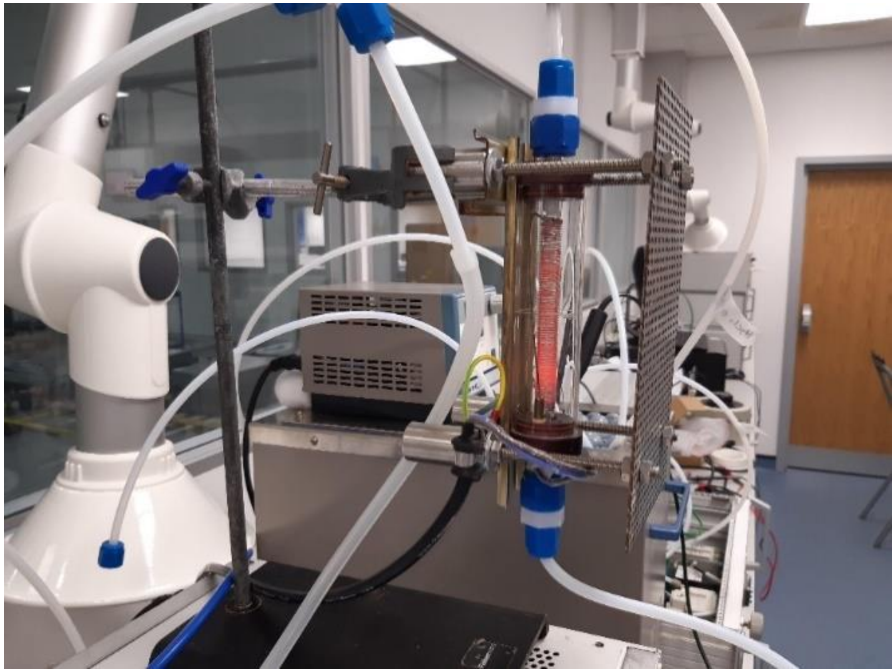
Saturator Conditions:					
Temp., C	**-17.8**		**Dilution Flow, slpm**	**18**	
Pbar, in Hg	**30.74**				
dp, in H2O	**0**		**Diluted Output Concentration, ng/l @ ref. Condition:**		**0.0009 Hg(II) as HgCl2**
Flow, smlpm	**2**				
Ref. Temp, C	**20**		Uncorrected output concentration		0.0011
sat. flow, amlpm	1.69734			Ratio =	0.84867
sat. conc., ng/ml	9.98E-03				
Saturator Output, ng/min:		**0.016945**			

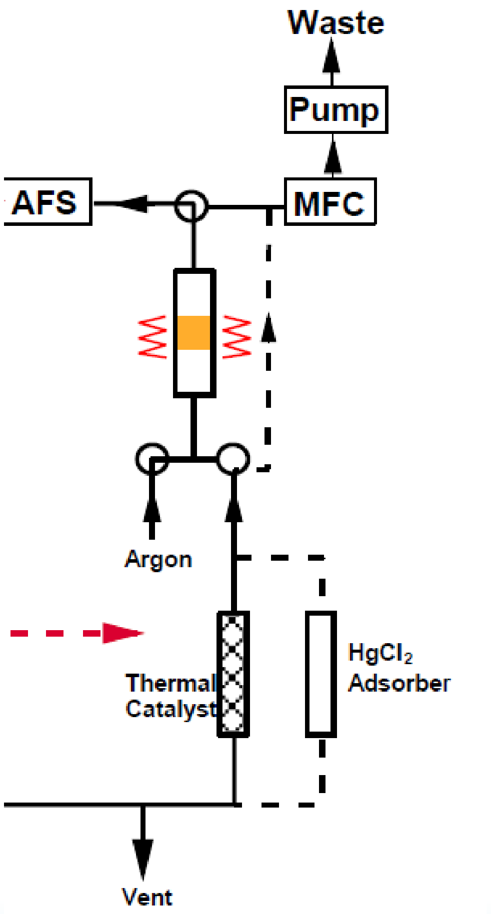
amlpm = actual milliliters per minute
smlpm = milliliters per minute at standard conditions (1 atm, 20 deg. C)



PSA

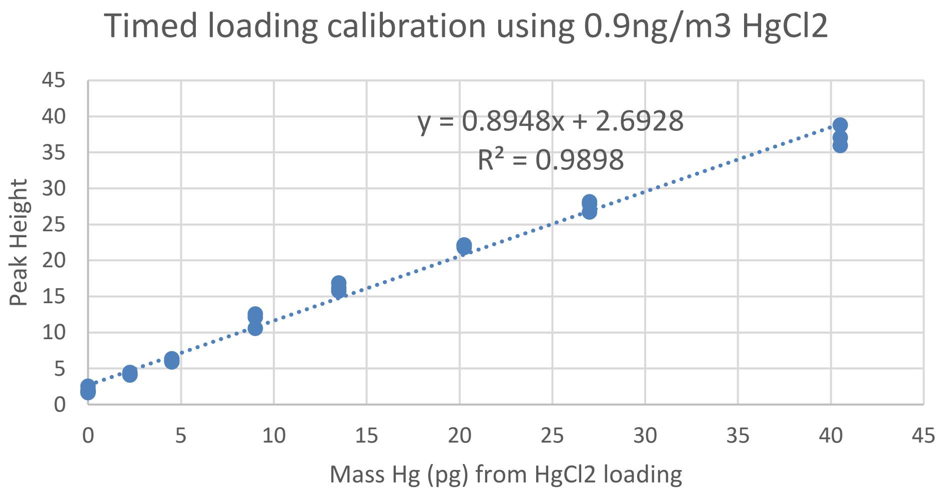
Thermal Conversion with Sir Galahad





PSA

Comparison Data for low level model Z Generators – Agreement is within 4% 100% Oxidized Hg as Zero response when thermal convertor bypassed

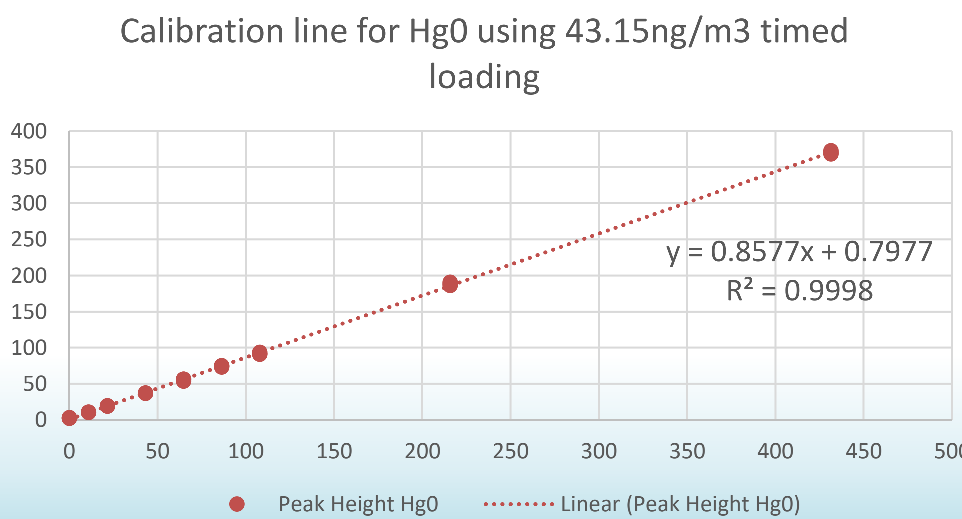


Loading based on 0.5L/min pg 0.9 ng/m3 for 0, 5, 10, 20. 30, 45 and 90 min

Concentration equivalent for 10L sample- 0.225ng/m3 to 4.0ng/m3 oxidized Hg

Loading based on 0.25 L/min of 43.15 ng/m3 for 0, 1, 2, 4, 6, 8, 10, 20 and 40 min.

Concentration equivalent for 10L sample- 1ng/m3 to 43ng/m3 oxidized Hg



Questions?