Accurate determination of trace elements emissions using AFS

Dr Warren Corns

Coal Research Forum 2016

PSA

PSA Experience in the Trace Element Emissions

- Numerous Hg in stack gas analysers worldwide have been sold since 1996 and these have been used to test in excess of 250 power plants worldwide. These are installed on sites using various fuel types producing different stack gas compositions.
- Instrument locations include upstream and downstream of particulate removal devices (ESP, bag-houses), deNOx units, wet/dry scrubbers and flue gas.
- Typical applications include coal fired power stations, waste incinerators, cement kilns, coal gasification syngas, natural gas and crematorium. More than 90% of these installations use the Hg CEM for speciation measurements to establish the efficiency of control technology
- New developments include the use of 30B iodated carbon traps sorbent traps for Hg, As and Se measurements for stack gas
- Recent focus on Hg, As and Se in FGD wastewater using online and offline measurement systems

PSA

HgCEM Options

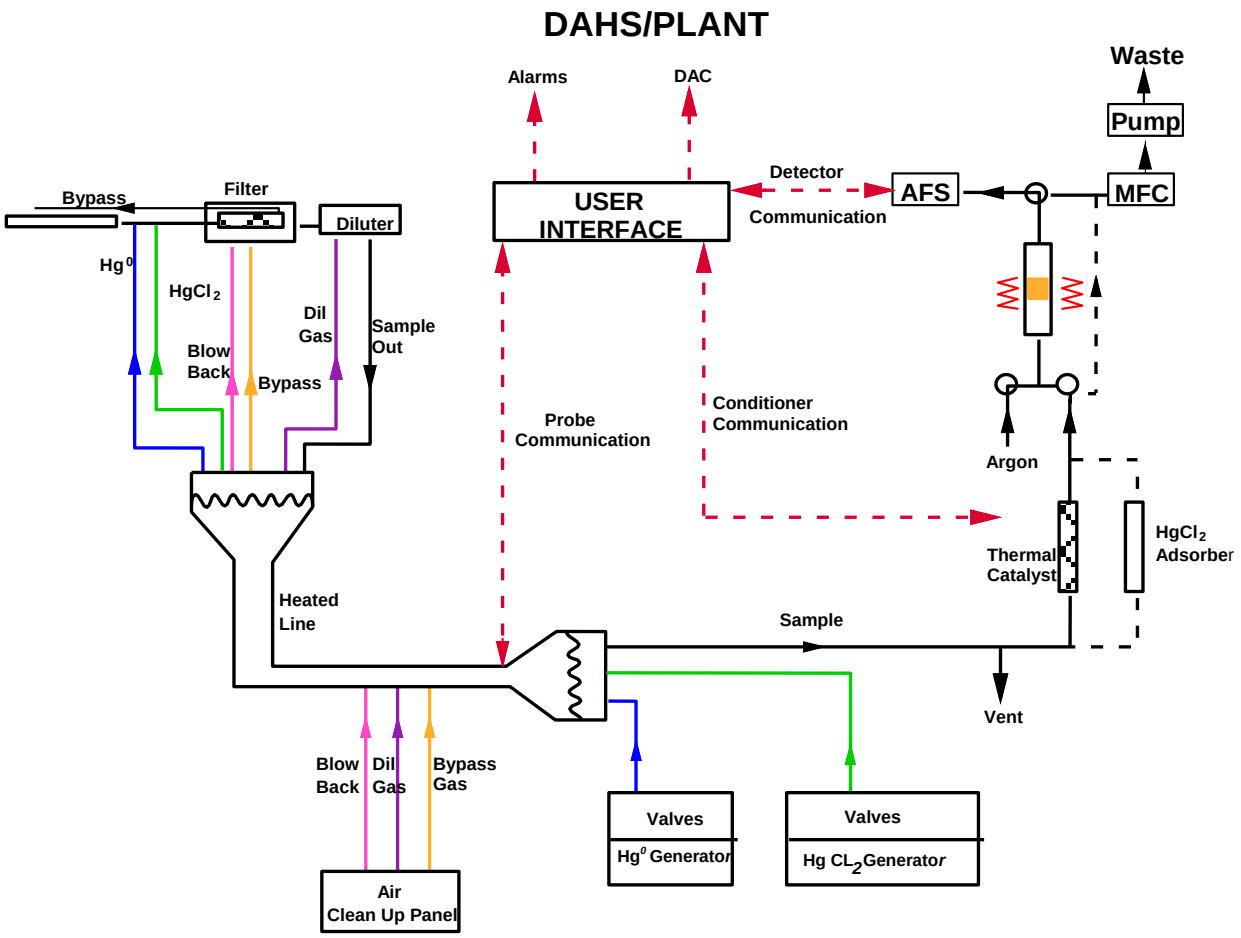
- Process Monitors to control and optimize performance of Hg Control Technology.
- Compliance Monitors for coal fired power stations, waste incinerators and crematorium
- Research Instruments to assist in the development of control technologies for bench-scale, pilot scale and field tests. Mass Balance Studies.
- Portable Stack Gas Monitoring Systems – IRM and short term testing

PSA

PSA 50.100 Hg CEM Stack Gas Typical Configuration

- Sample Conditioner
- Graphical User Interface
- Mercury Detector (Amalgamation – AFS)
- Controller and Alarm Module
- Stream Selector and Hg^0 and $HgCl_2$ Vapour Generator – calibration and span gases

Hg CEM Schematic

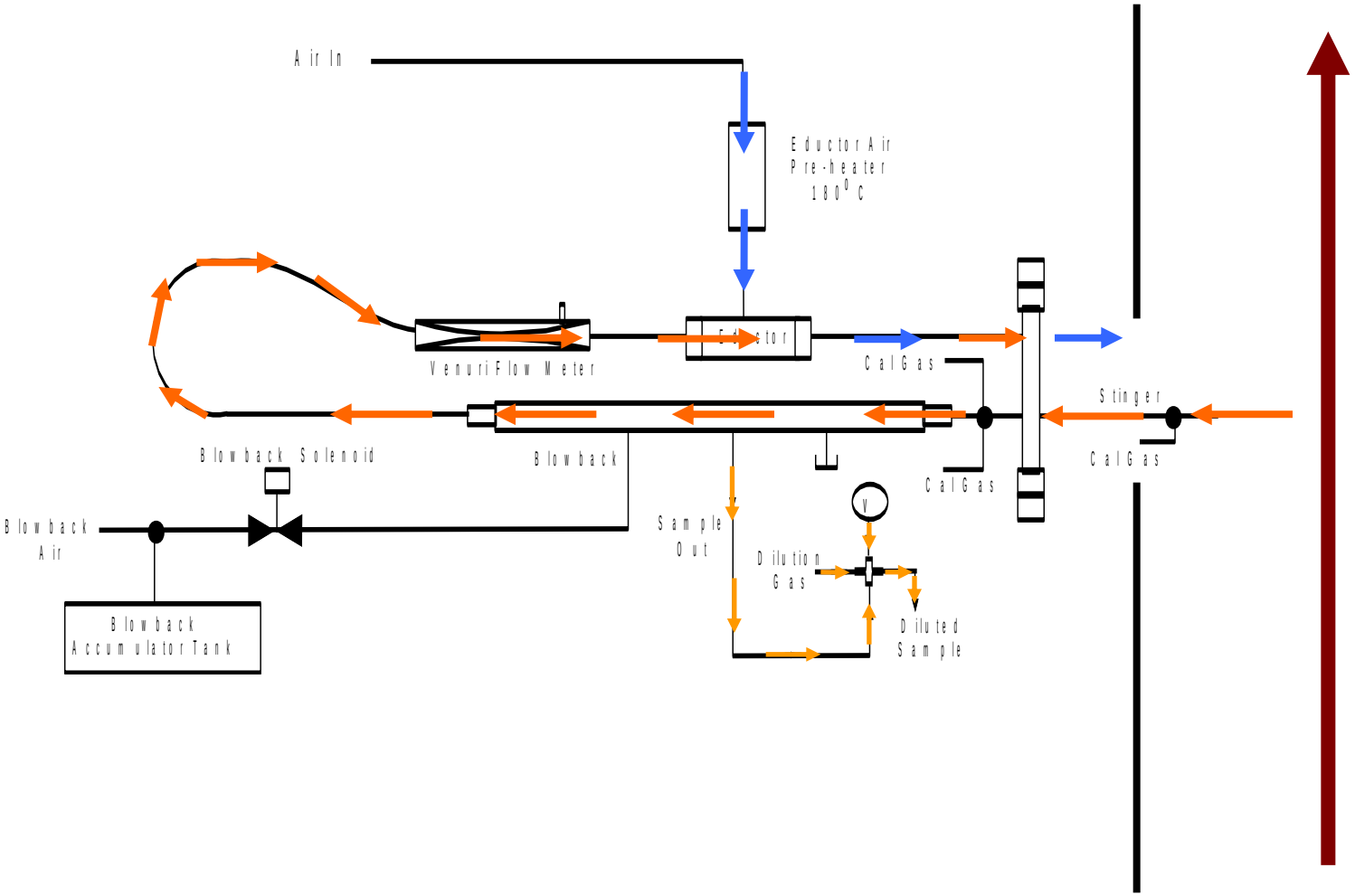


Probe Options

- Inertial Probe with dilution. Typically used on the inlet of ESP/Bag house where the ash content is very high. Can be used at all locations.
- Dilution probe with low flow bypass. Typically used for compliance monitoring.
- Speciation Dilution Probe for Pilot scale or IRM probe.

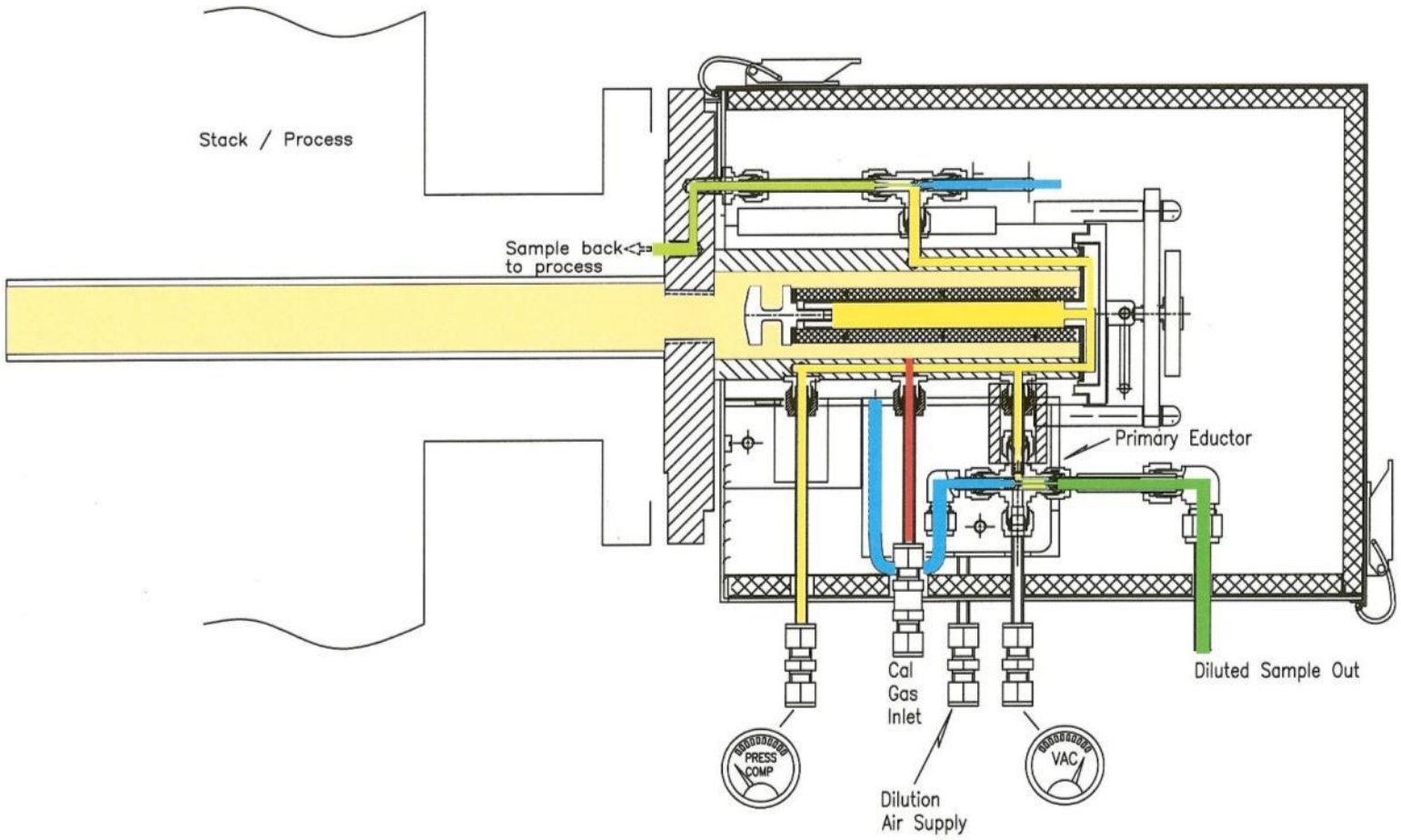
PSA

Inertial Probe Schematic



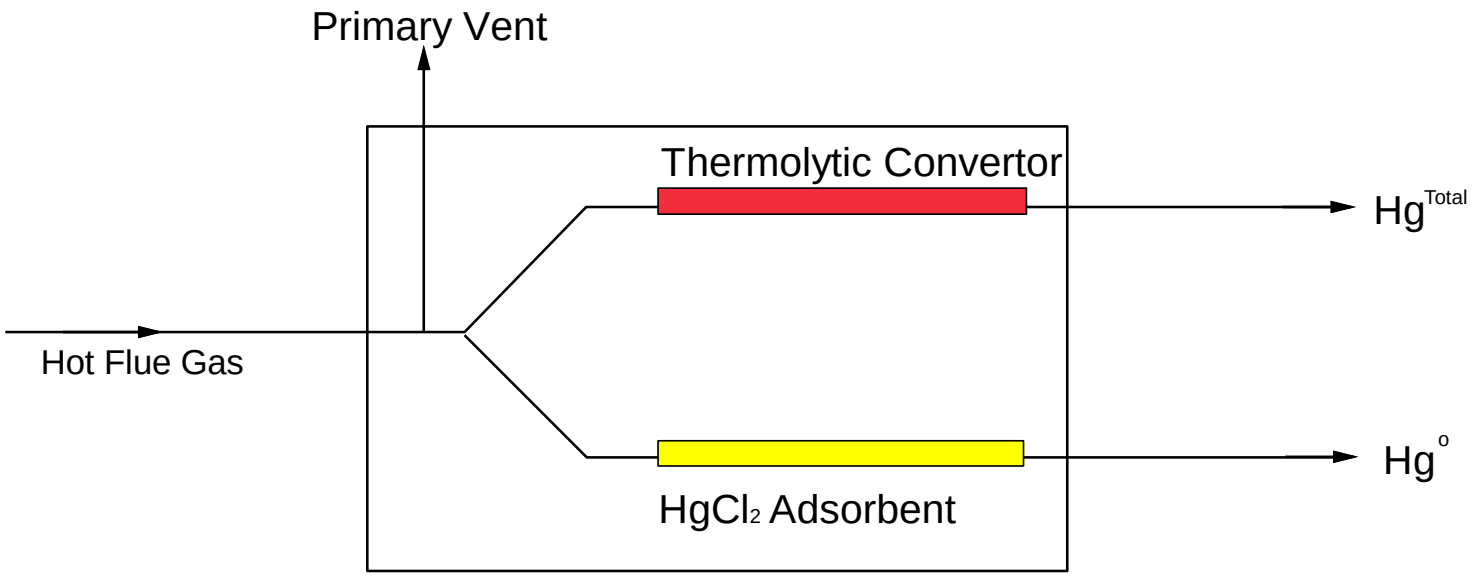
PSA

Dilution Probe Schematic



PSA

Schematic of Dry Based Speciation Module



PSA

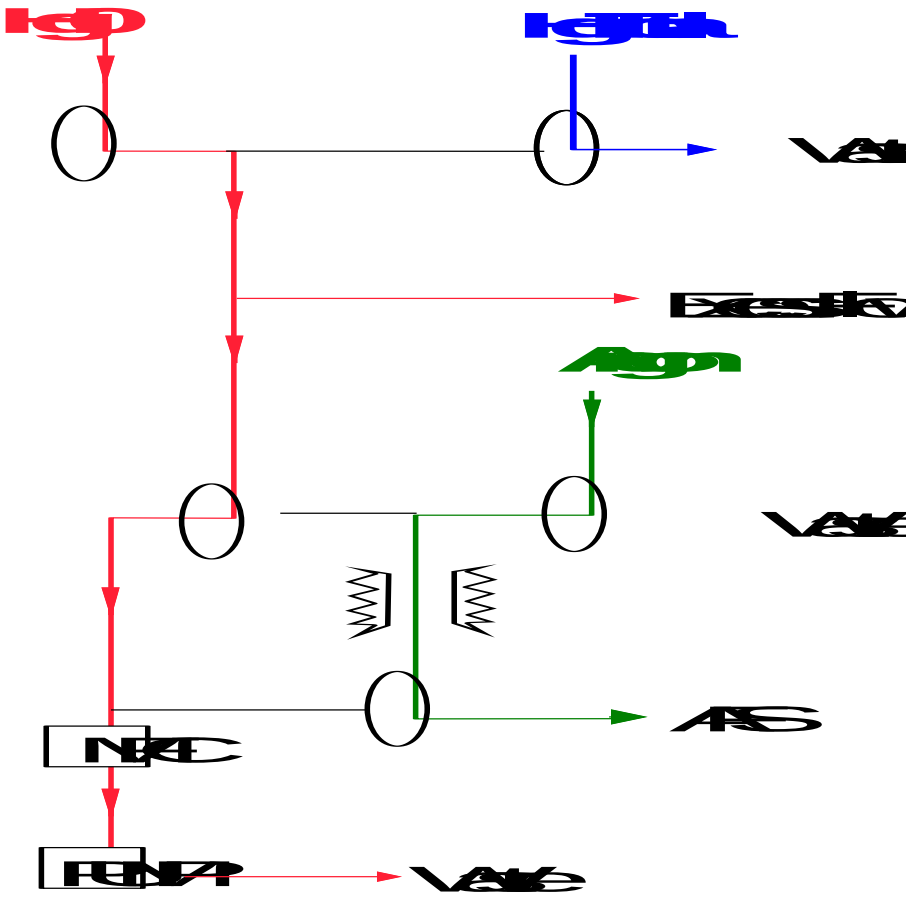
Hg in Gas - Sir Galahad II

Sir Galahad Analyser Specification

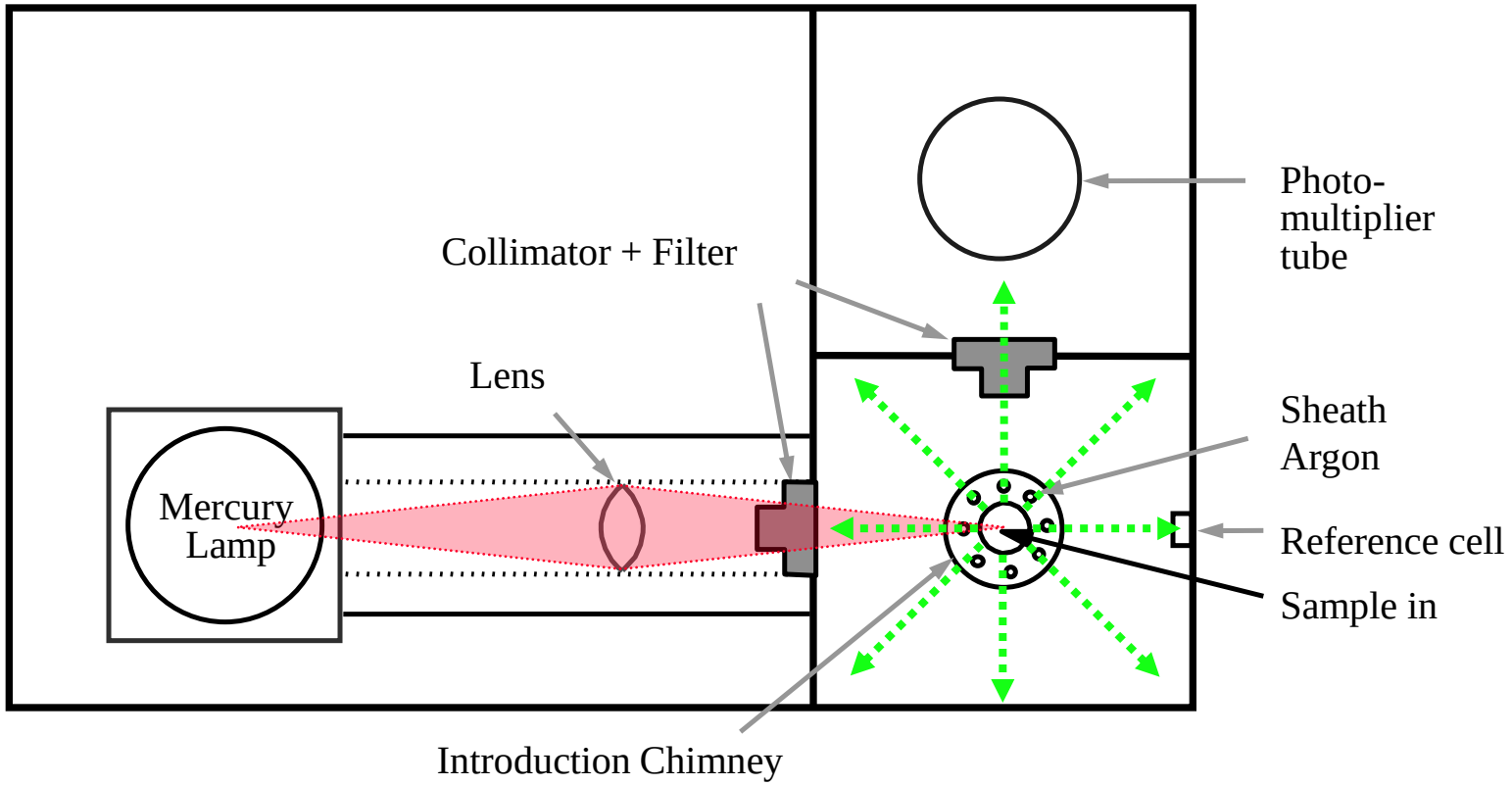
- Atomic Fluorescence Detection.
- 0.1 pg detection limit (0.1 ng m^{-3} for 1 litre sample volume).
- Easy to use.
- Excellent accuracy and precision.
- Excellent stability.
- Excellent selectivity and no interferences.
- Upper linear range to 5000 µg m^{-3}.
- Typical 3-4 minutes per sample.
- Single Amalgamation with continuous sampling for dilution systems.

PSA

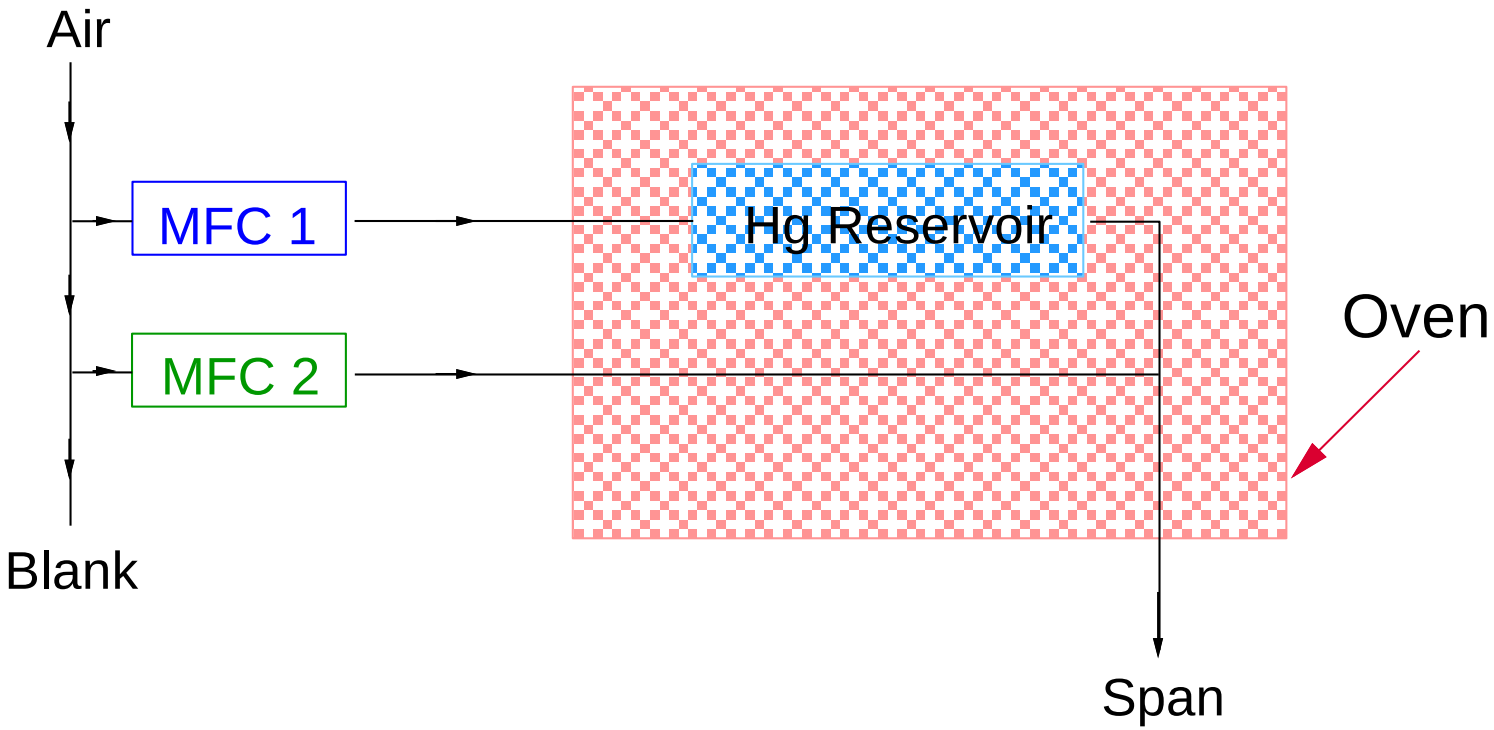
Schematic Diagram of Desorption Cycle



Schematic Diagram of AFS (plan view)

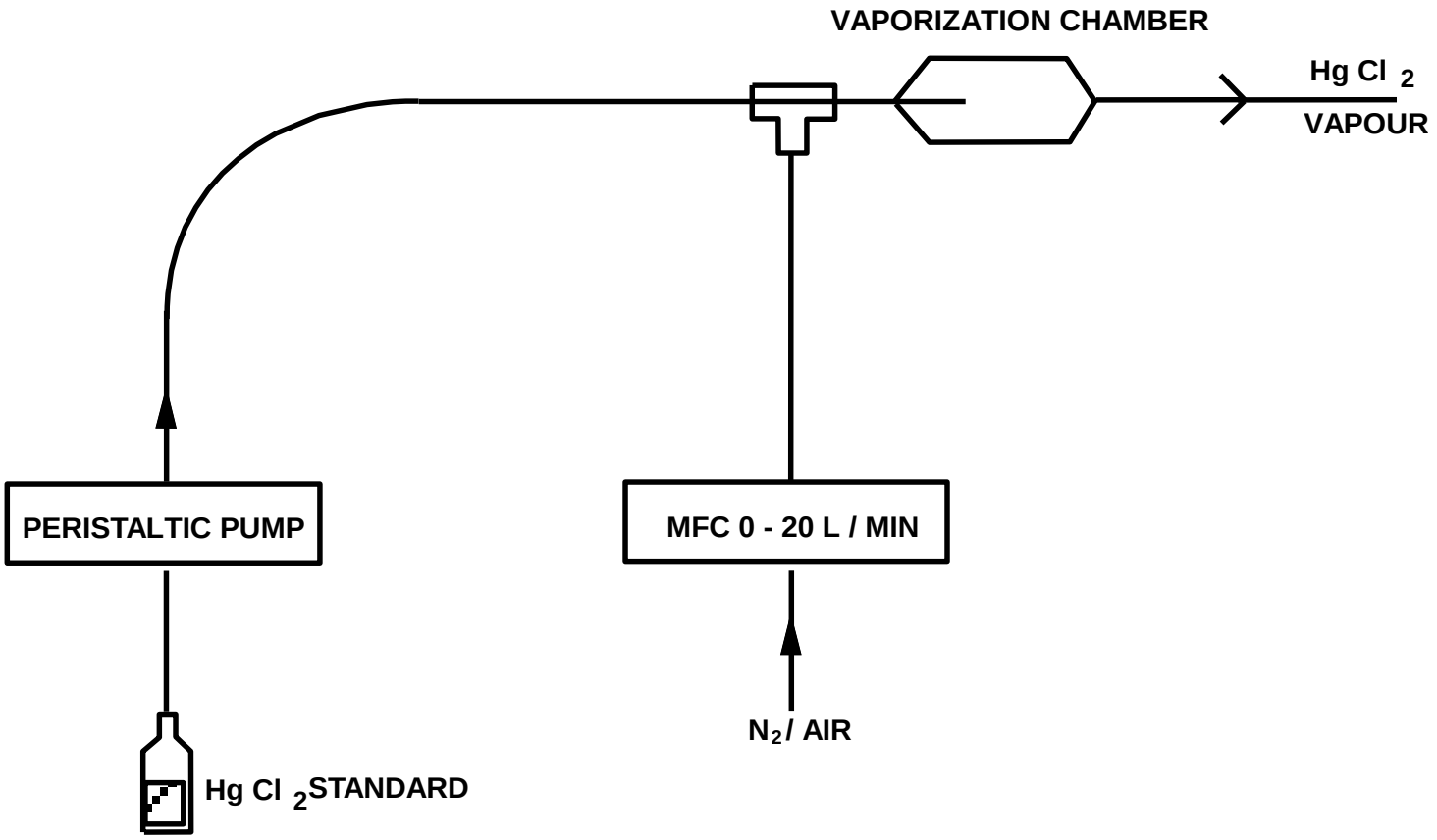


Cavkit Online Calibration System
Dilution of a Saturated Source



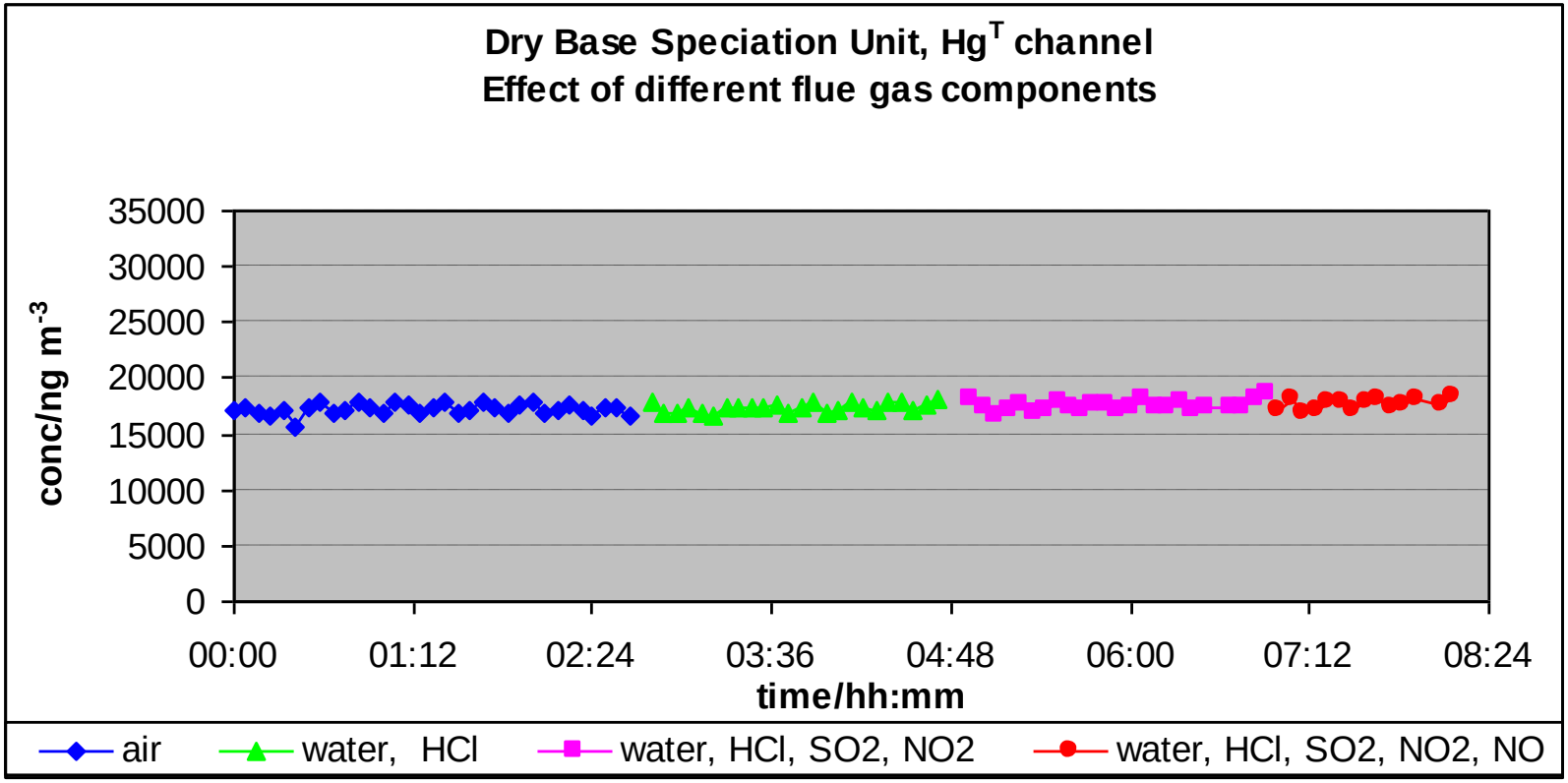
PSA

$HgCl_2$ Generator



PSA

Interference Study for Flue Gas. No Interferences.



(Concentrations: 5% water, 20 ppm HCl, 1400 ppm SO_2, 20 ppm NO_2, 250 ppm NO)

PSA

Validation tests Clean Air Mercury Rule (CAMR PS12A)

Test		Span Levels*	Initial Certification	Routine Frequency
Linearity Check		L, M, H	✓	Quarterly
System Integrity	1-level	M or H	–	Weekly
	3-level	L, M, H	✓	–
Calibration Error	7-day	Z, H	✓	–
	daily	Z, H	–	Daily
Cycle Time		Z, H	✓	–
RATA		–	✓	annually

*uses elemental mercury, oxidised mercury, uses either

Span levels (% of span): Z = 0-20 L=20-30 M=50-60 H=80-100

PSA

7 Day Calibration Error Test "PASS"

Day	Zero Span (0.00)			High Span (10.07)		
	/µg m^{-3}	|% Span|		/µg m^{-3}	|% Span|	
1	0.02	0.2	Pass	10.22	1.5	Pass
2	-0.02	0.2	Pass	10.40	3.3	Pass
3	0.01	0.1	Pass	10.33	2.6	Pass
4	0.01	0.1	Pass	10.03	0.4	Pass
5	0.00	0.0	Pass	10.20	1.3	Pass
6	-0.03	0.3	Pass	10.01	0.6	Pass
7	-0.03	0.3	Pass	9.86	2.1	Pass

PSA

Linearity Check Test
"PASS"

Span Level	Expected Value /µg m^{-3}	Average Result /µg m^{-3}	|expected-average|	Pass/Fail
Low	2.42	2.75	0.33	**Pass**
Mid	5.14	5.31	0.17	**Pass**
High	**9.98**	**9.45**	**0.53**	**Pass**

PSA

System Integrity Test "PASS"

Span Level	Expected Value /µg m^{-3}	Average Result /µg m^{-3}	Cal. Error (% of span)	Pass/ Fail
Low	5.00	5.03	0.15	Pass
Mid	9.98	9.96	0.10	Pass
High	19.94	19.94	0.00	Pass

PSA

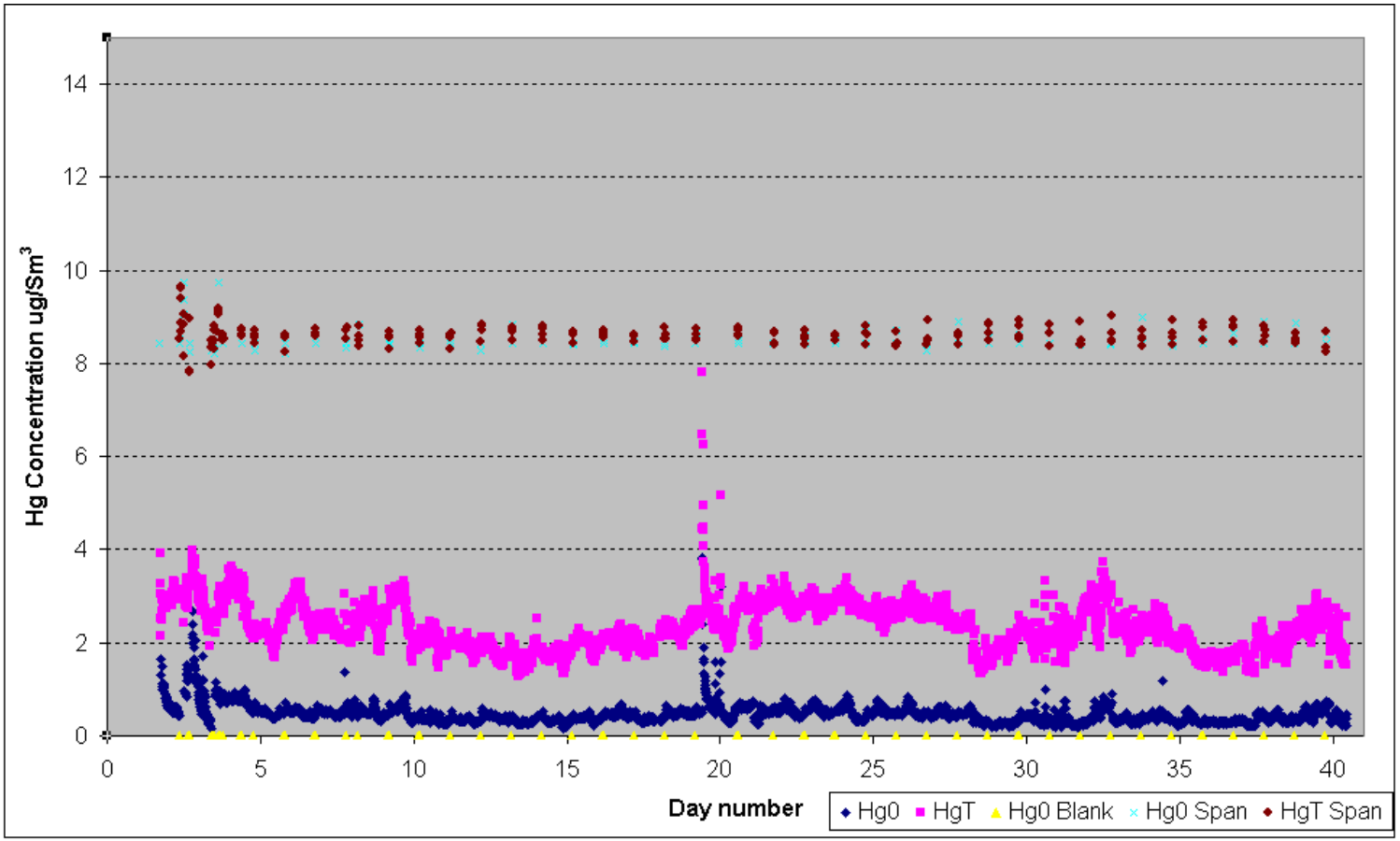
Relative Accuracy Test Audit "PASS"

CEM result /µg m^{-3}	OHM result (RM) /µg m^{-3}	Difference (d) /µg m^{-3}
17.36	17.29	0.07
12.46	12.02	0.44
20.93	19.28	1.65
19.90	18.04	1.86
8.39	8.73	-0.34
8.94	9.11	-0.17
7.82	7.38	0.45
7.03	6.49	0.55
7.97	6.83	1.14
7.98	6.90	1.08
9.22	8.25	0.97
7.64	8.14	-0.51
11.30	10.70	0.60

PSA

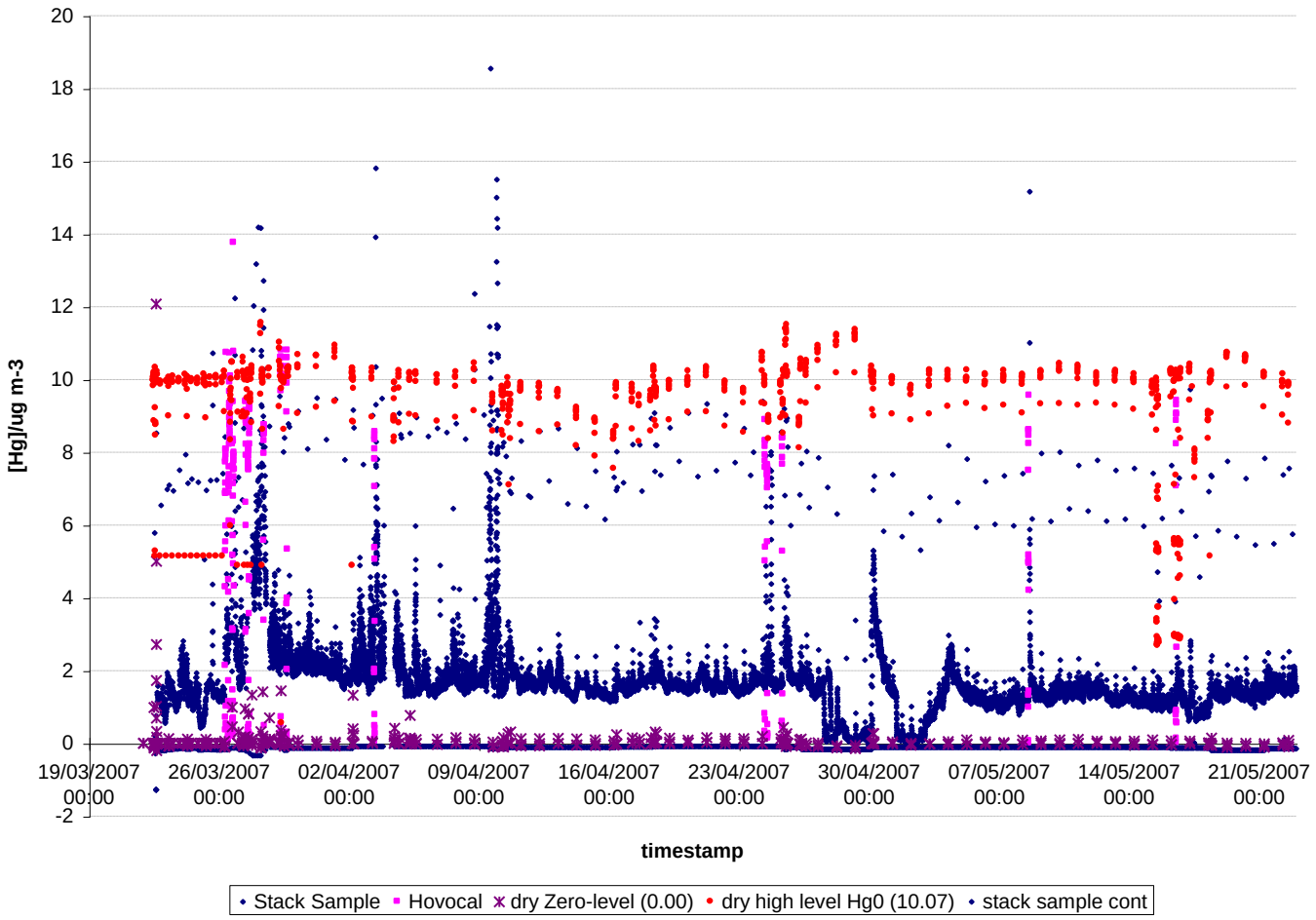
US Power Plant

Inertial dilution probe, speciation, daily zero and span checks, PS 12A 7 day drift check PASS



PSA

A Power station in Kentucky
Typical long term data – Wet scrubber site

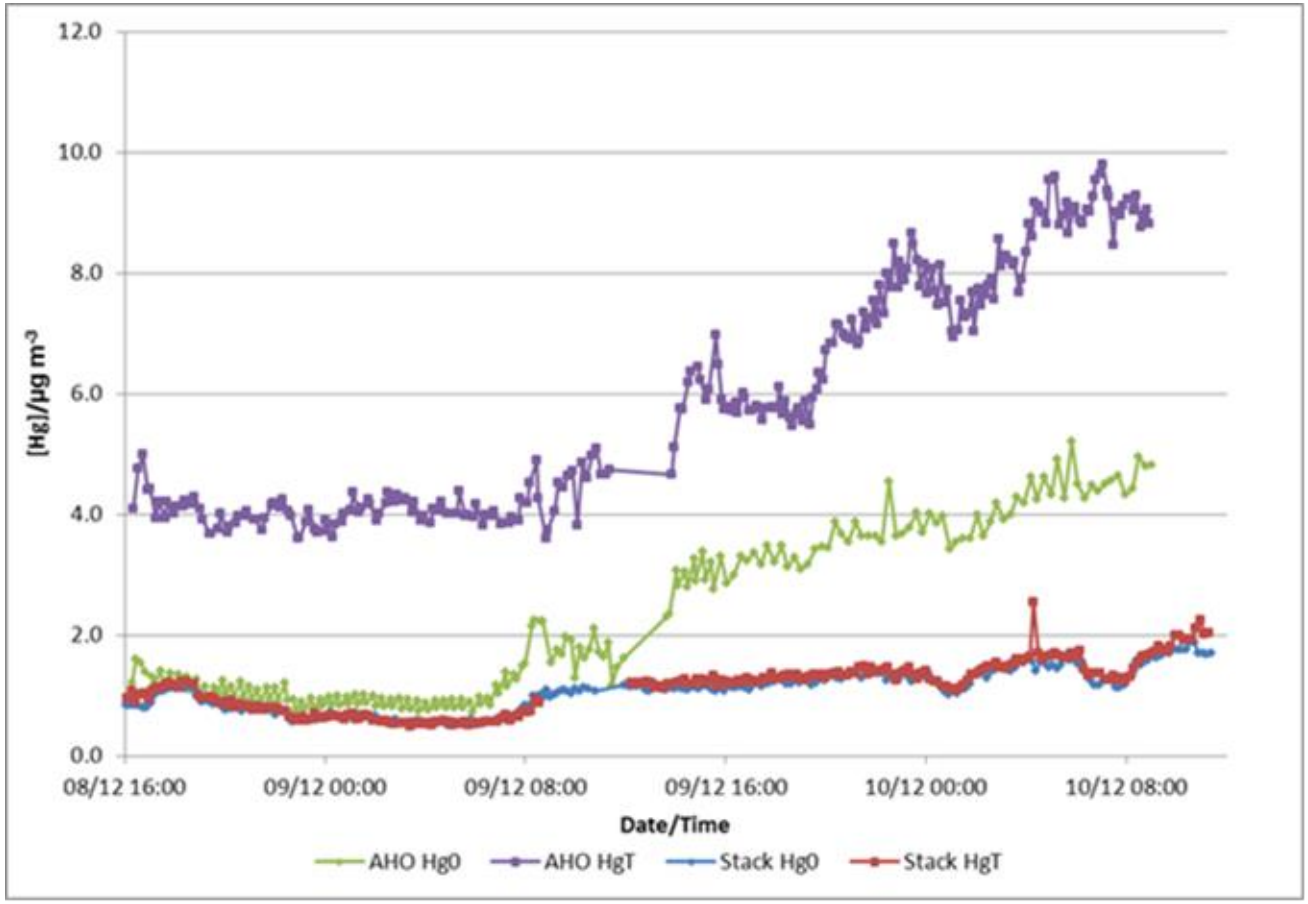


PSA

European Power Station

645 MW Unit with SCR, ESP and wet FGD

Firing bituminous coal with 15% biomass

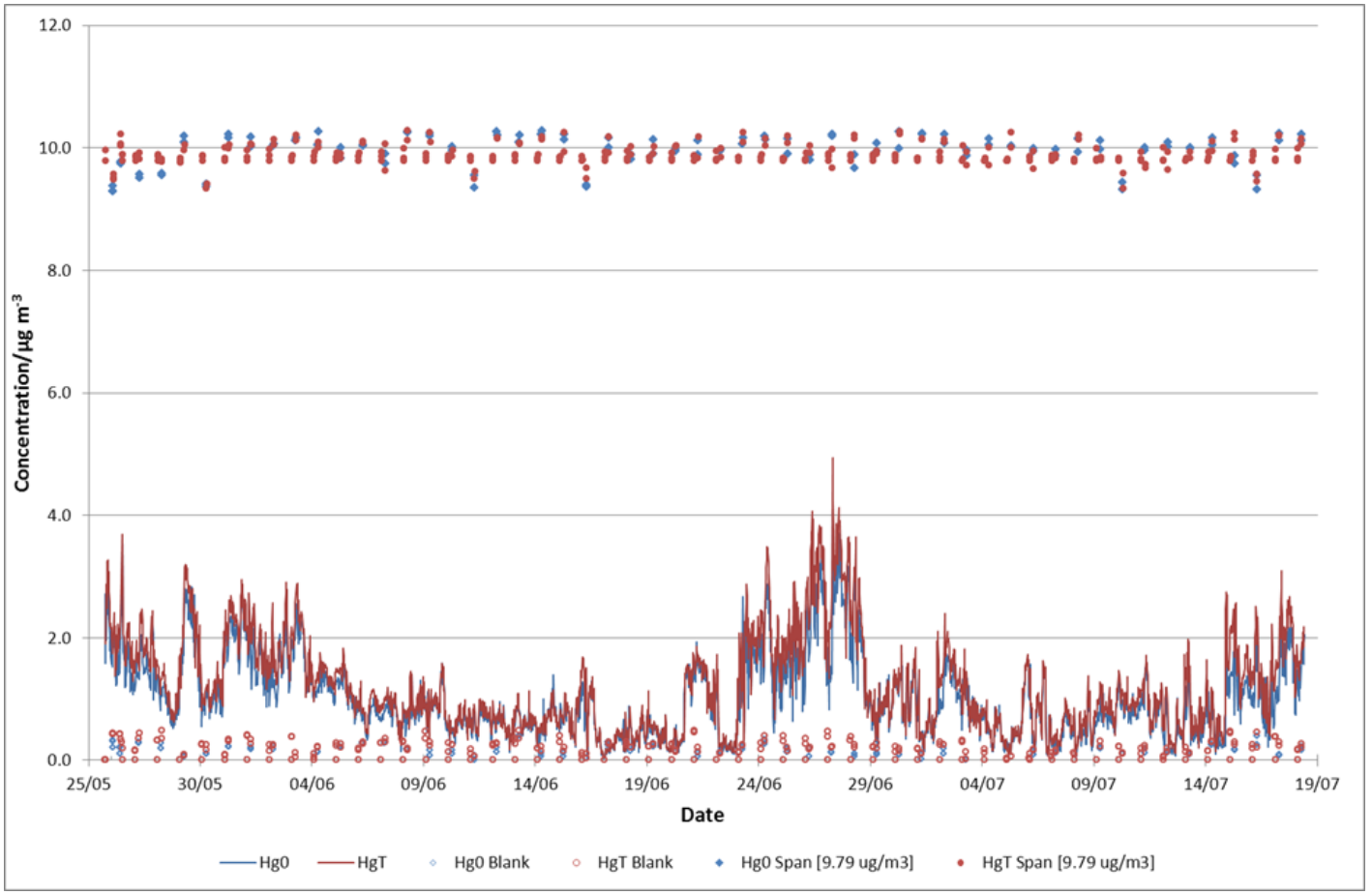


PSA

Power Station

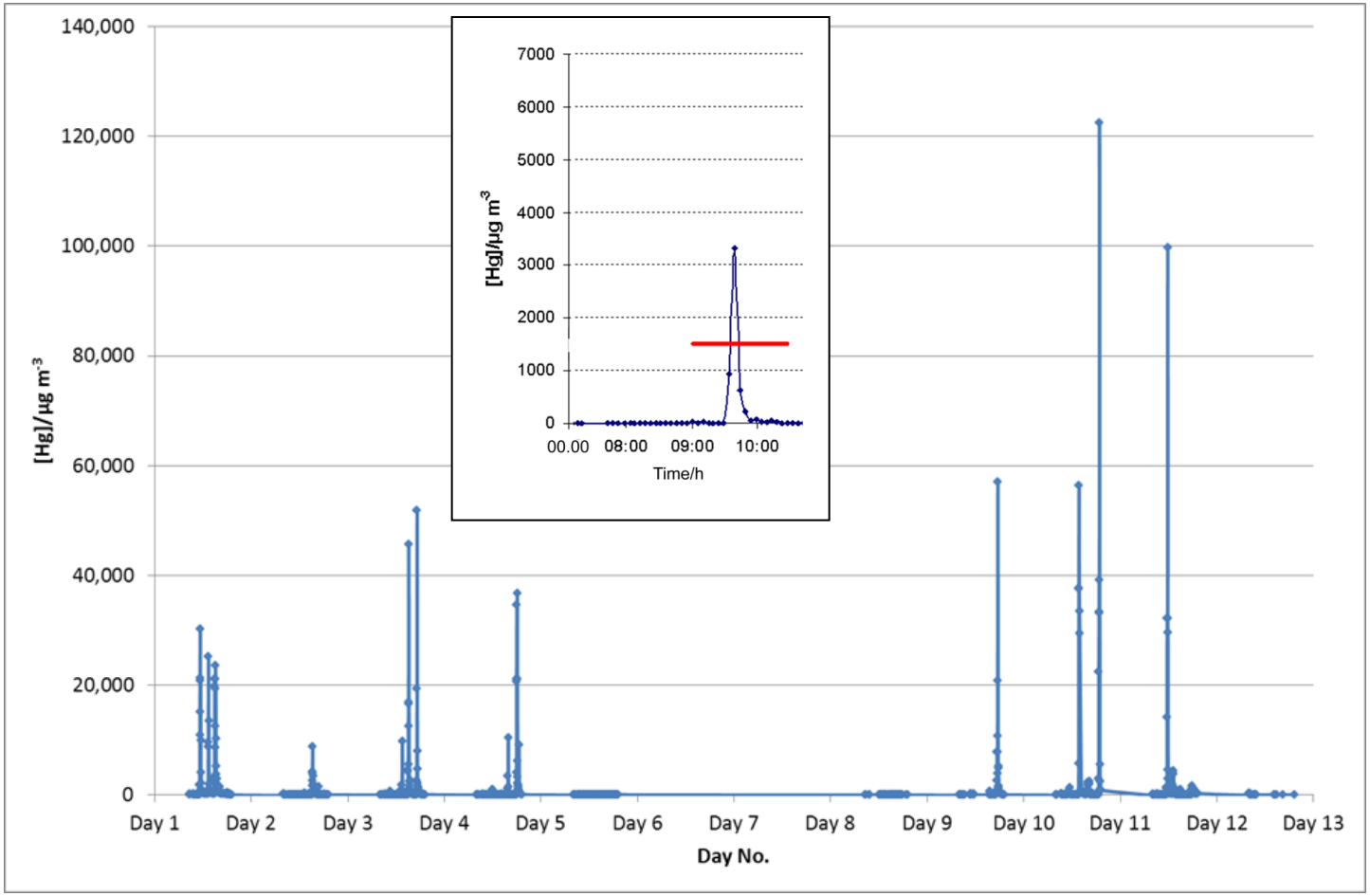
Unit has ESP & FGD

Firing various bituminous coals including PRB.

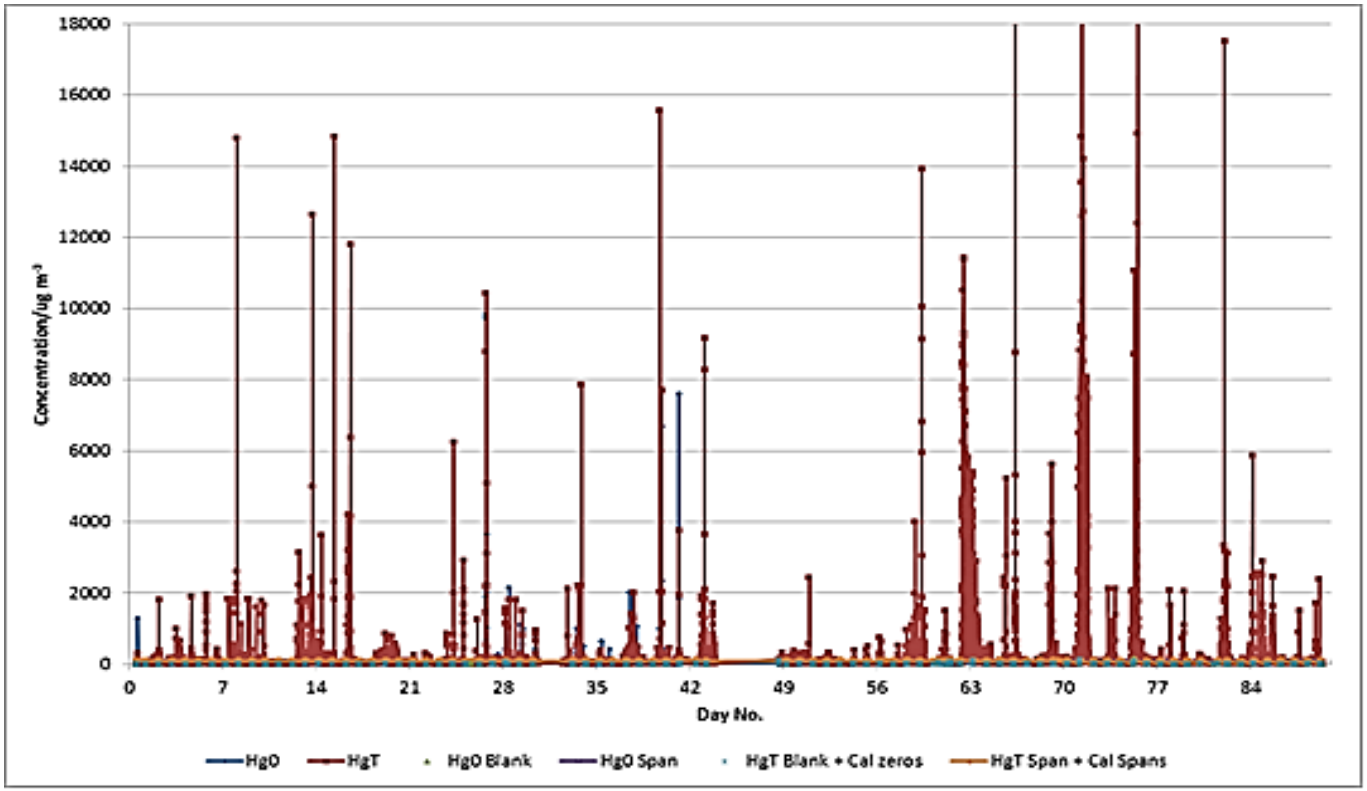


PSA

Data from Crematorium in UK



Data from a UK Waste Incinerator



PSA

Other Applications

PSA

Millennium Merlin – CVAFS and 1631-Hg

- Lab analyser based on Cold Vapour – AFS
- EPA 1631 Method uses gold amalgamation
- Chemical digestion with acidic oxidants
- Stannous chloride reduction of Hg^{2+} to Hg^{o}

$$Hg(II) + Sn(II) \rightarrow Hg^{o} + Sn(IV)$$

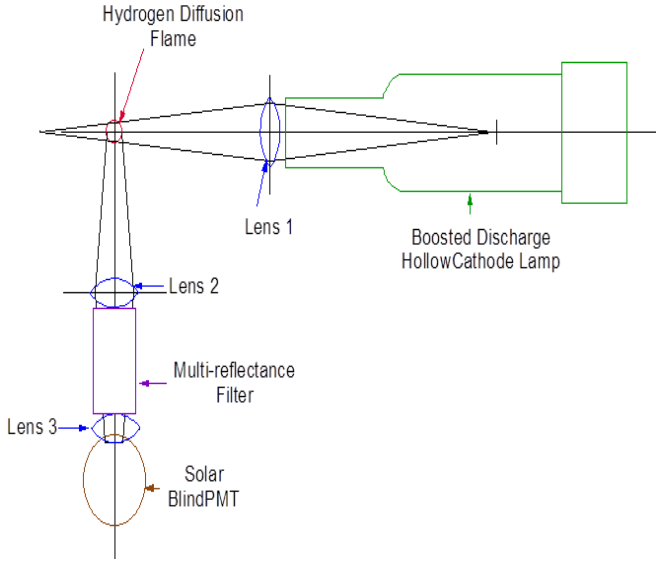
- Automated with 2 min cycle times and optional UV automated digestion
- Detection Limits less than 1 part per trillion. Linearity 5 orders of magnitude.
- No quartz atom cell to avoid carryover between samples
- Suitable for all types of wastewater and plant samples (coal, coke, ash, leachates, gypsum, sorbent traps, impinger solutions etc)

Millennium Excalibur
Hydride Generation AFS – As, Se, Sb

- Laboratory Analyser for As, Se, Sb, Te and Bi Single Element detector defined by lamp.
- Samples require preparation prior to measurement, digestion and conversion to optimal oxidation state
- Automated NaBH4/Acid chemistry to produce gaseous hydrides and hydrogen diffusion flame.

$$NaBH_4 + HCl + 3H_20 \rightarrow 8H + H_3BO_3 + NaCl \rightarrow MH_x + H_2$$

- Part per trillion detection limits. Linearity to 10ppm. 1 min cycle time. Optional UV auto-digestion and species conversion.
- Lower MDL than ICPMS as less dilution required
- Suitable for all types of wastewater and plant samples (coal, coke, ash, leachates, gypsum, sorbent traps, impinger solutions etc)



PSA

DETERMINATION OF ARSENIC, MERCURY AND SELENIUM ON SORBENT TRAPS SUITABLE FOR GAS PHASE MEASUREMENTS

SAMPLE PREPARATION

280 mL nitric acid, 160 mL sulphuric acid and 80 mL 0.1 N bromine solution are mixed and are used for the digestion of the sample.

(1) Add 300 mg of the spiked sorbent sample and 10 mL of the mixed acid solution to a 40 mL glass vial. Close the vial tightly with a PTFE-lined cap

(2) Place the glass vials in a hot block at 100 °C and heat for 3 hours. Check the vials every 20 min to ensure that the cap is still closed.

(3) Cool the samples to room temperature.

(4) Add 1 mL ascorbic acid reagent (10%m/v) to the solution and then top-up to 40 mL

(5) Filter the digest with ash-free filter paper.

(6) Take 5 mL of the digested filtered solution and depending on the element to be determined treat in different ways:

For arsenic: To 5 mL sample add 15 mL HCl, 15 mL water and 1 mL KI/ascorbic acid (50 g KI and 10 g ascorbic acid in 100 mL water). Top up the solution to 50 mL with water. Leave the solution for at least 30 min to allow As (V) to be reduced to As (III) prior to hydride generation

For mercury and selenium (with on-line pre-reduction): To 5 mL sample add 2.5 mL HCl. Top up the solution to 50 mL

For selenium (with off-line pre-reduction): To 5 mL sample add 5 mL deionised water and then 15 mL HCl in a plastic vial. Heat in a hot block at 120 °C for one hour loosely capped. Let the solution cool down and top it up to 50 mL.

PSA

Spike Recoveries for Hg, As and Se on Sorbent Traps

Spike Amount (As/Hg/Se)	Recovery(As) / %	Recovery(Hg) / %	Recovery(Se) / %
100 ng spike	97.2	96.3	104.4
250 ng spike	103.3	98.2	101.8
500 ng spike	106.4	103.2	102.1

PSA

FGD Wastewater Background Information

- In September 2015 EPA finalized the rule “40 CFR Part 423” entitled “Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category”. This appeared in the federal register on November 2015
- Previous regulations for wastewater did not account for the new waste streams that have essentially shifted pollutants from air to water.
- The intention of the new rule is the limit the amount of toxic metals, nitrogen and total dissolved solids discharged from power plants to surface water
- Main toxic metals of concern are Mercury, Arsenic and Selenium. These bio-accumulate in the environment harming wildlife and human health.

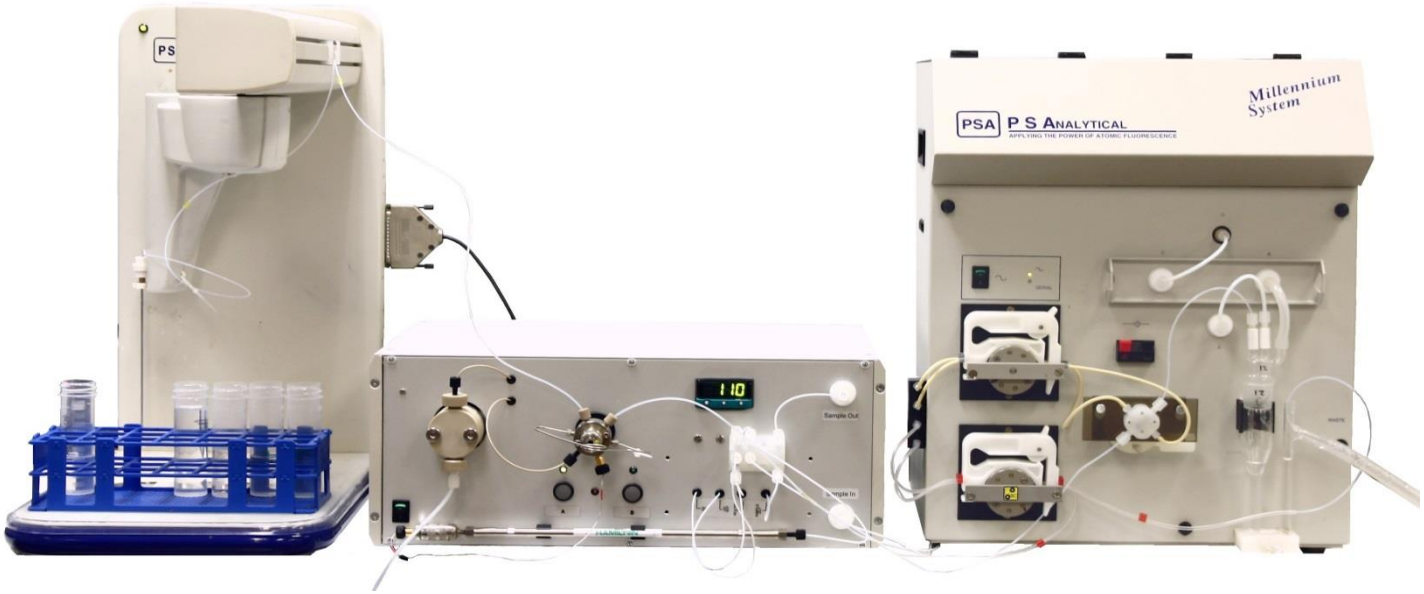
PSA

Some typical Results for FGD Wastewater

Element	Plant	WWTP Inlet µg/L	WWTP Outlet µg/L	Spike Recovery %	MDL µg/L
Hg	A B C	437.9 ± 4.9	0.010 ± 0.003 0.005 ± 0.002 <0.002	100.1 92.3 97.9	0.002
As	A B C	1395 ± 168	0.122 ± 0.003 5.86 ± 0.08 0.483 ± 0.005	94.5 97.5 100.0	0.012
Se	A B C	5652 ± 10 4824 ± 46	37.08 ± 0.97 - 9.81 ± 0.28	102.0 98.7 93.0	0.008
Sb	A B	79.7 ± 0.4	6.33 ± 0.07 3.08 ± 0.07	95.7 98.3	0.020

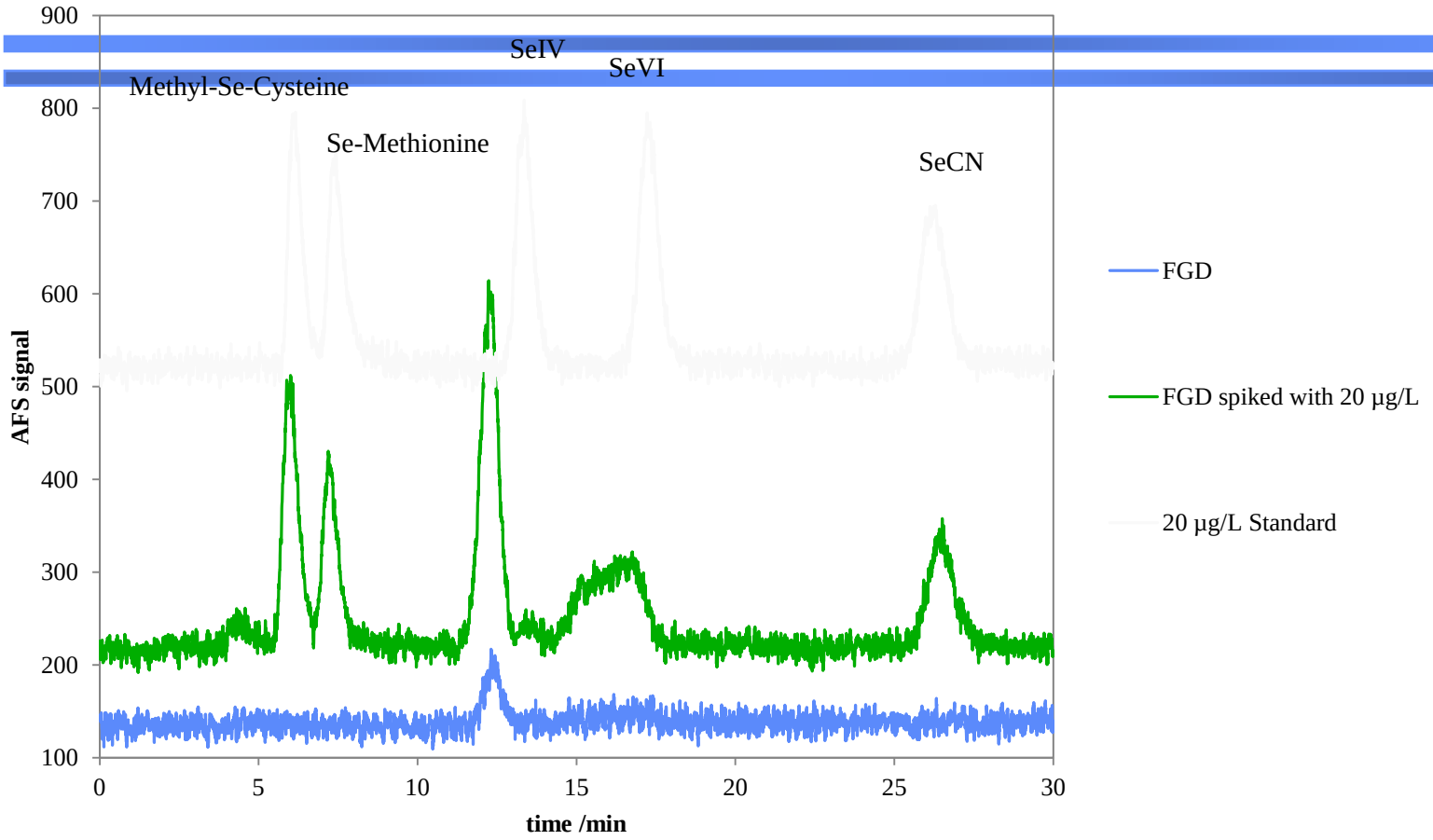
PSA

Speciation using IC-UV-AFS



PSA

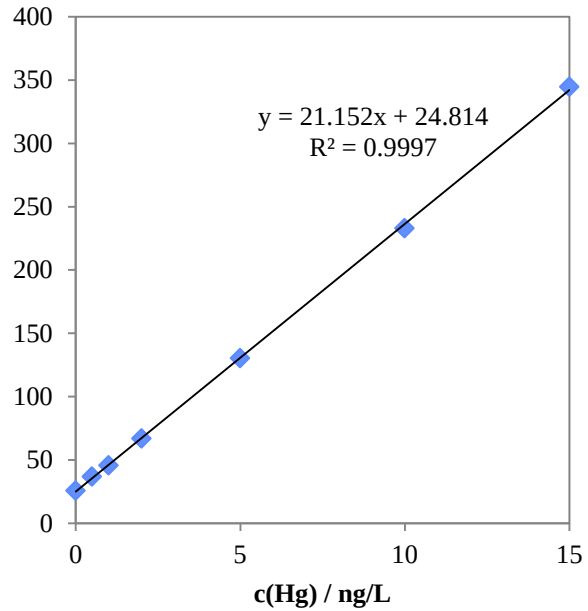
FGD Selenium Speciation?



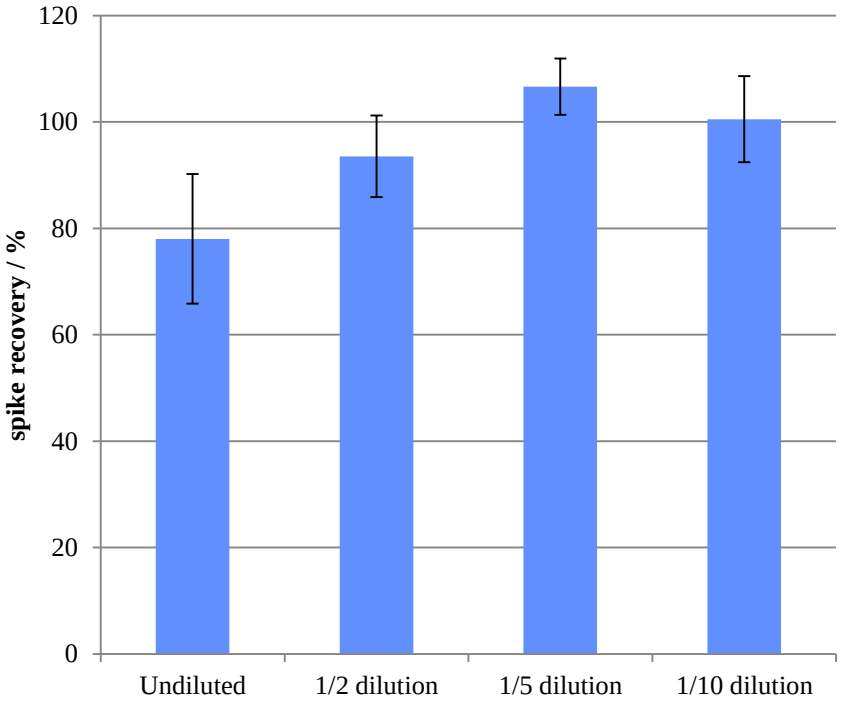
10.225/10.255 Liquid Online Hg, As & Se

PSA

Low Level Hg Calibration & Recoveries with batch amalgamation AFS



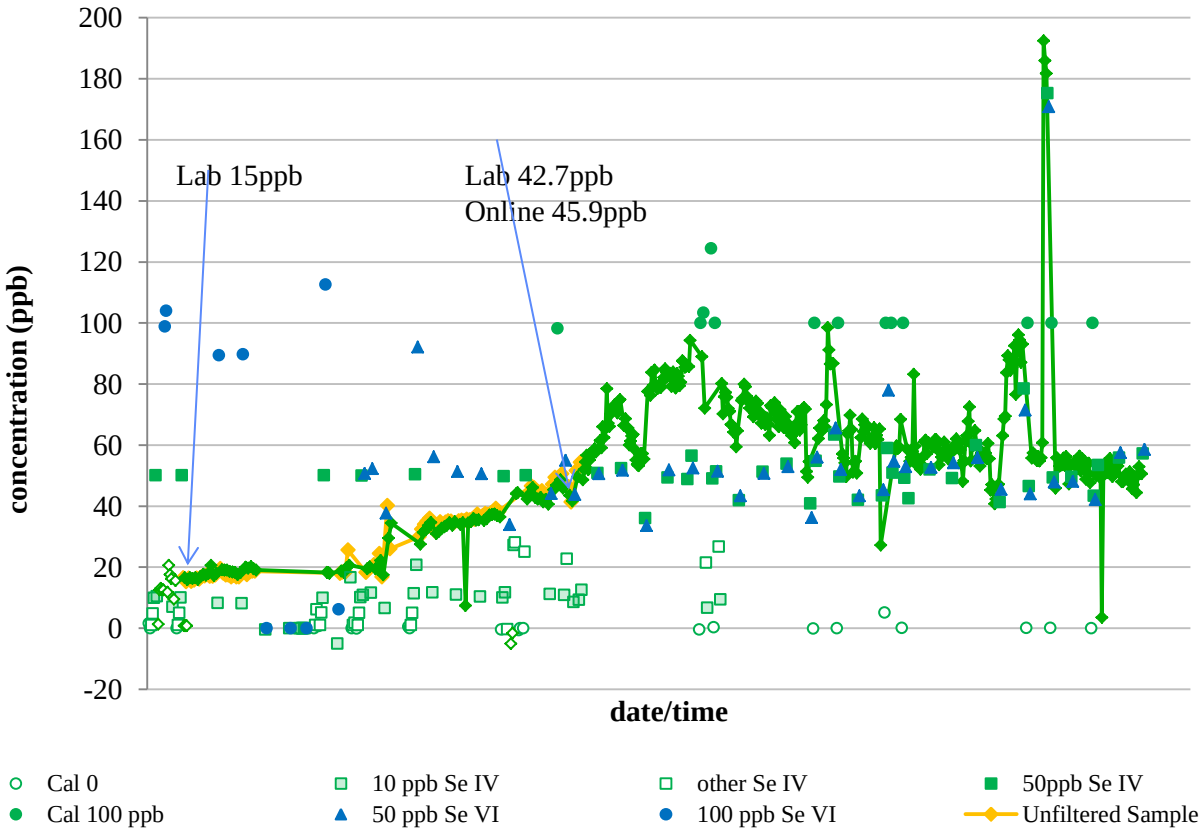
Instrumental Limit of detection
LOD(T-Hg)=0.035 ng/L (n=10)



Method Limit of Detection
0.07 ng/L

PSA

Online Selenium



Further Information

For more information please contact P S Analytical

- P S Analytical, Arthur House, Crayfields Industrial Estate, Main Road, Orpington, Kent, BR5 3HP, UK
  Tel: +44 (0) 1689 891 211 E-mail: **psa@psanalytical.com**

www.psanalytical.com

PSA