An Overview of Mercury Monitoring Options

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Introduction

- **What do we need to measure?**
  - Total mercury $Hg^T = Hg^0 + Hg^{2+} + Hg^P$
  - $Hg^P << (Hg^0 + Hg^{2+})$
  - Vapour phase Hg sufficient for coal fired plant with modern control technology

- **What is emitted?**

  Depends on PM control technology
  - ESP only: Hg^0 and Hg^{2+}

  Hg^{2+} is water soluble
  - ESP + FGD: mostly Hg^0
  - ESP + FGD + SCR: mostly Hg^0

  $Hg^0 \rightarrow Hg^{2+}$ enhanced by the SCR catalyst

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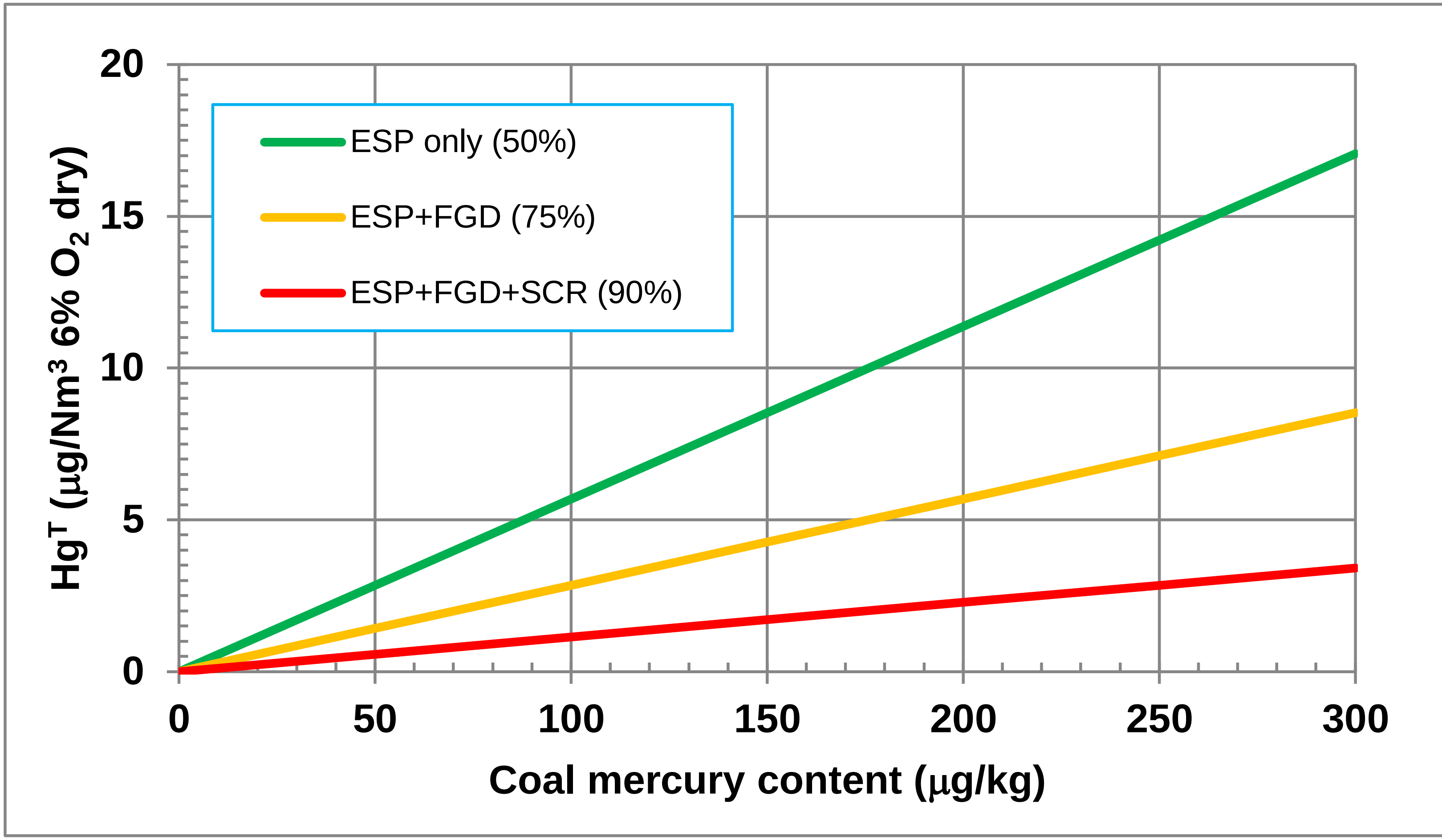
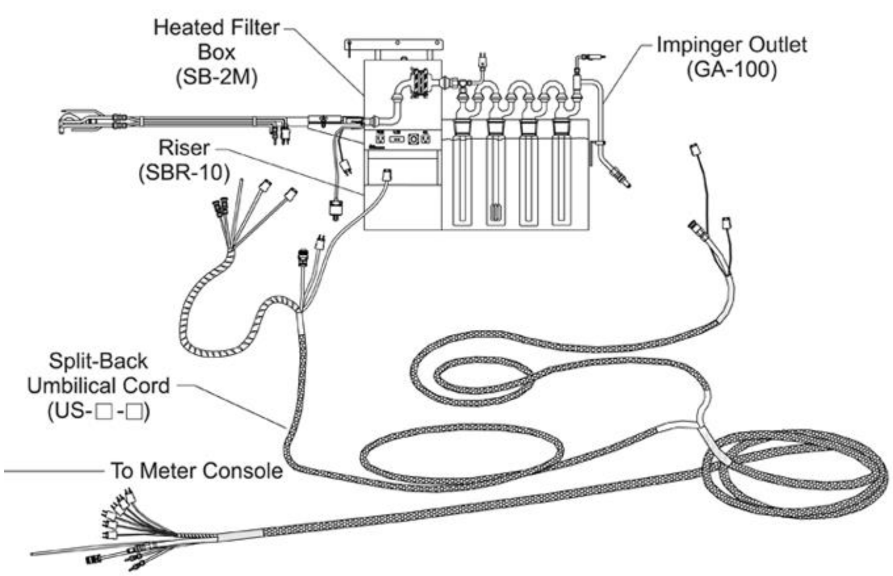
Anticipated range of mercury concentration?

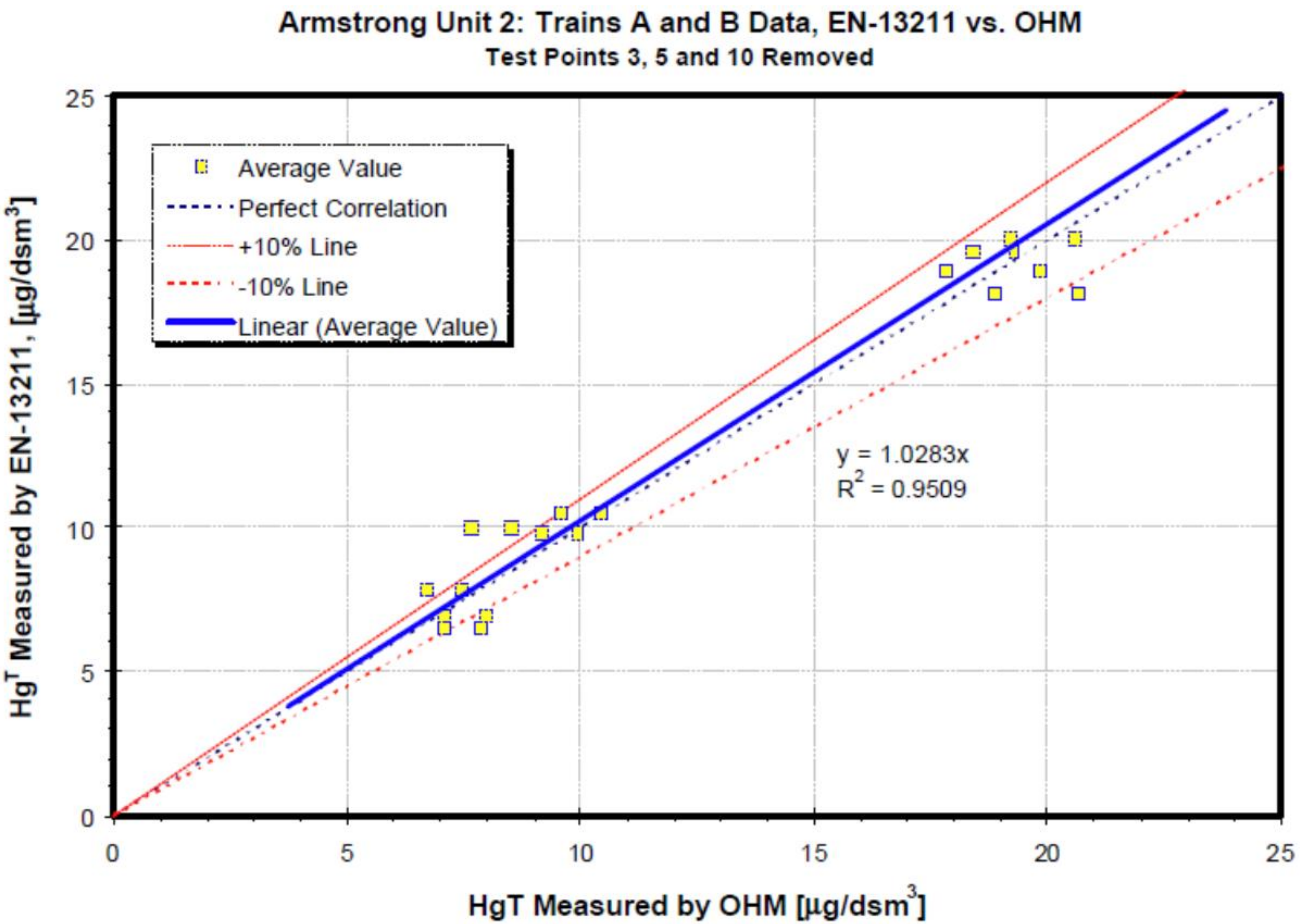


Options for mercury monitoring I

- **Periodic measurement to EN 13211:2001**
  - Industrial Emissions Directive ‘For combustion plants firing coal or lignite, the emissions of total mercury shall be measured at least once per year.’
  - Flue gas @ 20 to 30 l/min, for 1 to 2 h, >1Nm^3
  - Probe/filter >120°C
  - Cooled impingers ($KMnO_4/H_2SO_4$) (Breakthrough<5%)



EN13211 ≡ Ontario-Hydro Method (OHM)



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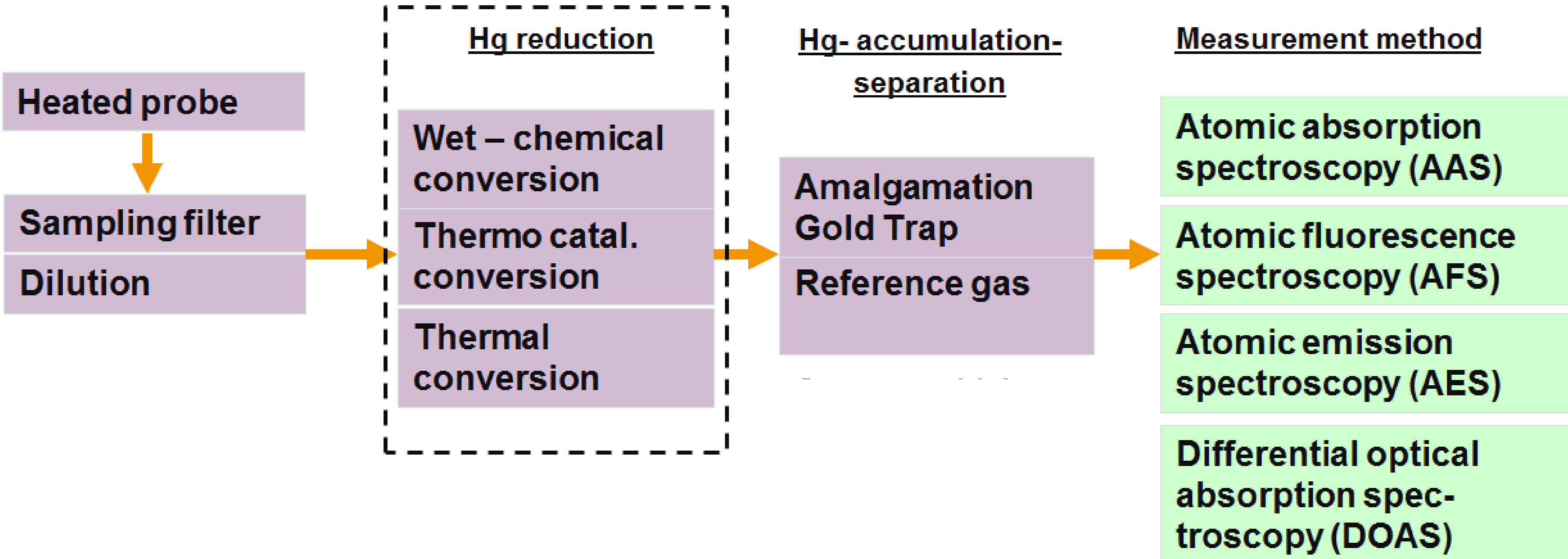
EVALUATION AND COMPARISON OF U.S. AND EU REFERENCE METHODS FOR MEASUREMENT OF MERCURY, HEAVY METALS, PM2.5 AND PM10 EMISSIONS FROM FOSSIL-FIRED POWER PLANTS Dr. Nenad Sarunac, Energy Research Center, Lehigh University Feb 2007 (tested in July 2006 at Armstrong PP)

Options for mercury monitoring II

- **Continuous measurement to EN 14884:2005**
  - LCP BREF Continuous monitoring required unless it can be demonstrated by other means that the ELV will not be exceeded



Courtesy Sick Gmbh

Options for mercury monitoring II

- **Continuous measurement to EN 14884**
- Instrumental methods
- Primary measurement is Hg^0
- Convertor $Hg^{2+} \rightarrow Hg^0 \rightarrow Hg^T$
- Speciation by:
  - Converter switching in/out
    - $Hg^{2+} = Hg^T (in) - Hg^0 (out)$

Courtesy Tekran Instrument Corporation

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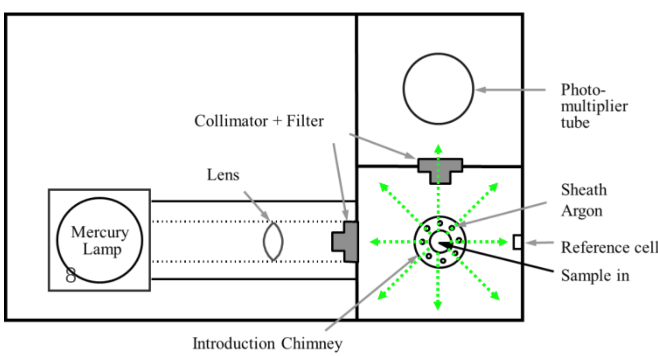
Continuous analysis - Approach 1A CVAFS

- **Sample dilution with gold trap amalgamation**
- Inertial probe to exclude particulate (M&C)
- Heated inert transfer lines
- Dilution ratios 40:1 (PSA); 30:1 (Tekran)
- Thermo-catalytic converter → Hg^T
- Dual gold traps - continuous sampling – 3min cycle - Ar
- CV Atomic Fluorescence Spectrometry
- Very linear and selective (no SO_2 interf.)
- Detection limits (PSA):
    - 0.1 pg (absolute mass)
    - 4 ng/m^3 (40:1, 1 dm^3 sample vol)



Courtesy PS Analytical

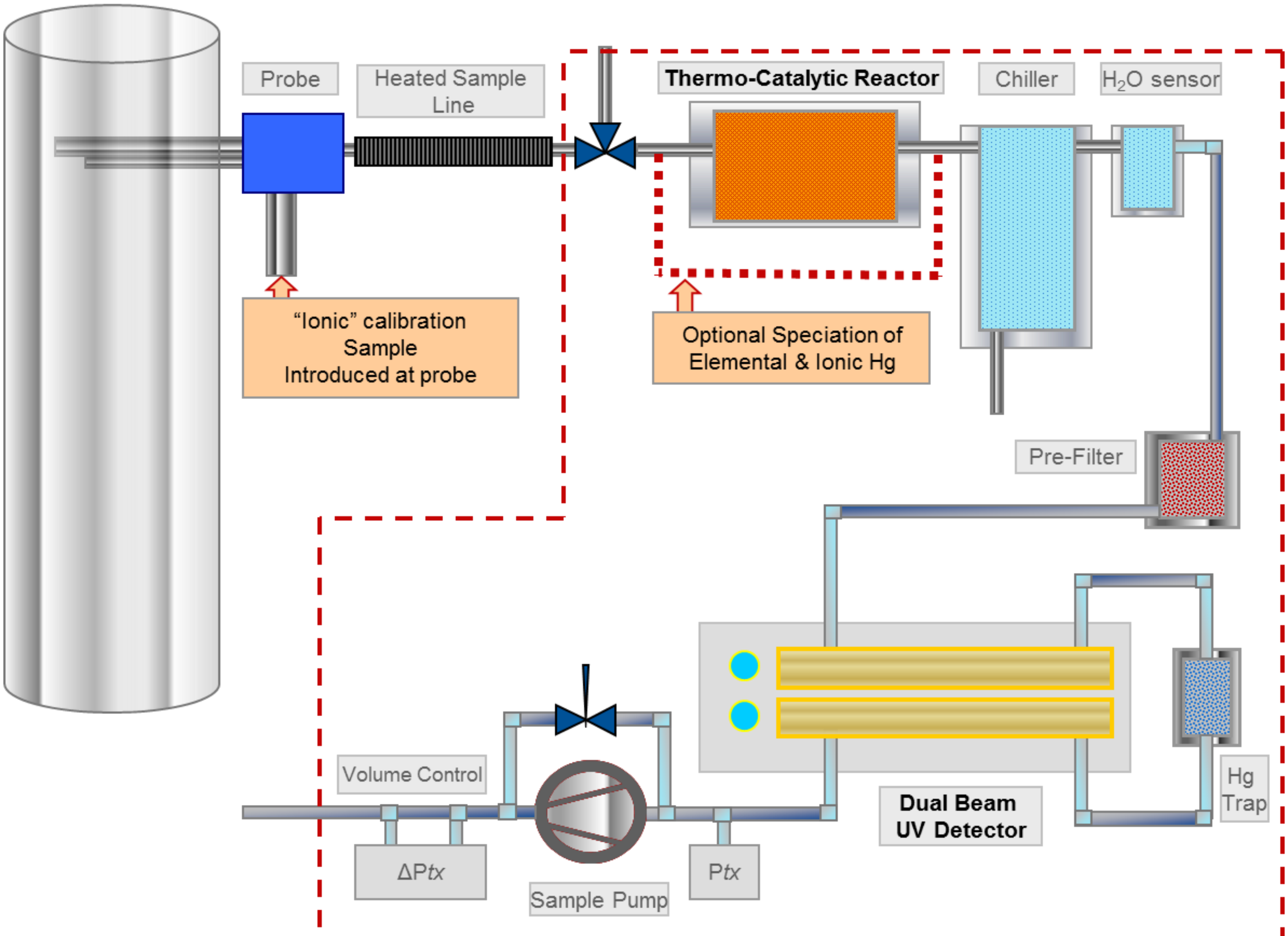
Continuous analysis - Approach 1B CVAFS

- **Sample dilution without gold trap amalgamation**
- Inertial probe to exclude particulate
- Heated inert transfer lines
  (Thermo – converter at stack – simplifies transport)
- Dilution ratios 40:1 (Thermo); 50:1 (Gasmet)
- Thermo-catalytic converter → Hg^T
- Thermo-Scientific and Gasmet direct reading CVAFS
- Diluted sample (no gold traps) Carrier N_2

Courtesy ThermoFisher

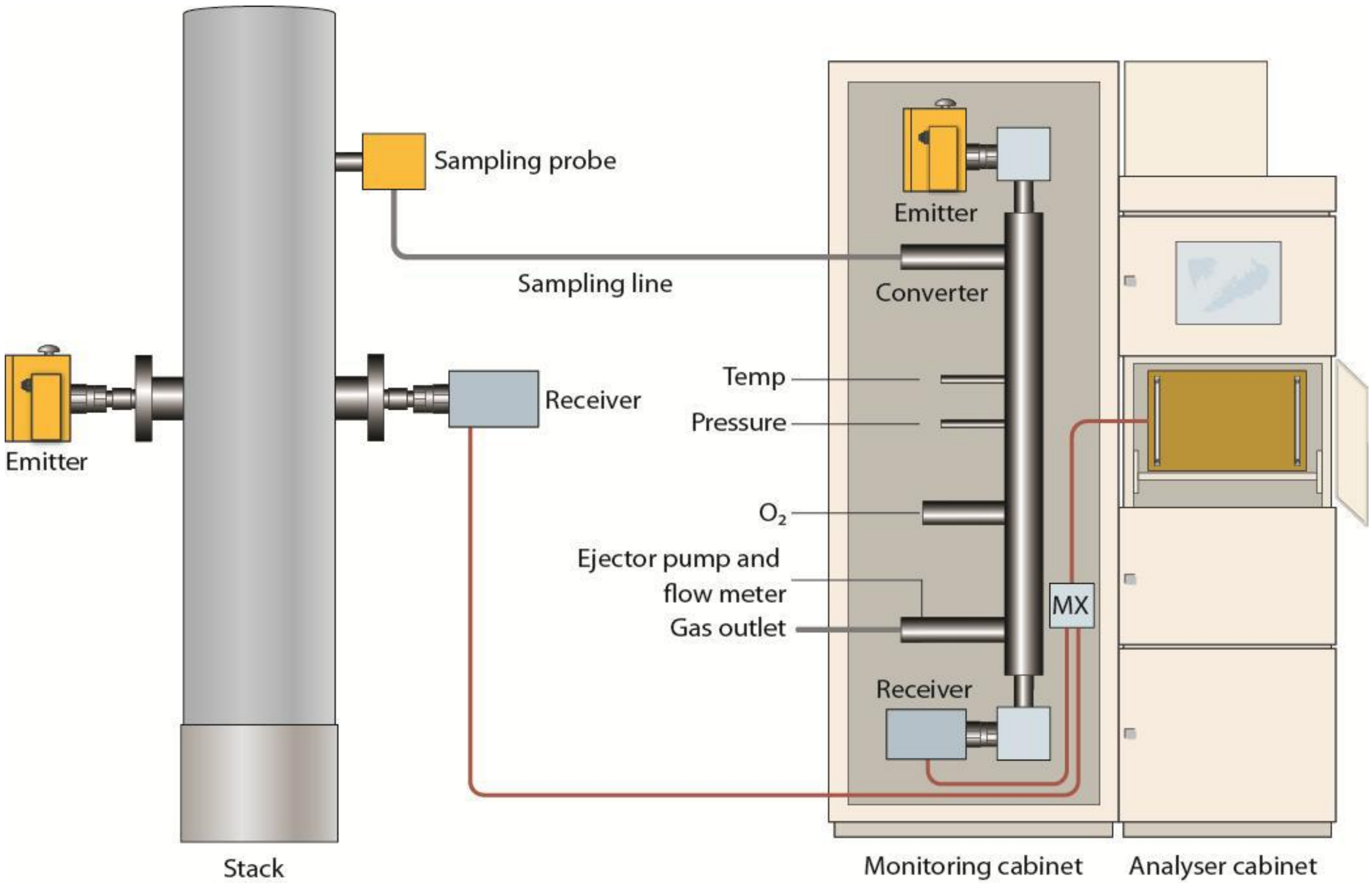
Courtesy Ohio-Lumex

Continuous analysis - Approach 2 AAS (no dilution)



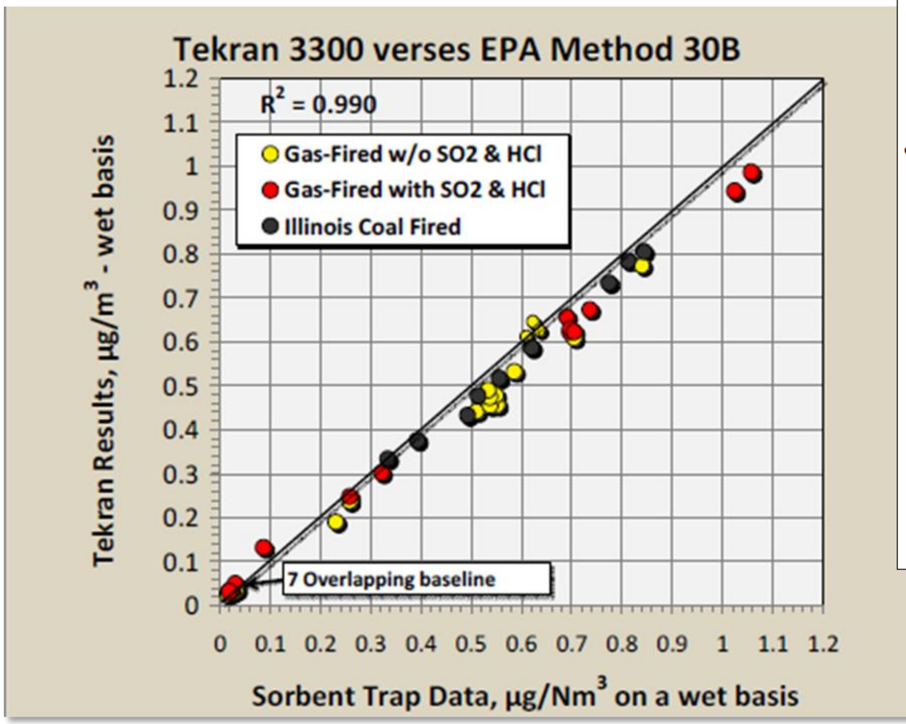
Courtesy Durag

Continuous analysis - Approach 3 DOAS

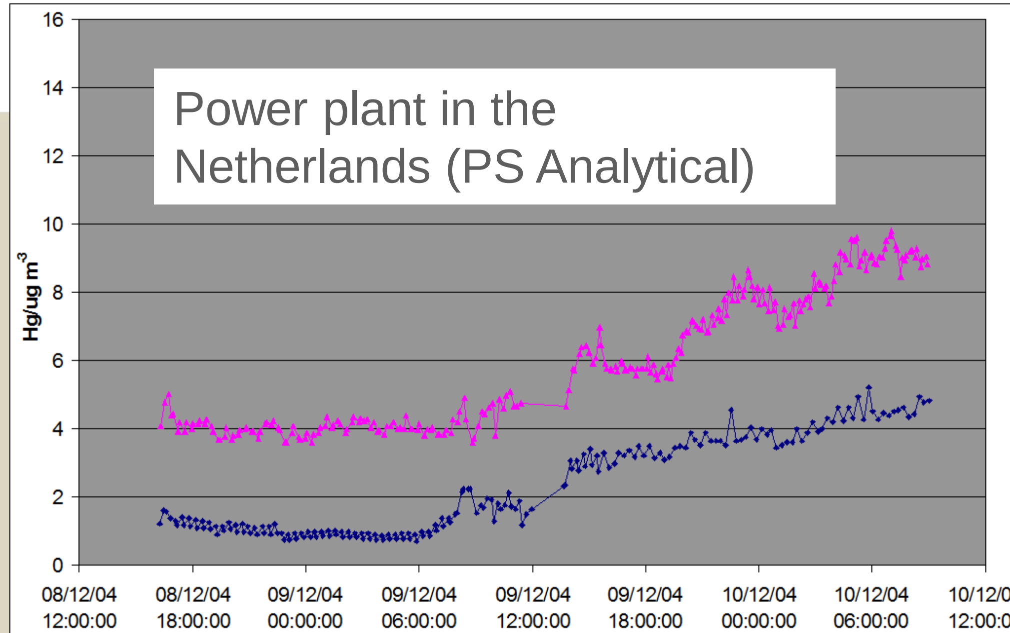


Courtesy Opsis

Continuous analysis - Approach 1A results



Courtesy Tekran Instrument Corporation



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

Courtesy PS Analytical

Power plant in the USA (PSA)

Continuous analysis - Approach 1B results

Facility [redacted]
Unit Number: [redacted]
Test Location: Stack
Monitor / Calibrator: Thermo Model 80i / Model 81i

Test Date: 11/4 and 11/5/2008
Project #: M22M0486
Site Name: [redacted]
Serial Numbers: 0803527419 / 0803527425

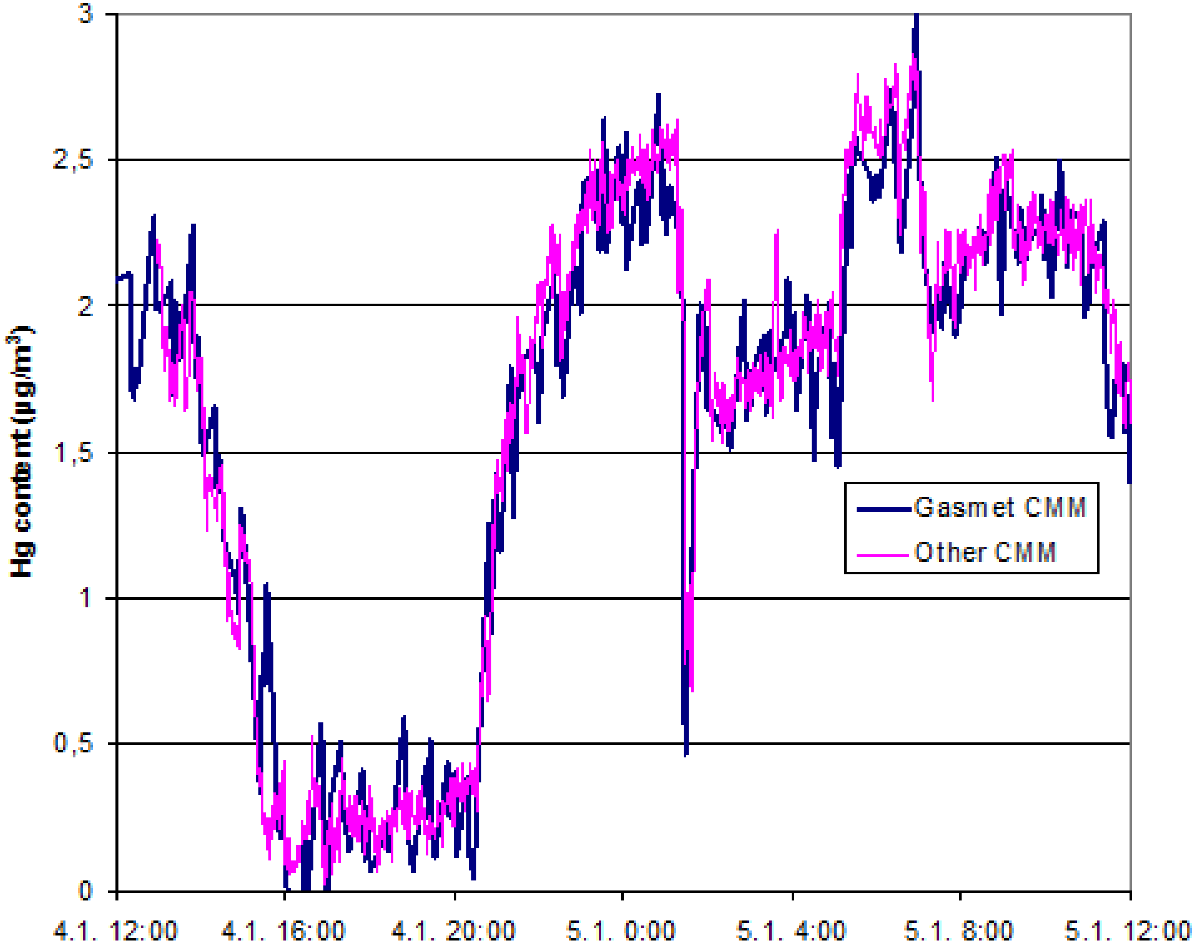
	Test Run	Date	Start Time	End Time	Reference Method Hg µg/scm	CEM Output Hg µg/scm	(RM-CEM) Difference (di)	Difference^2 (di^2)
1	1	11/04/08	1522	1552	3.0	2.8	0.15	0.02
1	2	11/04/08	1615	1645	3.0	2.8	0.13	0.02
1	3	11/05/08	1027	1057	1.3	1.2	0.09	0.01
0	4	11/05/08	1117	1147	0.6	1.0	-0.39	0.15
1	5	11/05/08	1203	1233	0.8	0.9	-0.09	0.01
1	6	11/05/08	1246	1321	0.9	0.9	0.05	0.00
1	7	11/05/08	1340	1430	0.7	0.9	-0.14	0.02
1	8	11/05/08	1545	1631	0.7	0.7	0.02	0.00
1	9	11/05/08	1646	1729	0.6	0.7	-0.06	0.00
1	10	11/5/2008	1749	1819	0.9	0.8	0.08	0.01

Standard Deviation	0.101	sd
Confidence Coefficient	0.078	CC
Relative Accuracy based on % of RM Value	7.8	%
Relative Accuracy based on difference	0.0	Mean Difference
Calculated Bias Adjustment Factor	1.000	BAF
Default BAF (Hg <5.0 ug/scm)	1.000	BAF

Meets specifications for annual RA

Courtesy Thermo Fisher Scientific

Continuous analysis - Approach 1B results



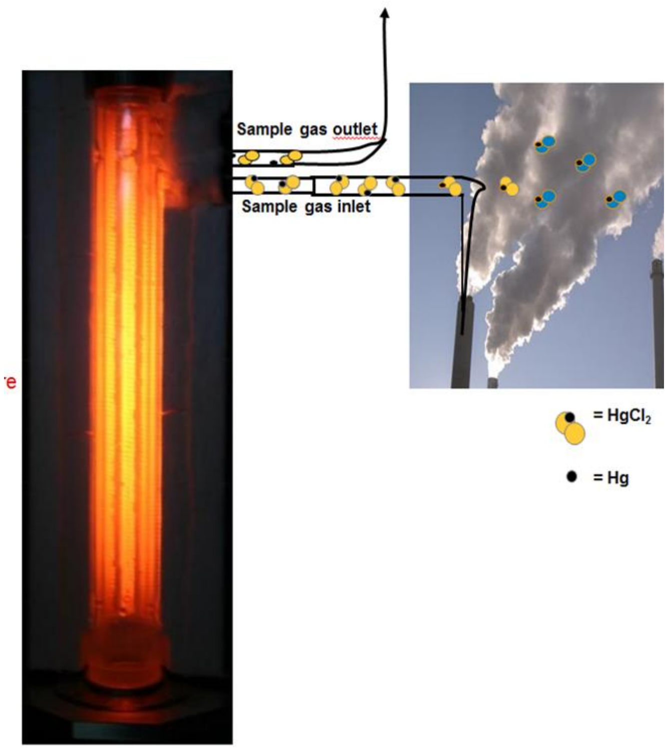
Courtesy Gasmet

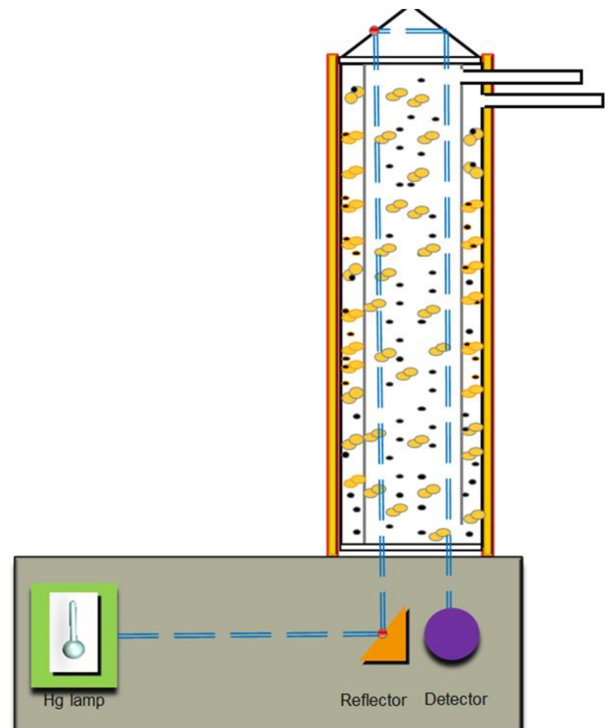
Continuous analysis – High temperature

Hg reduction

Measurement method

Heated probe → Sampling filter → Thermal Conversion → Atomic absorption spectroscopy (AAS) with integrated Zeeman cross sensitivity correction

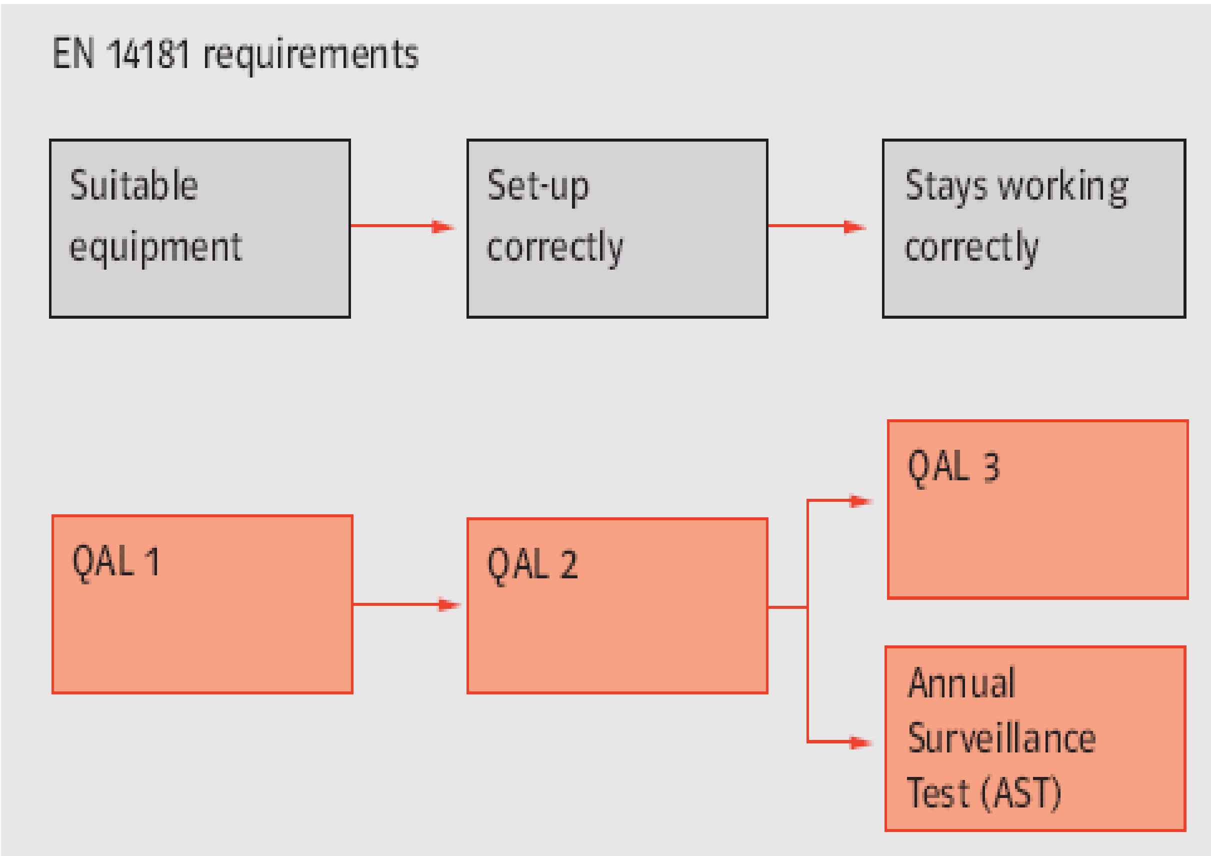




Courtesy Sick Gmbh

European QA standards

EN 14181: 2014 ‘Stationary Source Emissions - Quality Assurance of Automated Monitoring Systems’



Operator’s responsibilities:

- Installation of compliant equipment (QAL1)
- In-situ calibration of CEMs using an accredited test laboratory (QAL2) (audit)
- Annual check of the calibration (AST)
- Ongoing QA based on regular zero and span checks (QAL3)
- Submission of QAL2 & AST reports and ongoing maintenance of records
- Checking of hourly averages against the Valid Calibration Range (weekly)

Certification of CEMs - MCERTS

Certificate Holder	Model	Certified Range
Durag GmbH	HM 1400 TRX Mercury Analyser	0 to 45 µg/m³ 0 to 75 µg/m³
Opsis AB	AR 602Z/Hg	0 to 45 µg/m³ 0 to 100 µg/m³
SICK MAIHAK GmbH	MERCEM300Z Mercury Monitoring System	0 to 10 µg/m³ 0 to 45 µg/m³

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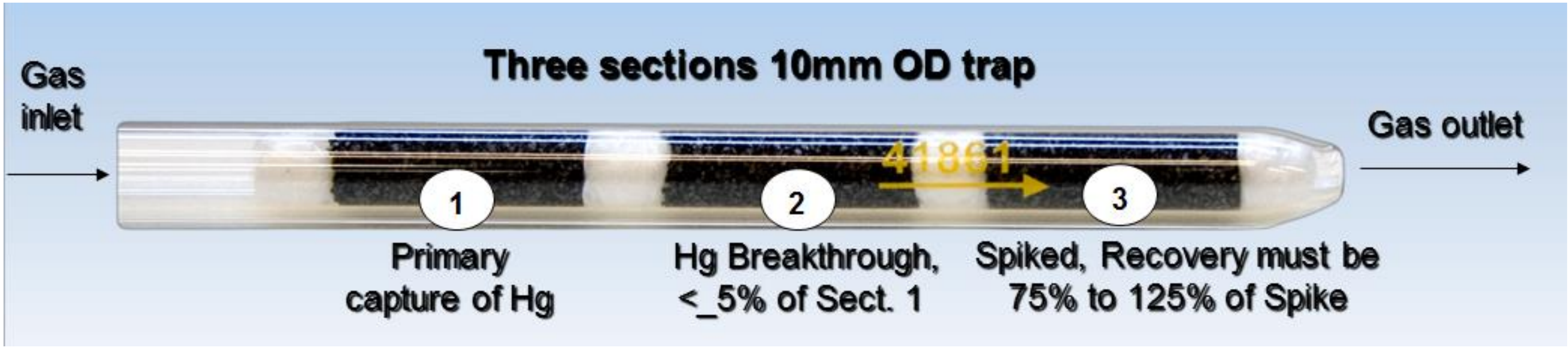
Options for mercury monitoring III

- **Semi-Continuous measurement to prEN XXXX (ex US)**
  - LCP BREF Semi-Continuous monitoring allowed

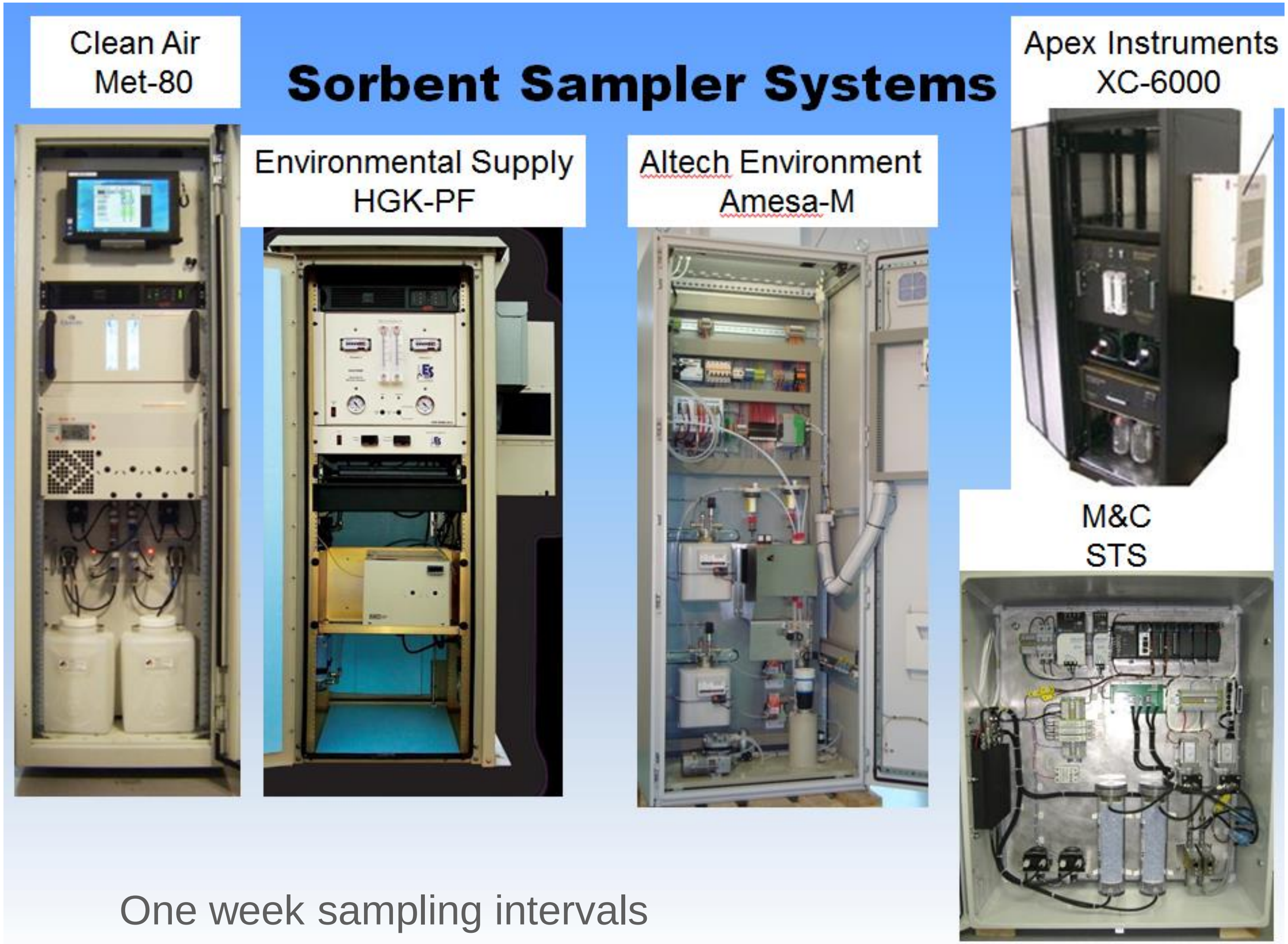


Relative Deviation <= 10%

Laboratory analysis following …
Thermal desorption
Leaching or
Digestion

Courtesy Ohio-Lumex

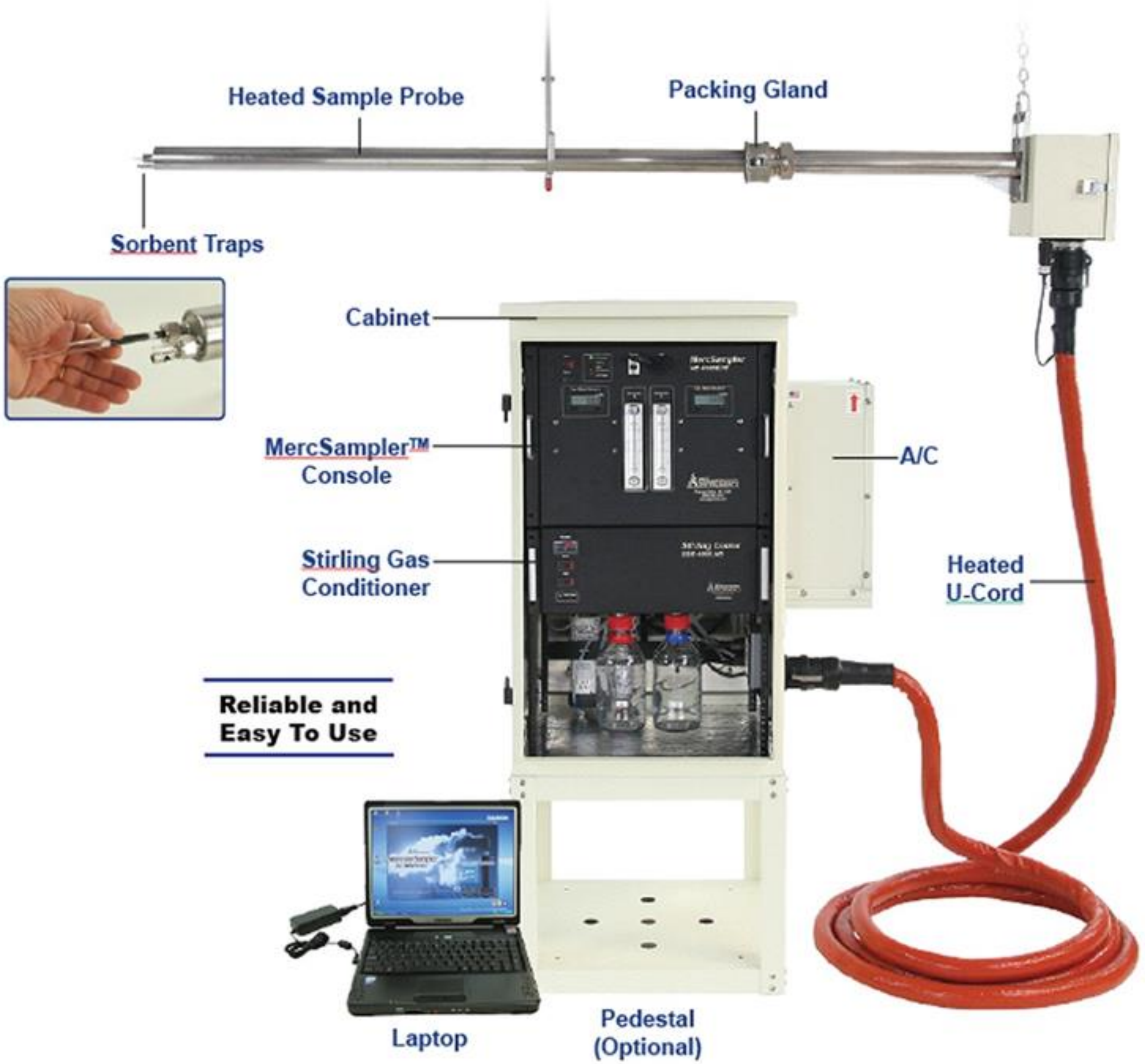
Options for mercury monitoring III



One week sampling intervals
Also used as an SRM in the US

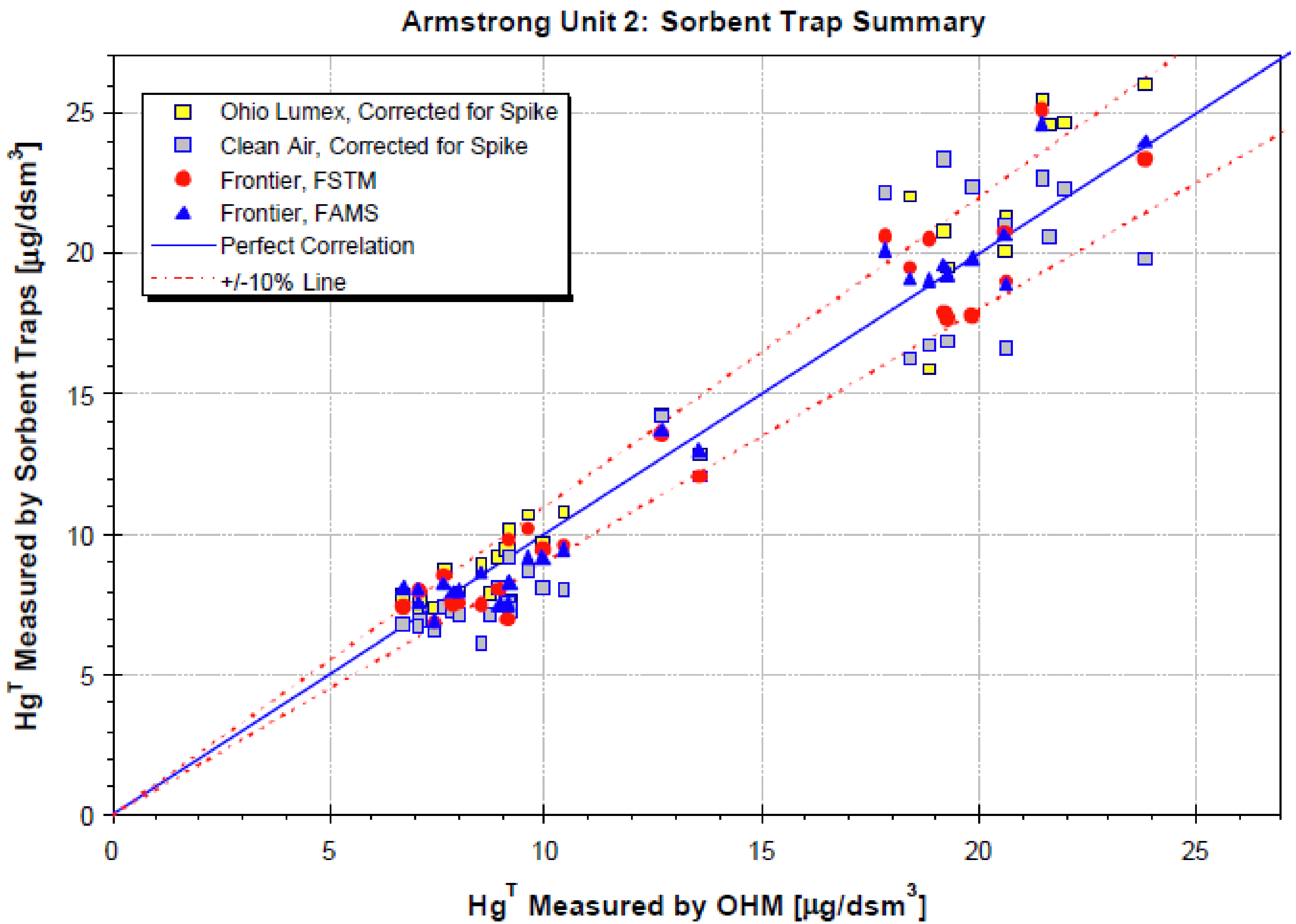
Courtesy Ohio-Lumex

Options for mercury monitoring III



Courtesy Apex Instruments

Sorbent Trap Method ≡ OHM ≡ EN13211



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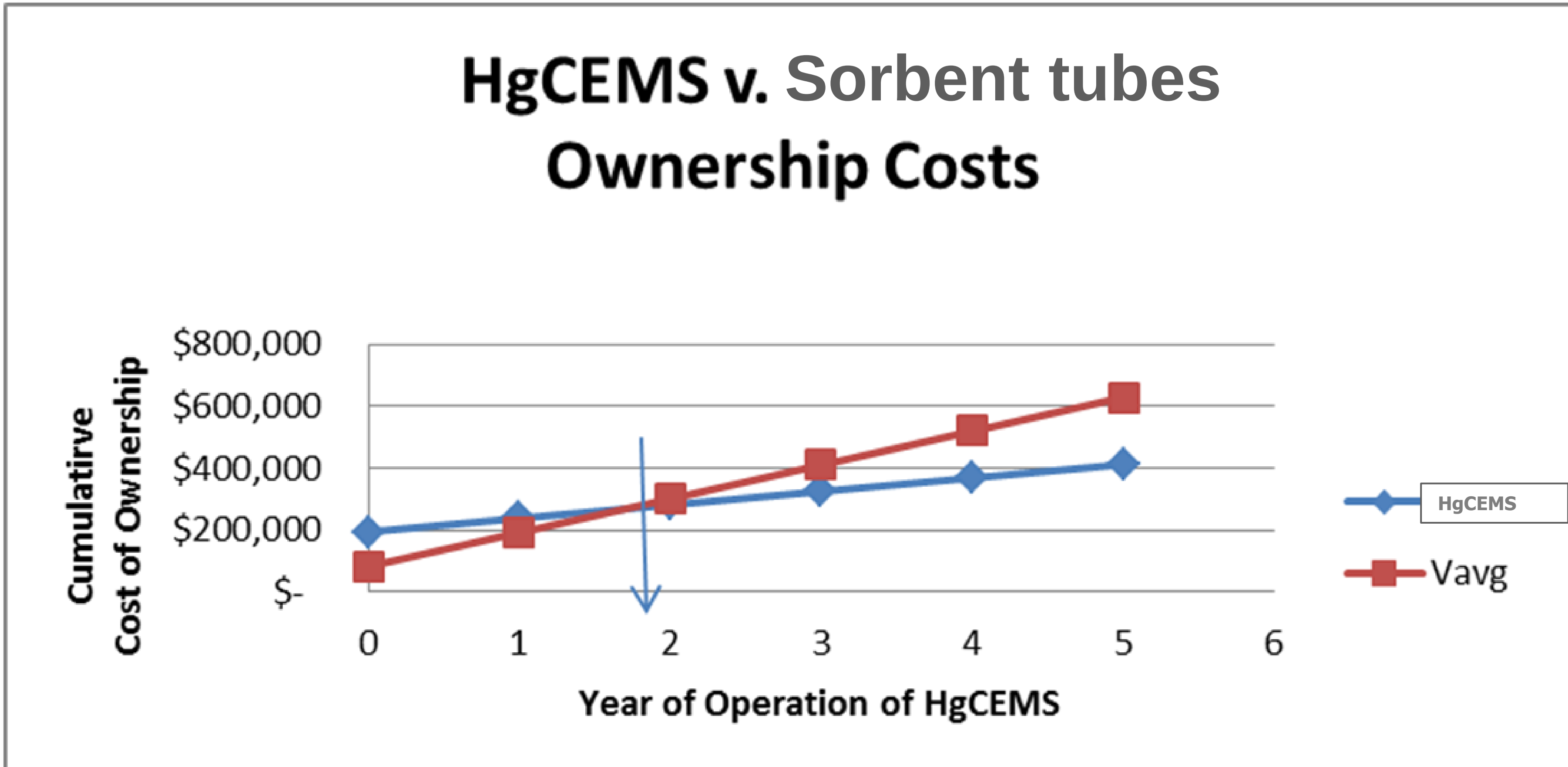
How much does it all cost?



Courtesy Tekran Instrument Corporation

Concluding Remarks

- EU mercury monitoring requirements are increasing
- Concentration levels are low for coal fired plant
- Periodic measurement to EN 13211:2001
  - Annual test under IED (from 1 Jan 2016)
  - Accredited Test Laboratory (ISO 17025)
- Continuous measurement to EN 14884:2005
  - LCP BREF requires this unless alternative means of demonstrating compliance (2021?)
  - Various techniques available (Hg^T as Hg^0)
  - Certification is limited but UK, European & US instruments have the required sensitivity
  - Capital outlay and running costs are high
- Semi-Continuous measurement to prEN XXX
  - Simple measurement with rigorous QA
  - Capital outlay lower but analysis costs to consider

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