# VGB Research Project 341: Measurement of Low Mercury Concentrations in Flue Gases of Power Plants

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Determination of low total mercury concentration and mercury species distribution in flue gases from coal-fired power plants by the sorbent trap method – Validation of the Dowex/AC measuring method –

- 1. Measuring Campaign in Oct. 2011 at a hard coal fired PF power plant
- 2. Measuring Campaign in Dec. 2012 at a lignite fired CFB power plant

Participants in the VGB field testing programme:

- E.ON New Build & Technology GmbH
- Otto von Guericke Universität Magdeburg
- Laborelec / GDF Suez
- Enel Engineering and Research

Further participants:

- Plant operators (with their CEMs)
- Environnement SA (with the AMESA M)
- Sick AG











## Background

- Public perception for mercury emissions from coal fired power plants is increasing.
- New emission limits in the range of 1 3 µg/m<sup>3</sup> are in discussion and already agreed in particular cases.
- The referred lower application limit of the Standard Reference Method (SRM) for mercury emission testing EN 13211 is 1 µg/m<sup>3</sup>.
- Differentiation between elemental Hg(0) and oxidized Hg(ox) is not possible with EN 13211 but important for development of effective mercury mitigation procedures.
- Alternative methods for mercury measurements at low concentrations and in different species are available but not validated for low concentrations and are not acknowledged by authorities in Europe.











# **Benefits**

- Reliable monitoring of mercury emissions from (new) coal fired power plants in the range of 1 µg/m<sup>3</sup> and below to demonstrate compliance with emission limit values.
- Improved acceptance of New Build projects by optimized and reliable emission monitoring.
- Verification of mercury mitigation measures as part of the permit obligations.
- Validation of an alternative measuring method that allows differentiation of mercury oxidation state and thus reduction of costs for legally required baseline and performance measurements for the authorities.











## **Work Programme**

- Field testing of mercury emissions at two different power plants with preferably low mercury emissions.
- Comparison of four different sampling and measuring methods for determination of mercury emissions.
- In addition methods for long-term sampling and continuous mercury emission monitoring have been included.
- Evaluation of the test results according to European standards and validation of alternative adsorptive sampling methods in the lower concentration range.











#### **1. Measuring campaign in Oct. 2011 at a hard coal-fired PF power plant**

Methods applied by the participating research institutes:

- 1. European Standard Reference Method EN 13211 (E.ON)
- 2. Dowex-Activated Charcoal Method (OvGU)
- 3. US-EPA Method 30B (Laborelec / GDF Suez)
- 4. PSA Continuous Mercury Emission Monitoring System (Enel E&R)

Additional methods applied by plant operator and equipment manufacturer:

- 5. Sick Mercem (official, calibrated CEM for Hg emissions)
- 6. AMESA M (Environnement SA Deutschland, long-term sampling system)
- 7. Sick Mercem300Z (test installation by Sick, not calibrated)

#### 2. Measuring campaign in Dec. 2012 at a lignite-fired CFB power plant

Methods applied by the participating research institutes:

- 1. European Standard Reference Method EN 13211 (E.ON)
- 2. Dowex-Activated Charcoal Method (OvGU)
- 3. US-EPA Method 30B (Laborelec / GDF Suez)

Additional methods applied by plant operator:

4. Mercury Instruments - SM4 (test installation)











### **1. Measuring Campaign: Description of the sampling location**

Hard coal-fired PF power plant, 510 MW<sub>el</sub>

- Sampling location: Downstream of the FGD at the emission measuring platform
- Flue gas duct: Horizontal, 7 m diameter, four access points on each half axis (45° out of the vertical) plus 2 bigger horizontal flanges







- Clean gas parameters: 55°C, water saturated, < 5 μg/m<sup>3</sup> Hg
- Coal input: Southafrican (0,1 mg/kg Hg; 0,04-0,06 % Cl) and Columbian (~0,05 mg/kg Hg; ~0,009% Cl











(1) European Reference Method EN 13211

Applied by E.ON New Build & Technology

Air quality - Stationary source emissions -Manual method of determination of the concentration of <u>total mercury</u>



 $H_2SO_4$  / KMnO<sub>4</sub> sampling train













(2) Dowex® / Activated Charcoal Method

Applied by Otto-von-Guerike Universität Magdeburg



Dowex/activated charcoal adsorption unit

**Elemental and oxidized**, vapour phase **mercury** in flue gas from stationary sources













#### (3) EPA Method 30B

Applied by Laborelec / GDF Suez



Activated charcoal traps inside the duct

Determination of **total vapor phase mercury** emissions from coal-fired combustion sources using carbon sorbent traps













#### (4) PSA Online Stack Gas system for Continuous Emission Monitoring (CEM) of Mercury

Continuous monitoring of **elemental and oxidized**, vapour phase **mercury** in flue gas from stationary sources

Applied by Enel Engineering and Research



Dilution unit installed straight to the duct













(5) Sick MERCEM for Continuous Emission Monitoring (CEM) of Mercury

**Applied by Plant Operator** 

Continuous monitoring of **total**, vapour phase **mercury** in flue gas from stationary sources; **approved** by German authorities



Wet chemical reduction of oxidized mercury













(7) AMESA M Automatic Sampler for Mercury using Adsorption Traps Short-term and long-term sampling system for **total mercury** in flue gas from stationary sources; installed for **validation trials** 

**Applied by Environnement SA Deutschland** 













#### (6) Sick MERCEM300Z Continuous Emission Monitoring (CEM) of Mercury

Applied by Sick Maihak Germany

Continuous monitoring of **total**, vapour phase **mercury** in flue gas from stationary sources; installed for **validation trials (QAL1)** 















### **Measurement Schedule**

Day	Cont. Measuremt.	Discont. Sampl.	Sick CEMs	AMESA M	
	Enel E&R	E.ON, OvGU,	<b>Operator /</b>	Environnement	
		Laborelec	Provider	SA	
Mon. Oct. 3rd	set-up		measuring		
Tue Oct. 4th	1. series	set-up	measuring		
Wed Oct. 5th	2. series	1. series	measuring		
Thu Oct. 6th	3. series	2. series	measuring	set-up	
Fri Oct. 7th	dismatling,	3. series	measuring	1. series	
	deptarture				
Sat Oct. 8th		dismatling,	measuring		
		deptarture			











### **Measurement Requirements**

- All sampling points / probe tips as close together as possible (preferably in the centre of the duct)
- All samplings and measurements starting and terminating simultaneously
- 6 samplings / measurements per day, each lasting 1 hour
- Each sampling performed as duplicate (with exception of CEMs)
- Measuring campaign resulting in a set of 36 flue gas samples per sampling method and a set of 24 samples per method comparable with the PSA CEM
- 12 flue gas samples to be comparable with the corresponding AMESA M samples











### Results of the 1. Measuring Campaign 05. – 07.10.2011



## **Conclusion from the 1. Measuring Campaign**

- The results of all 7 sampling / measuring methods are very close together, especially in consideration of the very low concentration level of about 2 3 μg/m<sup>3</sup>.
- The results of all 7 methods follow the enforced course of mercury concentration in almost the same way.
- The discontinuous sampling methods incl. automated EPA and AMESA M method are in a mid range close together.
- The calibrated continuous measuring method delivers the lowest values.
- In the row of the continuous emission monitors the new Sick Mercem300Z shows the best analogy with the standard reference method.
- The results of mercury species determination with the Dowex/AC and the PSA method were inconsistent and need further investigation.











### 2. Measuring Campaign: Description of the sampling location

Lignite-fired CFB power plant, 108 MW<sub>el</sub>

- **Sampling location:** Downstream of the ESP at the emission measuring platform
- Flue gas duct: Vertical, 4 m diameter, two access points on each half axis



- Clean gas parameters: 160°C, ca. 23 Vol.-% water, < 20 μg/m<sup>3</sup> Hg
- Fuel input: Lignite, waste derived fuel, sewage sludge











### **Results of the 2. Measuring Campaign 11. – 13.12.2012**



### **Comparison of the Methods applied in both Campaigns**



VGB Conference "Chemistry in Power Plants 2013", 30 and 31 October 2013 in Leipzig

# **Requirements for Application of DIN CEN/TS 14793**

- Up to 30 pairs of comparative values for each method.
- Outliner test according to Grubbs for each set of comparative values.

## **Test for Acceptance of Alternative Method**

- Repeatability of the alternative method must not be higher than the repeatability of the standard reference method.
- Linear regression must be evaluated ( $y = C_1x + C_0$ ).
- The following conditions must be fulfilled:

Condition:	Condition:	Condition:
R ≥ 0,97	$1-Sr(Zq)/Zq \le C1 \le 1+Sr(Zq)/Zq$	$C0 \leq Sr(Zq)$

Standard Reference Method EN 13211:  $Zq = 10 \mu g/m^3$ , Sr(Zq) = 1,2











## **Evaluation of EN 13211 and Dowex/AC Methods acc.**

OvGU	OvGU Alternativ Method					to DIN CEN/15 14/93							
		Comparative No. of Mea Measurements surements		- Averages		Variances							
Test Nr.	1			surements	s								
		$X_{r1}$	$X_{I2}$	$n_{i}$	$\overline{X_t}$	$\overline{X}^{2}$	$S^2_t(X)$	$X_i - Z_i$	$(X_{i1} - \overline{X}_{i})^2$	$\left(X_{cl} - \overline{X}\right)$	$\left(X_{i2} - \overline{X}\right)$	$\left(X_{i}-\overline{X}\right)^{2}$	$\left(X_{B} - \overline{X}\right)^{2}$
Test4		2,76	2,59	2	2,68	7,16	0,01445	7,35625	0,007225	-2,77	-2,94	7,67	8,64
Test6				-									5,29
Test7		Number of Samples for Evaluation acc. CEN/TS 1/702										7,07	
Test8		Number of Samples for Evaluation acc. CEN/15 14/93									5,33		
Test9													4,58
Test10		<ul> <li>36 samplings with each method in total</li> </ul>									5,29		
Test11		ou sumplings with cach method in total.									4,12		
Test12												5,61	
Test13		<ul> <li>30 sets of repeat samplings evaluable</li> </ul>									13,54		
Test14											14,51		
Test15		E acts of compliants aliminated by Chubba Test									13,54		
Test16		<ul> <li>5 sets of samplings eliminated by Grubbs Test</li> </ul>									12,60		
Test17													12,60
Test18		• 2	5 10	rified	sets c	of ren	eat sa	mnleg	s rema	inina	for		12,25
Test19		25 venneu sets ur repeat samples remaining fur									68,40		
Test20			02	ch m	othod								180,38
Test21			ъa		ethou								37,46
Test22													55,81
Test23		2,84	2,73	2	2,79	7,76	0,00605	5,645562	0,003025	-2,69	-2,80	7,23	7,84
Test24		2,25	2,06	2	2,16	4,64	0,01805	6,0890895	0,009025	-3,28	-3,47	10,76	12,04
Test25		6,43	5,96	2	6,20	38,38	0,11045	41,220347	0,055225	0,90	0,43	0,81	0,19
Test26		8,47	8,21	2	8,34	69,56	0,0338	/1,146914	0,0169	2,94	2,68	8,65	7,18
Test27		7,76	8,20	2	7,98	63,68	0,0968	65,322345	0,0484	2,23	2,67	4,97	7,13
Test28		9,77	9,37	2	9,57	91,58	0,08	99,754782	0,04	4,24	3,84	17,98	14,75
Test30		1,/4	1,61	2	1,68	2,81	0,00845	3,9701497	0,004225	-3,79	-3,92	14,36	15,36
					$\overline{\overline{X}}$	$SSD(X_b)$	$S_2(\overline{X})$	$SPD(\overline{BiZ})$	$S_r^2(X)$	R	C1	$S_r^2(X)$	
					5,35	536,0	22,33	545,73	0,03	0,996028	0,978187	-0,063747	











#### **Results of Method Comparison acc. to DIN CEN/TS 14793**













## **Summary and Conclusions**

- All applied sampling and measuring methods showed pretty well comparable results (as long as applied properly).
- All adsorption methods (Dowex/AC, EPA 30b, Amesa M) didn't show systematic deviations from the Standard Reference Method (SRM) EN 13211.
- The continuously measuring systems (CEMs) showed partly higher deviations from the SRM.
- The Dowex/AC method could be successfully validated according to CEN/TS 14793 as an alternative method to the SRM in the concentration range of 1 to 20 µg/Nm<sup>3</sup>.
- A validation of the differentiation between Hg(0) and Hg(ox) with the methods Dowex/AC and PSA was not possible with the available data.











#### Thanks to the teams for a good job!











