# Continous Emission Monitoring of toxic and reactive gases

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#### EXAMPLE : CEMENT KILN EMISSIONS



Monitoring is normally required due to environmental regulations

A limited number of parameters are monitored, typically NOx,SO2,CO,O2 and Dust/Opacity





Cement manufacturing process



#### EMISSIONS FROM CEMENT PLANTS



NOX (Nitrogen Oxides) is developed during combustion of fuel and air, and is temperature dependent

SO2 (Sulfur Dioxide) is developed from sulfur in the raw material and the fuel, and the final emissions also depends on the process used.



CO (Carbon Monoxide) is typically a result of poor combustion

CO2 (Carbon Dioxide), is developed from carbon content in the fuel during combustion and from processing the raw material



#### SPECIAL EMISSIONS



TOC (Total Organic Carbon) is developed due to heating of raw material containing hydrocarbons, and from using certain alternative fuels ,mainly consiting of Methane (CH4) and may also contain VOC's such as Benzene, Toluene, Xylenes etc

Other gases of interest could be HCL(Hydrogen Chloride), HF,NH3 and Hg (Mercury) depending on the composition of the raw material or alternative waste coincineration



#### EXAMPLE, EUROPEAN REGULATION

EC Directive 2000/76/EC applies to Waste Incineration plants and Cement plants using co-incineration

Compound	Emission limit value 24 hour				
	(mg/m3 , NTP, 10 % O <sub>2</sub> )				
Particles	30				
ТОС	10				
HCI	10				
HF	1				
SO <sub>2</sub>	50				
NO <sub>X</sub>	800/500 (old/new plant)				
СО	Set by local authority				



#### NEW REGULATIONS FOR MERCURY

- USA, Proposed federal MATS rules for Coal Fired Power Plants, requires CEMS for continous monitoring by 2015. Limit value for coal fired plants, 0.013 lb/GWh
- USA, Existing MACT rules for Cement Plants, CEMS for continuous monitoring. Limit value 10 ug/Nm3 for existing plants, 4 ug/Nm3 for new plants
- EU has ongoing discussions for new Mercury regulations.Germany and Spain already have regulations for Mercury from Waste Incineration Plants and Coal Fired Power Plants



## THE DOAS MONITORING SOLUTION

( DOAS= Differential Optical Absorption Spectroscopy)



Absorption Spectrum

Analyser



#### IN-SITU,NON-CONTACT,CROSS STACK MONITORING



- Non-contact measurements works well with corrosive and reactive gases
- Non Sampling Monitoring Solution, for Maximum Reliability and Minimum of Maintenance !



#### DOAS APPLICATIONS FOR MERCURY

 UV DOAS can monitor Hg<sup>0</sup> in situ in raw (untreated) gas

 UV DOAS + converter can monitor Hg<sup>TOT</sup> in final emissions



#### OPSIS SYS400HG FOR TOTAL MERCURY





#### SYSTEM400HG OVERVIEW





#### MERCURY CALIBRATION

- Calibration of Hg<sup>0</sup> using closed cells
- Calibration of Hg<sup>TOT</sup> using Hovacal gas generator



#### SYS400 FLEXIBILITY

 Can be configured as a dedicated system for Hg<sup>TOT</sup> only

 Can be configured as a complete CEM system for Hg<sup>TOT</sup> + NO, NO<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, HCI, HF, CH<sub>4</sub>...



#### EXTRACTIVE HGTOT SYSTEM CAN BE ADDED TO EXISTING DOAS MULTIGAS CEMS





#### EXTRACTIVE HGTOT SYSTEM CAN BE ADDED TO EXISTING DOAS FAST LOOP SOLUTION





#### SYS400HG CERTIFIED BY TÜV

Calculation of overall uncertainty according to EN 141 Measuring system Name of measuring system Serial number of the candidates Measuring principle Test report Test aboratory Date of report Measured component Certification range Evaluation of the cross sensitivity (CS)	81 and Opsis AR60 1498 UV - 936/2 TOV 2011 Hg	AB 122/Hg 1499 DOAS 1215492 Rheinlan 10-10	267-3 IA		
Measuring system Manufacturer Name of measuring system Serial number of the candidates Measuring principle Test report Test laboratory Date of report Measured component Certification range Evaluation of the cross sensitivity (CS)	Opsis AR60 1498 UV - 936/2 TÜV 2011	AB (2Z/Hg / 1499 DOAS 21215492 Rheinlan	A		
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Measured component Certification range Evaluation of the cross sensitivity (CS)	Hg		1		
measured component Certification range Evaluation of the cross sensitivity (CS)	Hg				
Evaluation of the cross sensitivity (CS)	0.	45	ug/m²		
Evaluation of the cross sensitivity (CS)		40	P.S.		
, , ,					
(system with largest CS)					
Sum of positive CS at zero point		0.00	hð/w,		
Sum of negative CS at zero point		-0.50	hð/m.		
sum of penative CS at reference point		-1.10	µg/m²		
Maximum sum of cross sensitivities		1.10	ug/mª		
Uncertainty of cross sensitivity		0.694	µg/m³		
Calculation of the combined standard uncertainty					
lested parameter		U		u*	(under Die
Standard deviation from paired measurements under field conditions."	UD	0.730	µg/m²	0.042	(µg/m²)²
Zero drift from field test	Ultr	-0.442	ug/m <sup>a</sup>	0.195	(µg/m²)²
Span drift from field test	Uda	-0.650	ua/mª	0.423	(µg/m²)²
Influence of ambient temperature at span	U,	0.153	µg/mª	0.023	(µg/m²)=
Influence of supply voltage	Uv	0.208	µg/m³	0.043	(µg/m²)²
Cross sensitivity (interference)	u	0.694	µg/mª	0.481	(µg/m³)*
Influence of sample gas flow	u <sub>p</sub>	-0.049	µg/mª	0.002	(µg/m*)*
Uncertainty of reference material at 70% of certification range The larger value is used : "Repeatability standard deviation at span" or	Urm	U.304	hð/ш.	0.132	(µg/m*)*
"Standard deviation from paired measurements under field conditions"		_	_		
Combined standard uncertainty (uc)	u	√∑ (u_	m, ) <sup>2</sup>	1.42	µg/mª
Total expanded uncertainty	U = u	l,*k = u,	1.96	2.78	µg/m*
Relative total expanded uncertainty	U in 9	% of the	ELV 30 µg/i	m²	9.3
Requirement of 2000/76/EC and 2001/80/EC	U in 9	% of the	ELV 30 µg/	m'	40.0
Requirement of EN 15267-3	Uin	% of the E	LV 30 µg/m		30.0



#### **PROCESS CONTROL APPLICATIONS**



Cement manufacturing process

#### CEM information





Feedback to Process



#### SCRUBBER / REACTOR CONTROL



**CEM + Process control** 



#### MULTIPLE STACK MONITORING OF NH3,CL2,HCL AND HF AT SEMICONDUCTOR PLANT IN CHINA





#### 9 STACKS MONITORED BY TWO OPSIS SYS400





#### PICTURES FROM SITE



Station 1#



Station 2#



The Stacks



#### PICTURES FROM SITE





Receiver

-							
Path Path	1 1.250 m 3 1.250 m	21 °C 21 °C	181.3 kPa 181.3 kPa	Path 2 Path 4	1.258	21 °C 21 °C	101.3 kP
1 -		C12					
Conc Bev Lght		8.8 ng/n3 8.8 ng/n3 91.8 %					
Conc Bev Lght			8.4 ng/ni 8.8 ng/ni 91.4 %	3			
Conc Dev Lght				8.1 8.8 98.6	ng/n3 ng/n3 %		
Conc Bev Lght	8.7 ng/n3 8.8 ng/n3 53.1 %						

Measuring: HCL, 2			PO Disk : 511.6 MB		RAM :	888; 235 kB	30 Tim	) me : 17:00	
Path 1 Path 3	1.250 m 1.250 m	21 °C 21 °C	101.3 kPa 101.3 kPa	Path 2	1.250	n 21	°C	101.3 kPa	
1 Conc Dev Lght 2 Conc Dev Lght 3 Conc Dev Lght	HCL -0.2 ng/n3 0.1 ng/n3 64.0 % HCL 0.5 ng/n3 0.1 ng/m3 71.0 % HCL 0.1 ng/m3 0.1 ng/m3 68.0 %	HF 0.1 mg/n3 0.1 mg/n3 51.0 % HF 0.3 mg/n3 68.8 % HF 0.3 mg/n3 68.8 % HF 0.3 mg/n3 56.8 %							

The Measurement Data



#### MONITORING THC AND VOC'S





#### THC COMPARISON FID VS DOAS





## CALIBRATION OF TOXIC AND REACTIVE GASES



Opsis standard calibration kit can be used

Some gases requires a gas generator such as HgCL2 for HgTOT and HF, as they are not stable in gas cylinders

Higher concentrations and shorter cells will elimanate problems related to reactive gases

Closed cells with liquid/vapor can be used for some toxic gases such as Hg<sup>0</sup>



#### CALIBRATION OF DOAS SYSTEMS

 $(C_p \times L_p = C_c \times L_c)$ 

Example: 100 ppm x 2 m = 1000 ppm x 0.2 m

"Optical density"  $C_{p=}$  Concentration in the measuring path  $L_{p=}$  Length of the measuring path(/diameter)  $C_{c=}$  Concentration in the cell (=gasbottle)  $L_{c=}$  Length of the Calibration Cell



#### ZERO AND SPAN CALIBRATION





#### MULTIPOINT/LINEARITY CALIBRATION



OPSIS



#### MULTIPOINT/LINEARITY CALIBRATION





## OTHER MONITORING SOLUTIONS

#### **Complete AQM stations**



## www.opsis.se

#### Data presentation and reporting



#### Dust / PM10/PM2.5



Metereological masts



DOAS open path system



Public information





#### FENCE-LINE MONITORING OF FUGITIVE EMISSIONS IN INDUSTRIAL AREAS





## FENCE LINE MONITORING SOLUTIONS





#### WORLDWIDE OPSIS FENCELINE SYSTEMS



Saudi Aramco

Porto Marghera ,Italy









#### TOTAL MONITORING AND MANAGEMENT SOLUTION FOR INDUSTRIES





# Thank you for your attention!

