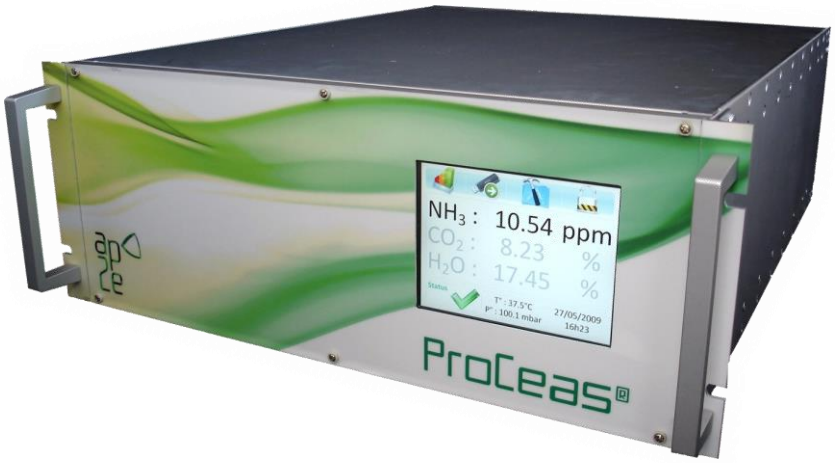
On-line gas analyzers

Resonant cavity laser spectrometry – Low Pressure Sampling : 2 patents dedicated to atmospheric emissions monitoring



Atmosfair
09.06.2015

David Chauvel – Sales Manager
d.chauvel@ap2e.com

Contents

- Overview
- Organization
- Markets
- Technologies/benefits
- Products
- Case study : atmospheric emissions monitoring on some incineration plant

Company overview

- 2006 : creation of AP2E
- 30 : years of experience in online gas analysis
- 2 : patents OFCEAS (technologie laser İR laser spectroscopy) and LPS (Low Pressure Sampling)
- 5 departments R&D : chemistry, optics, metrology, mechanics, electronics / software
- 29 : employees including 15 engineers / PhD
- 400 : analysers worldwide
- 25 : measured gases

Our partners

Investors

ACG MANAGEMENT

PACA INVESTISSEMENT
FINANCEUR D'INNOVATION - CRÉATEUR DE VALEUR

Technology

UNIVERSITE JOSEPH FOURIER
SCIENCES.TECHNOLOGIE.SANTÉ

Floralis
Cultivons l'innovation

spectro
Laboratoire de Spectrométrie Physique

Industrial clusters

AXELERA
catalyseur de croissance durable

Optitec
Pôle photonique & imagerie

PÔLE RISQUES

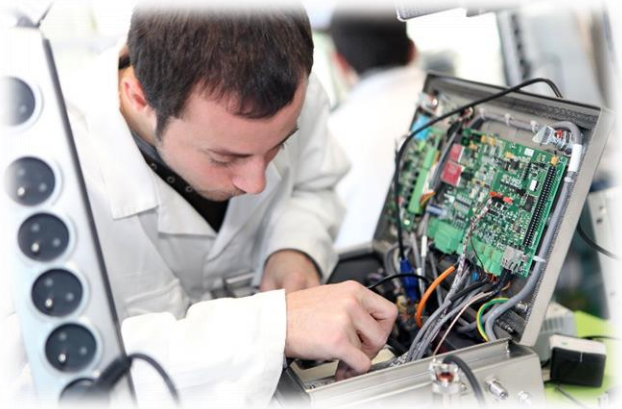
What we do

Sales

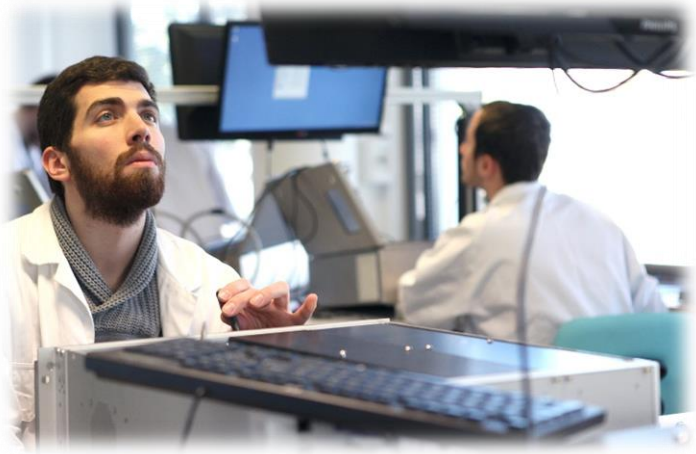
Production

R&D

Integration & commisioning



Training



After sales (diagnosis & maintenance)

Facilities : 1000 m², production capacity of 300 analysers / year

1 electronic labaratory

- Welding
- Oscilloscopes
- Signal generators

1 optical laboratory

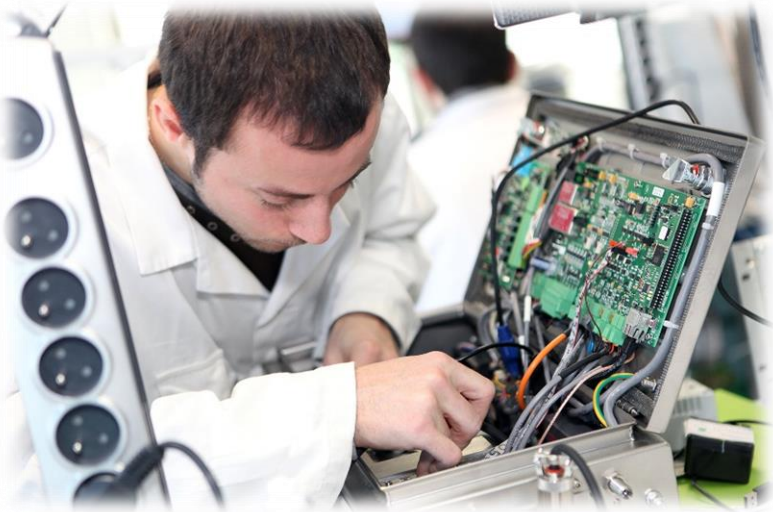
- Optical bench
- Infra-red camera

1 metrologic laboratory

- Standardised gases and gas expanders
- Gas mixers
- Humidity generator

1 engineering service for mechanics and thermics

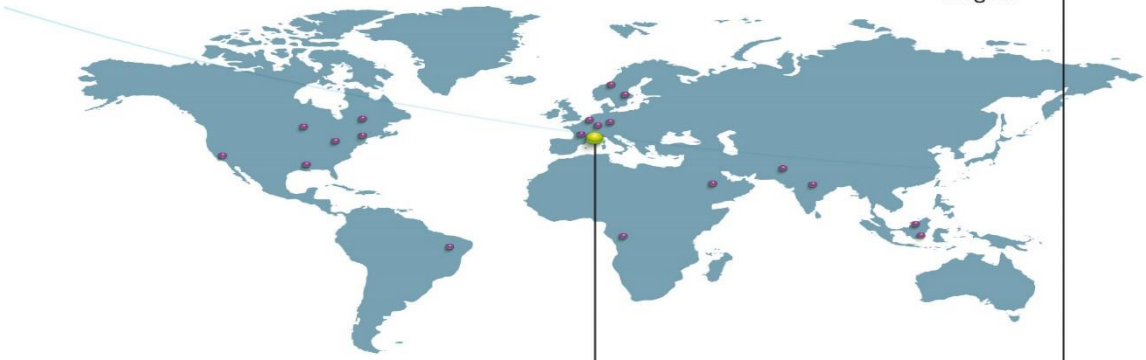
- CAO (Solid Works)
- Climatic room



Our analysers worlwide

NOS ANALYSEURS DANS LE MONDE
OUR ANALYSERS WORLDWIDE

France
USA
Pays bas
Norvège
Allemagne
Suède
Luxembourg
Malaisie
Pakistan
Inde
Brésil
Indonésie
Arabie Saoudite
Angola



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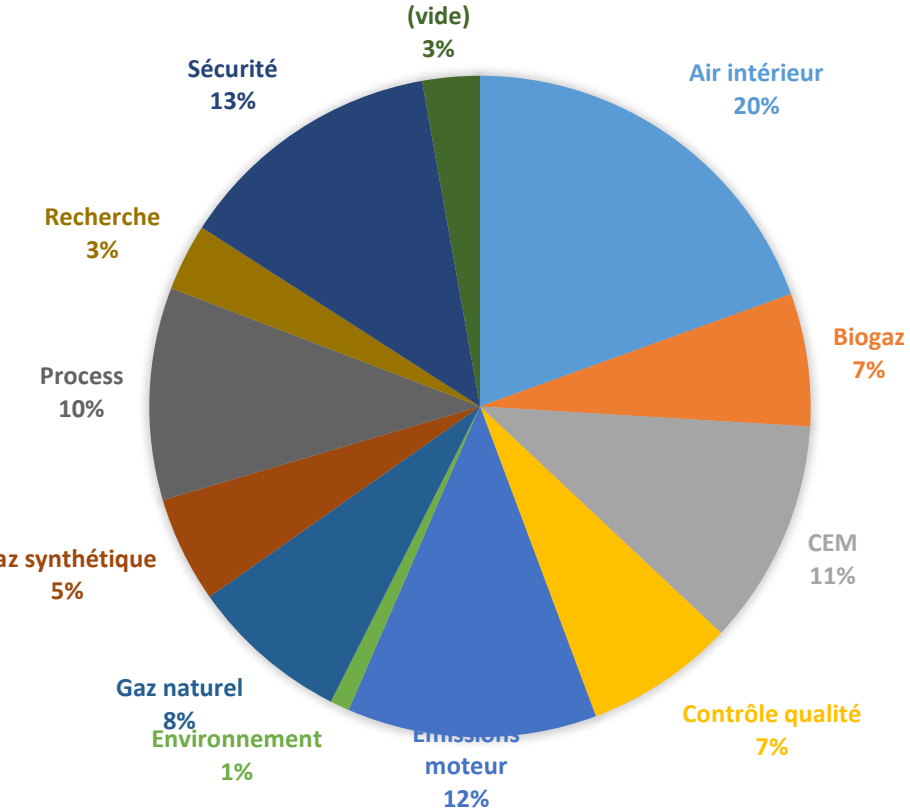
Applications



- Process optimisation for energy production : renewables and biofuel (Biogaz, Syngaz)
- Optimisation and control of the cycle of combustion gases of heavy burners (boilers, incinerators, refineries),
- Control of the greenhouse gases on engine test benches for the automotive industry
- Control of the indoor air (submarines, buildings)
- Quality of the natural gas and pure gases (nitrogen, hydrogen)
- Quality and safety of the powder drying (food, cosmetic, pharmaceutical industries)
- Regulatory emissions measurement (CEM)

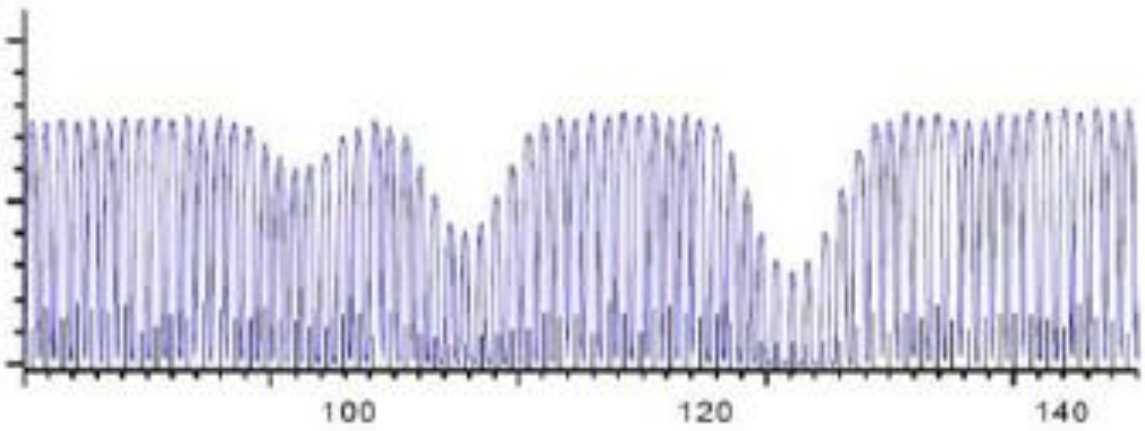
Some of our references

DGA
SIEMENS
Nestlé
ape
IFE Institute for Energy Technology
Elektronik-Kontor Messtechnik
MICHELL Instruments
AIR LIQUIDE
ARKEMA INNOVATIVE CHEMISTRY
DCNS
Creative Oxygen
cea
GDF SUEZ
PRAXAIR
university of groningen
INSA LYON
NOVARB
EAU & Industrie
ARTELIA
SP your Science Partner
SIMTRONICS Fire & Gas
AREVA
MIDREX
cnrs dépasser les frontières
hobré instruments bv
Centre de Recherche Public Gabriel Lippmann
VEOLIA PROPRETÉ
SARP Industries Gestion des Déchets Spéciaux
CLEMESSY
COFELY GDF SUEZ
EXXON
TERRABON
Esso
sensors

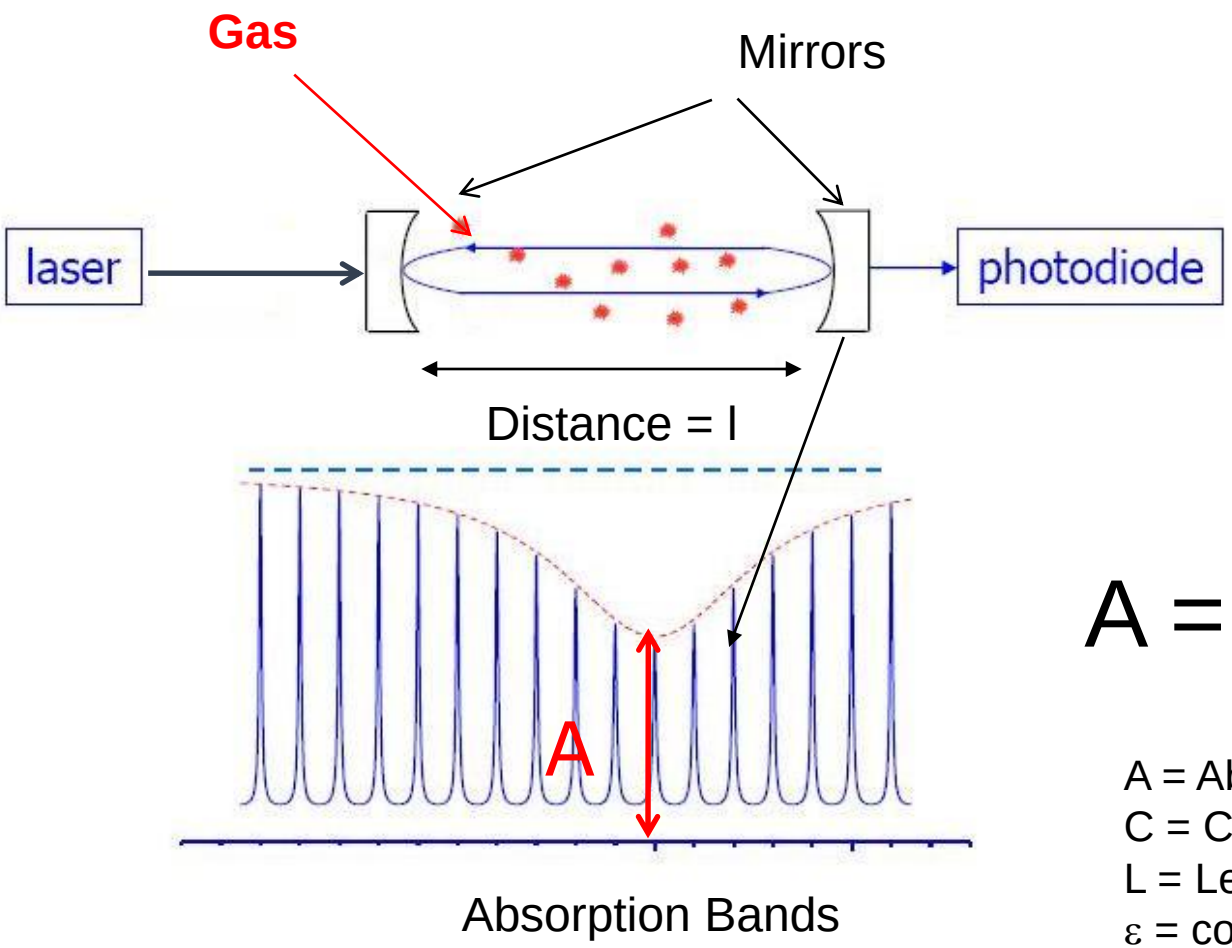
Laser spectroscopy working principle - Beer Lambert Law

- Each gas has a spectral absorption signature
- By measuring the absorption, we can characterize and quantify the gas

Raw spectrum for NH3



Laser spectroscopy working principle - Beer Lambert Law



$$A = C \times l \times \varepsilon$$

A = Absorption
C = Concentration
L = Length
ε = constant

OFCEAS Technology - Patent WO 03031949

Optical

Feedback

Cavity

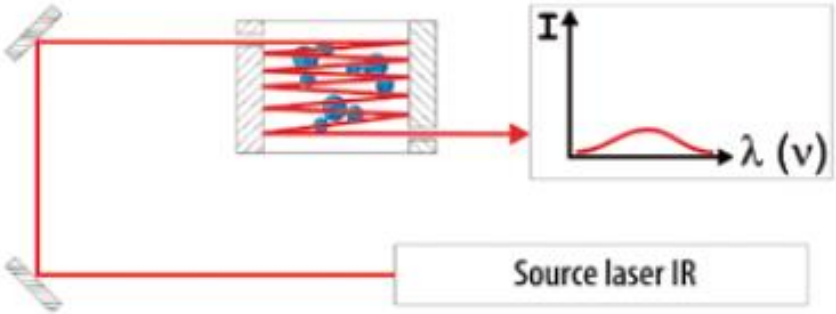
Enhanced

Absorption

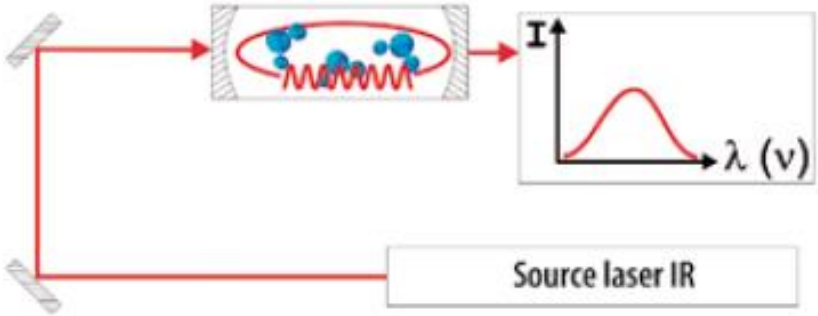
Spectroscopy

From IR Spectrometers to OFCEAS

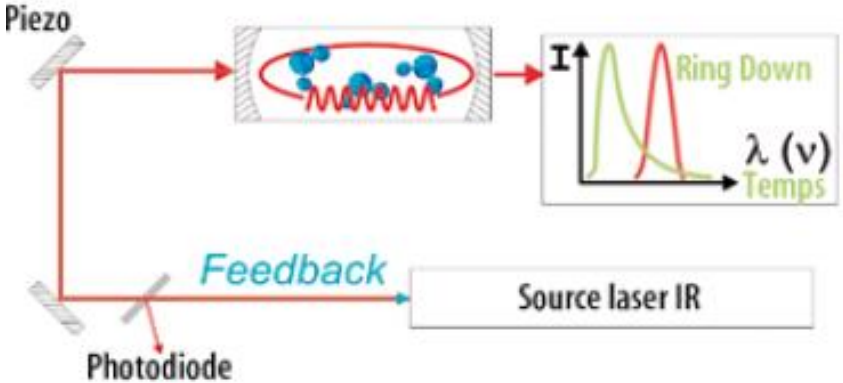
1. Traditionnnal IR spectroscopy:
Multipass Gas Cell
Pathlength = l_1 = 1 – 10 m



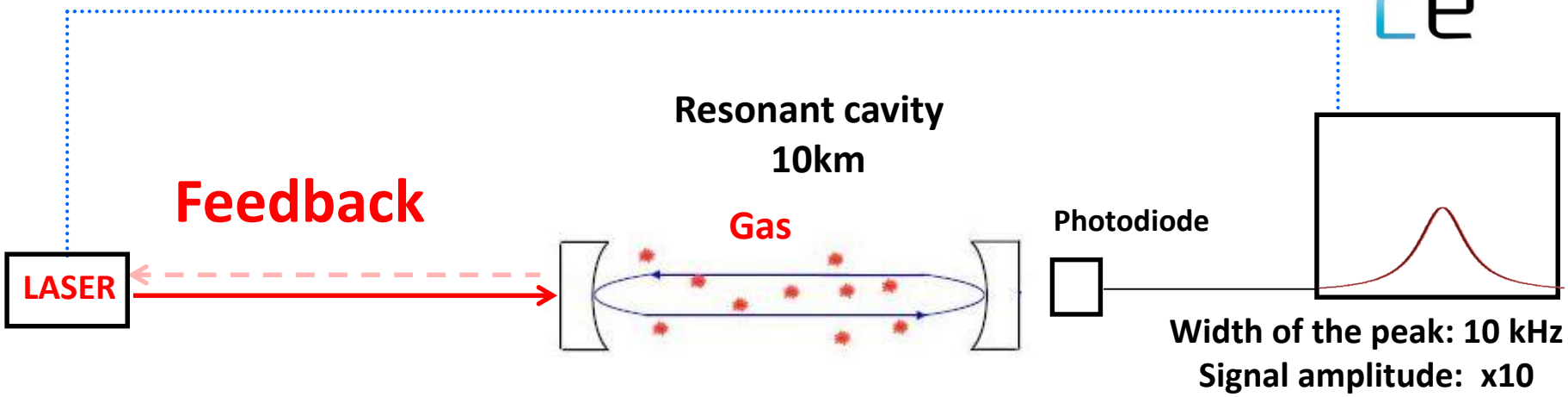
2. Improved spectroscopy
(hyper reflective gas cell – cavity resonance)
Pathlength = l_1 = 1 – 10 km
Increase the sensitivity by 1 000

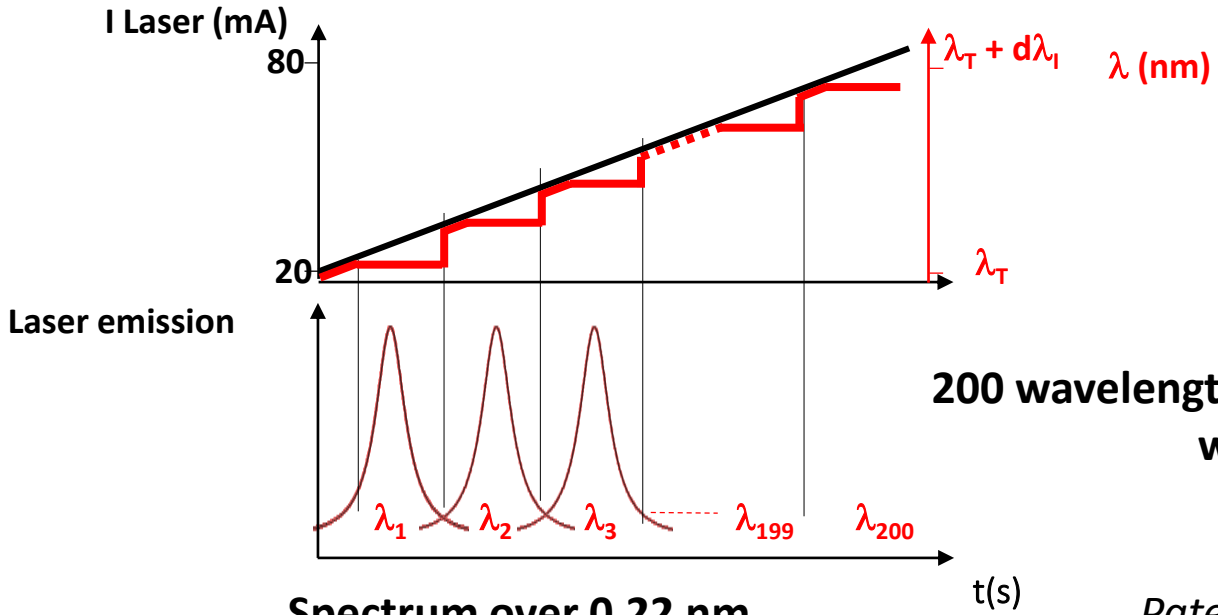


3. AP2E spectroscopy (OFCEAS)
Pathlength = l_1 = 1 – 10 km
Feedback (increases the laser purity, optical resolution)



Tehnology:
Optic principle (Feedback)





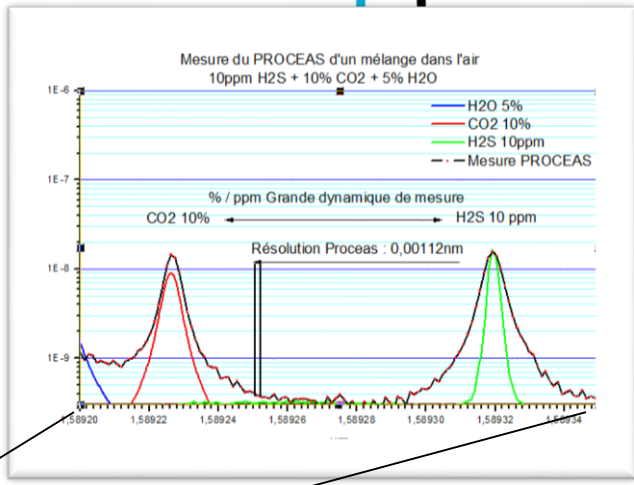
200 wavelengths of 0,00112 nm wide

Spectrum over 0,22 nm
«Sweep of 200 wavelengths»

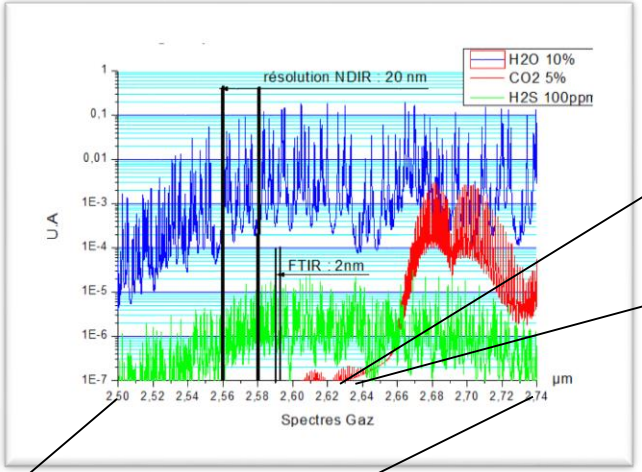
Patent WO03031949

From IR Spectrometers to OFCEAS

0,22nm

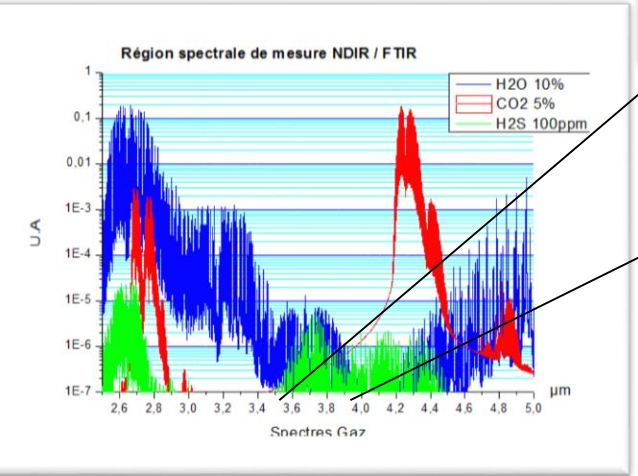


2 nm



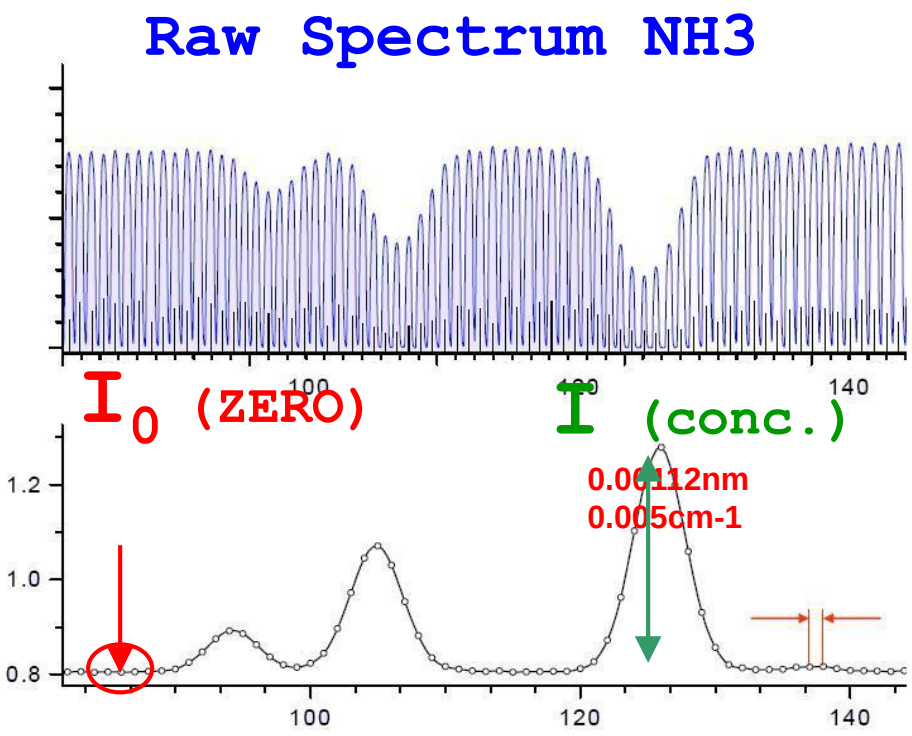
20 nm

FTIR / NDIR



OFCEAS
No risk of interference with matrix

From IR Spectrometers to OFCEAS

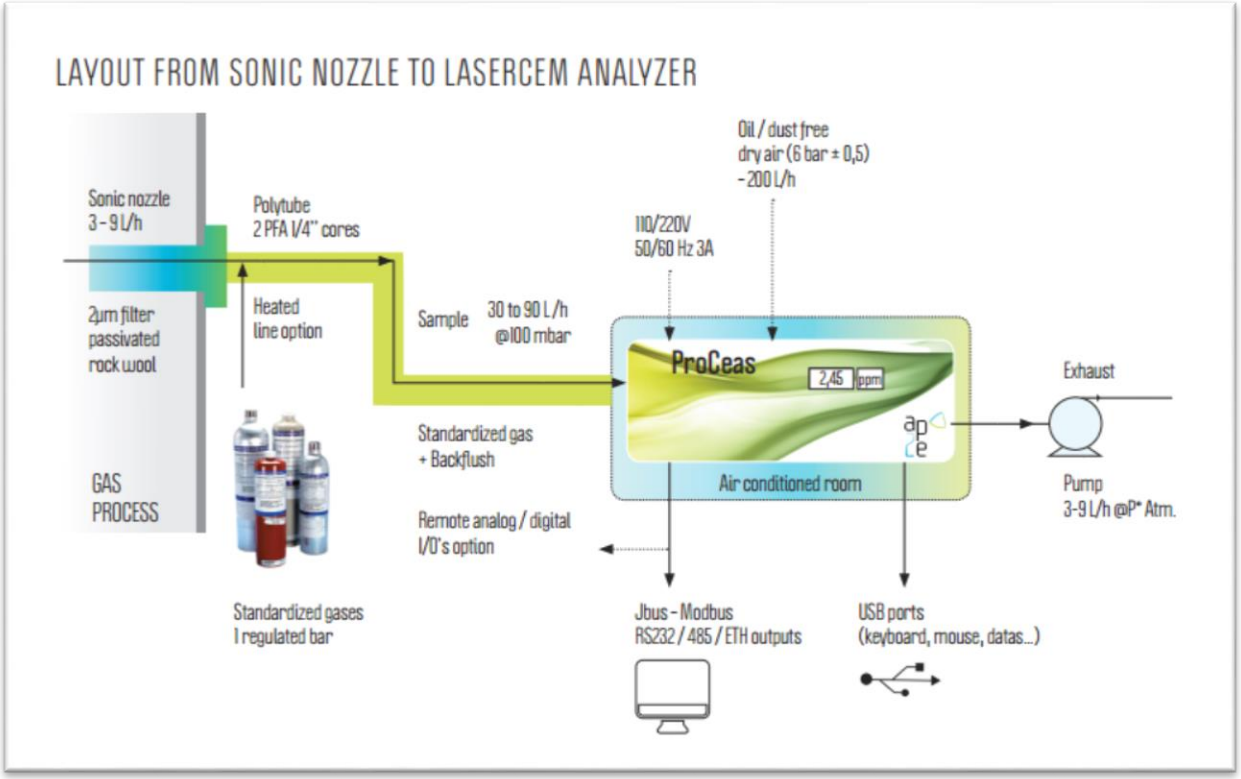


Each spectrum contains both **I** (concentration) and $\mathbf{I_0}$ (re-zero) information.

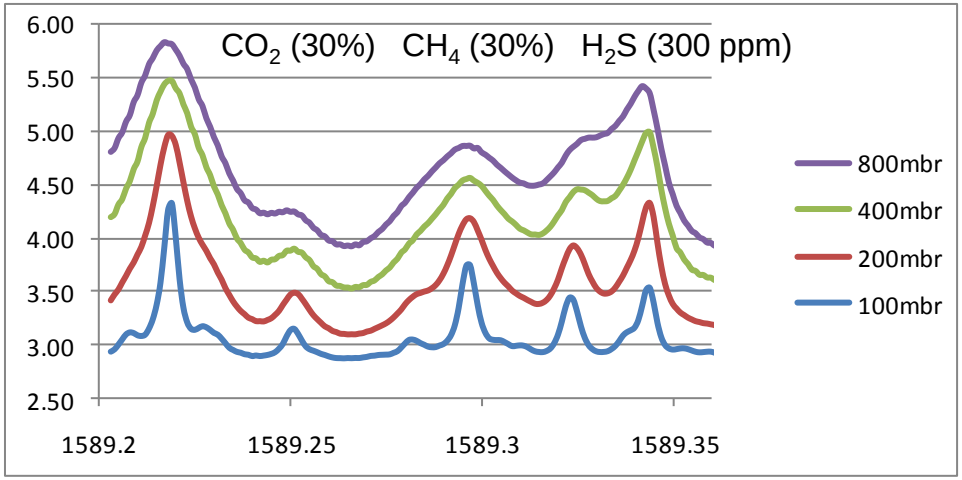
NO REFERENCE GAS REQUIRED.
NO RE-ZERO
NO DRIFT / NO CALIBRATION REQUIRED

LPS system - Patent WO 2010058107

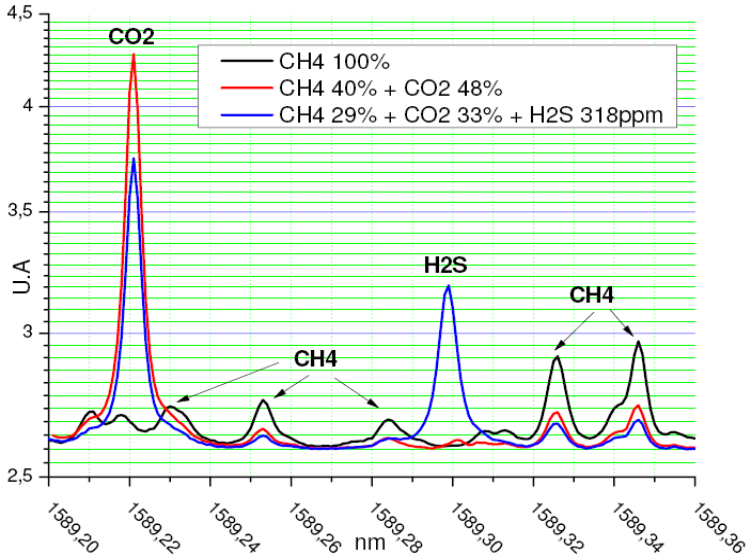
Low
Pressure
Sampling



Low Pressure (100 mBar) Sampling



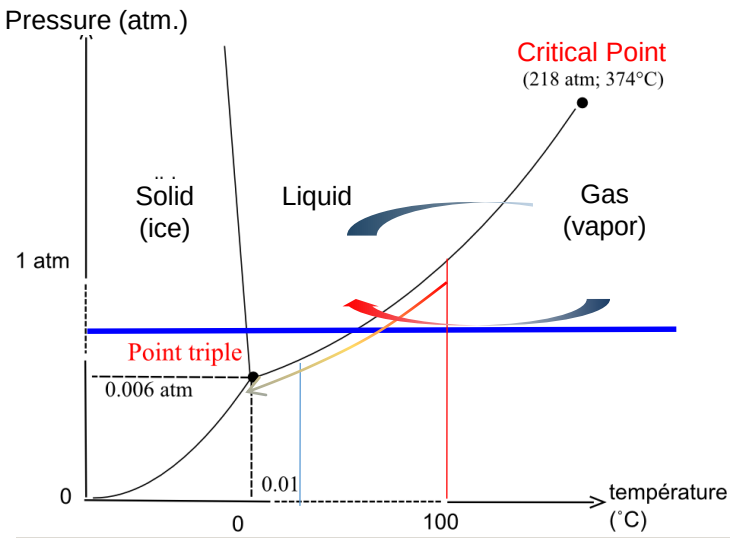
Narrows the bandwidth of the absorption bands to use the full potential of the extremely low optical resolution. Avoids interferences and false positive response.



Absorption Bands Narrowing, Matching Spectral Information To Optical Resolution

Low Pressure (100 mBar) Sampling

Avoiding Condensates in the Sampling Line



As pressure goes down …

… so does the boiling point …

… and so does the dew point..

Avoiding Condensates In The Sampling Line
No need of heated line

Low Pressure (100 mBar) Sampling

Flow Rate @ Sampling Probe	3 – 9 L/h
Flow Rate @ Inside Line	30 – 90 L/h
Transfer Time (4/6 tubing)	~ 5 sec / 10 m

Steel wool filter after 3 month of use sampling post-SCR emissions at a trash incinerator facility.

Self-Cleaning

Faster Sample Transfer Times

Summary of benefits / costs advantages

Analytical

1. Higher Sensitivity (more signal / less noise)
2. Multi-Gas Capable (CEM up to 7-8 gases in 1 analyser)
3. No Interference with matrix
4. 4 decades dynamic range (from ppm to %)
5. Fast Response

Industrial

1. No Sample Conditioning (no need of heated line)
2. Low Fouling (no filter clogging)
3. No consumables
4. Self-Referencing – No Re-Zero Required
5. Self-Stabilizing – No Drift with time
6. Fast Transfer Time

Low maintenance
Low cost of possession

GASES

GAZ ANALYSÉS*

ANALYZED GAS*

*Non-exhaustive list

Diatomic	H_2	O_2			
Nitrogen	NH_3	NO	N_2O	NO_2	HCN
Sulfur	H_2S	COS	CS_2		
Oxides	SO_2	SO_3	CO	CO_2	H_2O
Halogenides	HF	HBr	HCl	$ClCN$	
Alcohols	CH_3OH	C_2H_5OH			
Aldehydes	CH_2O	C_2H_4O			
Hydrocarbons	CH_4	C_2H_2	C_2H_4	C_2H_6	

*Liste non exhaustive

Versions/integratio

- 19’’ rack mounted in cabinet

- Wall mounted

- Navy – small size

Case study : Atmospheric emissions monitoring

Company : SAVE

Activity : Incineration

Location : Cornillé

Normative background

- In the framework of the French and European standards (NF EN 14 181), it is mandatory for industrials to monitor their polluants atmospheric emissions (CEM: Continuous Emission Monitoring) when it comes to combustion or waste incineration plants.

- CEM measurements (NOx, SOx, NH3, CO, CO2, HCl, HF, H2O, H2S etc.) are implemented to control the respect of these obligations by industrials.

QAL (Quality Assurance Level)

- QAL 1 : evaluation by manufacturer of the aptitude of the analyser to comply with uncertainties requirements (linearity, accuracy, repsonse time….)
- QAL 2 : evaluation / calibration of the analyser on site - reference method
- QAL 3: control of the drift and fidelity over time
- AST : annual monitoring to control variability and calibration of the analyser

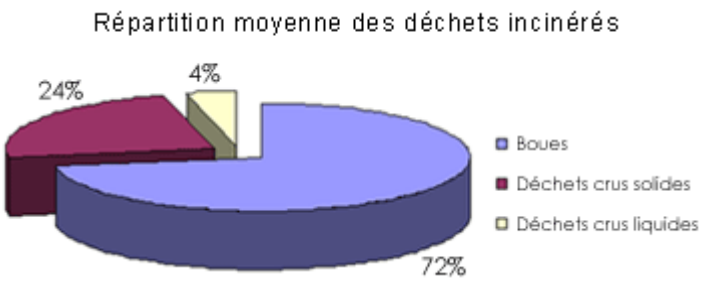
Activity

Incineration of Materials :

- sludge from wastewater of treatment plants
- organic waste unsuitable for material recovery , from the food business

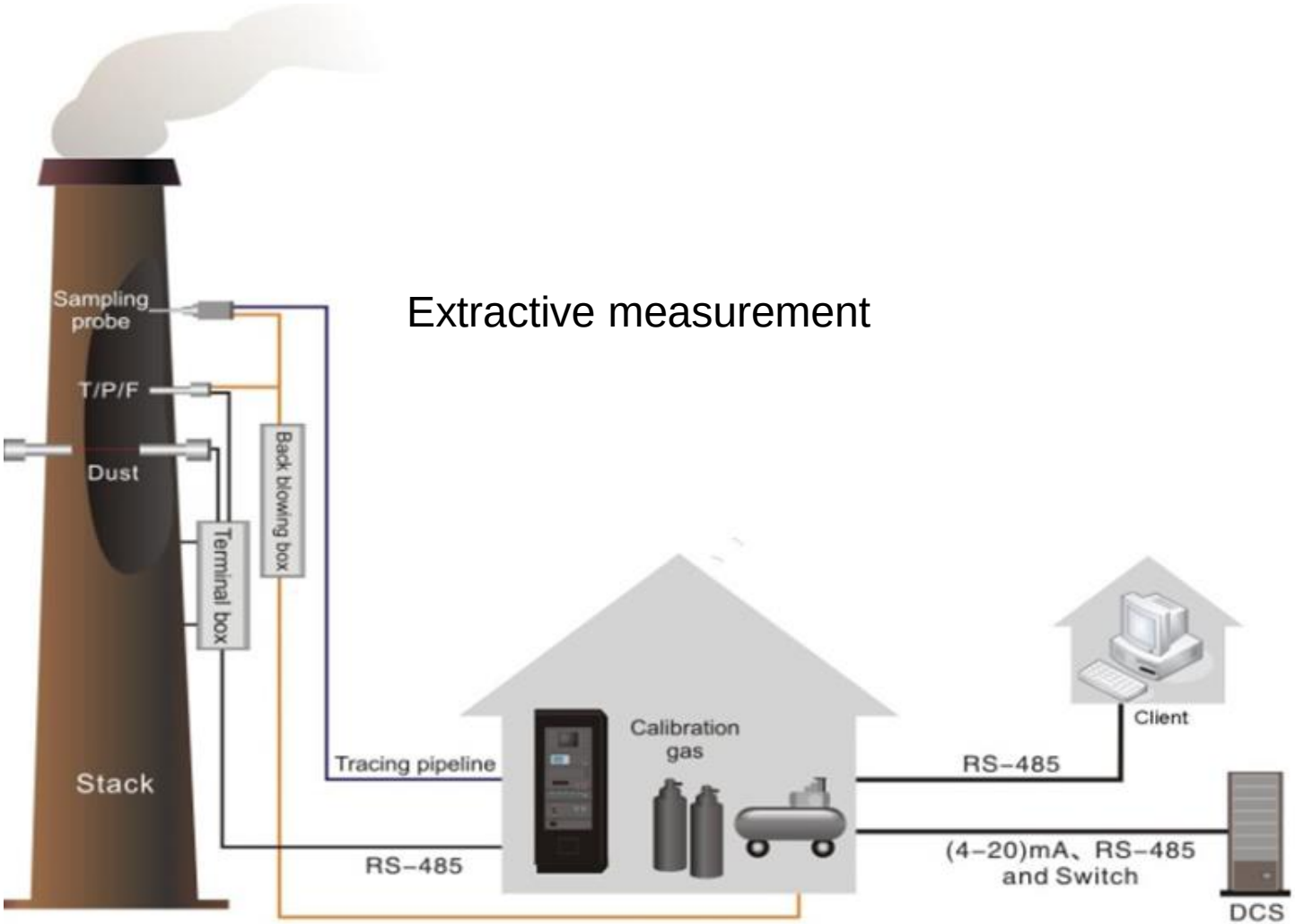
Energy → vapour

MATIÈRES INCINÉRÉES	TONNES DE MATIÈRES BRUTES
Sludge	35 000 T / an
Solid waste	12 500 T / an
Liquid waste	2 500 T / an
TOTAL	50 000 T / an



Typical CEM installation layout

Extractive measurement

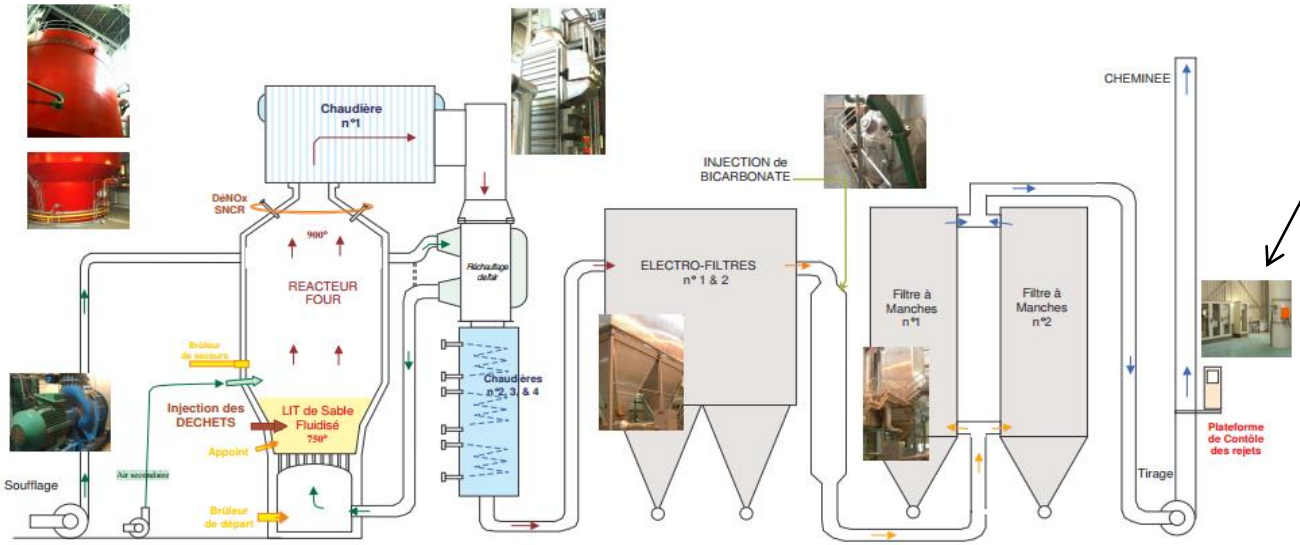


Atmospheric emissions

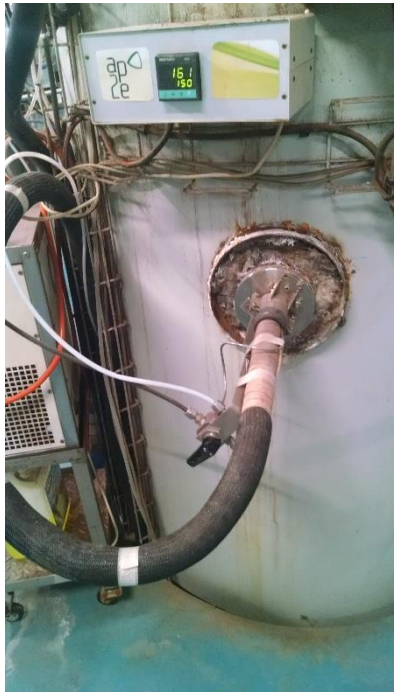
- Measurement of SO2, NO, HCl, H2O, NH3, CO, CH4 as a redundant system since 2012
- Sampling line : 20 meters
- DeNox SNCR system and condensing system

S.A.V.E.
Schéma synoptique de l'installation

On line CEM analysers



Sampling, cabinet, calibration bottles



Campaign of measures

Bilan des deux campagnes de mesures Année : 2013

Polluants de l'air en mg/Nm^3 Fractions solide et gazeuse		Mesure de avril 2013 Socotec	Mesure de oct.2013 Socotec	Limite Réglementaire	
Sur Gaz secs à 11% O_2 ↓		< LQ = ½LQ	< LQ = ½LQ	VLE ½h	VLE Jour
Débit fumées	Nm^3 sec				
	à 11% d'O_2	21 550	21 933		
Oxygène	%O_2	9,3%	10,2%		
Dioxyde de Carbone	CO_2	9,40%	8,7%		
44g/mole		184,6 g	170,9 g		
Monoxyde de Carbone	CO	13,0 mg	4,1 mg	100 mg	50 mg
Composés organiques	COV	3,0 mg	1,9 mg	20 mg	10 mg
Oxydes d'azote	NOx	61,4 mg	100,7 mg	400 mg	200 mg
Dioxyde de soufre	SO_2	1,2 mg	10,7 mg	200 mg	50 mg
Poussières	TSP	0,07 mg	0,79 mg	30 mg	10 mg
Acide chlorhydrique	HCl	0,6 mg	2,5 mg	60 mg	10 mg
Acide fluorhydrique	HF	0,1 mg	0,12 mg	4 mg	1 mg
Ammoniac gazeux	NH_3	20,3 mg	9,7 mg		
Protoxyde d'Azote	N_2O				
Dioxines et furanes	PCDD /-F	0,0011< y <0,0012	0,0035< y <0,0059	0,100 ng	
Sur Gaz secs à 11% O_2 ↓		< LQ = ½LQ	< LQ = ½LQ		
Σ Métaux Lourds	cf. AP	0,029< y <0,034	0,073< y <0,0764	0,500 mg	
Σ Cadmium + Tallium	Cd+Tl	0,0007< y <0,0013	0< y <0,0007	0,050 mg	
Mercure	Hg	0,013 mg	< 0,010 mg	0,050 mg	
Sur Gaz secs à 11% O2 ↓		< LQ = ½LQ	< LQ = ½LQ		
Arsenic	As	< 0,4 µg	< 0,4 µg		
Cadmium	Cd	< 0,3 µg	< 0,3 µg		
Cobalt	Co	< 0,3 µg	< 1,8 µg		
Chrome	Cr	21,5 µg	6,4 µg		
Cuivre	Cu	1,8 µg	< 31,3 µg		
Mercure	Hg	< 13,0 µg	< 10,4 µg		
Manganèse	Mn	1,6 µg	< 2,0 µg		
Nickel	Ni	< 2,7 µg	< 3,0 µg		
Plomb	Pb	3,1 µg	< 30,8 µg		
Antimoine	Sb	< 0,5 µg	< 0,5 µg		
Thallium	Tl	1,0 µg	< 0,5 µg		
Vanadium	V	< 0,2 µg	< 0,2 µg		

Feedback of customer :

- Reliable measure, no drift
- Very short reponse time (8 sec approx. in « CEM » application). 3 x times faster than other techniques. Very interesting for process
- Very easy calibration (remark : injection and measure of standardized gas in real matrix)
- Very good sensibility and precision.
- Compact
- Very friendly interface, data access
- Remote maintenance : easy and friendly.
- Benefit to work at low pressure. No 180°C heated line
- Very low signal interferences
- Low fouling - Low salt formation

Thank you for your attention