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Carbon Capture and Storage Program

EMISSION MEASUREMENTS TO A NEW LEVEL

Eerik Järvinen, Ramboll Finland Oy

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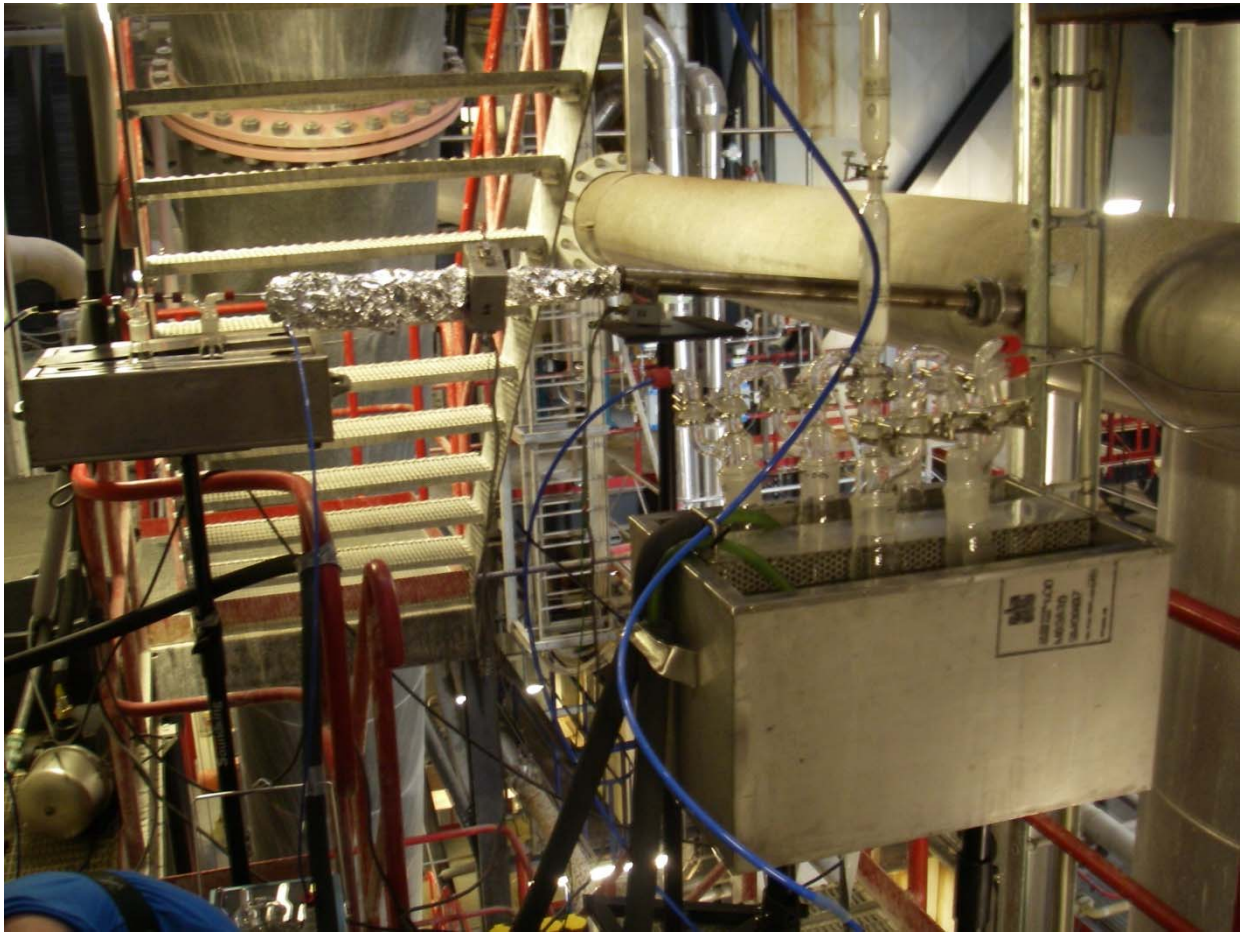
What we did?



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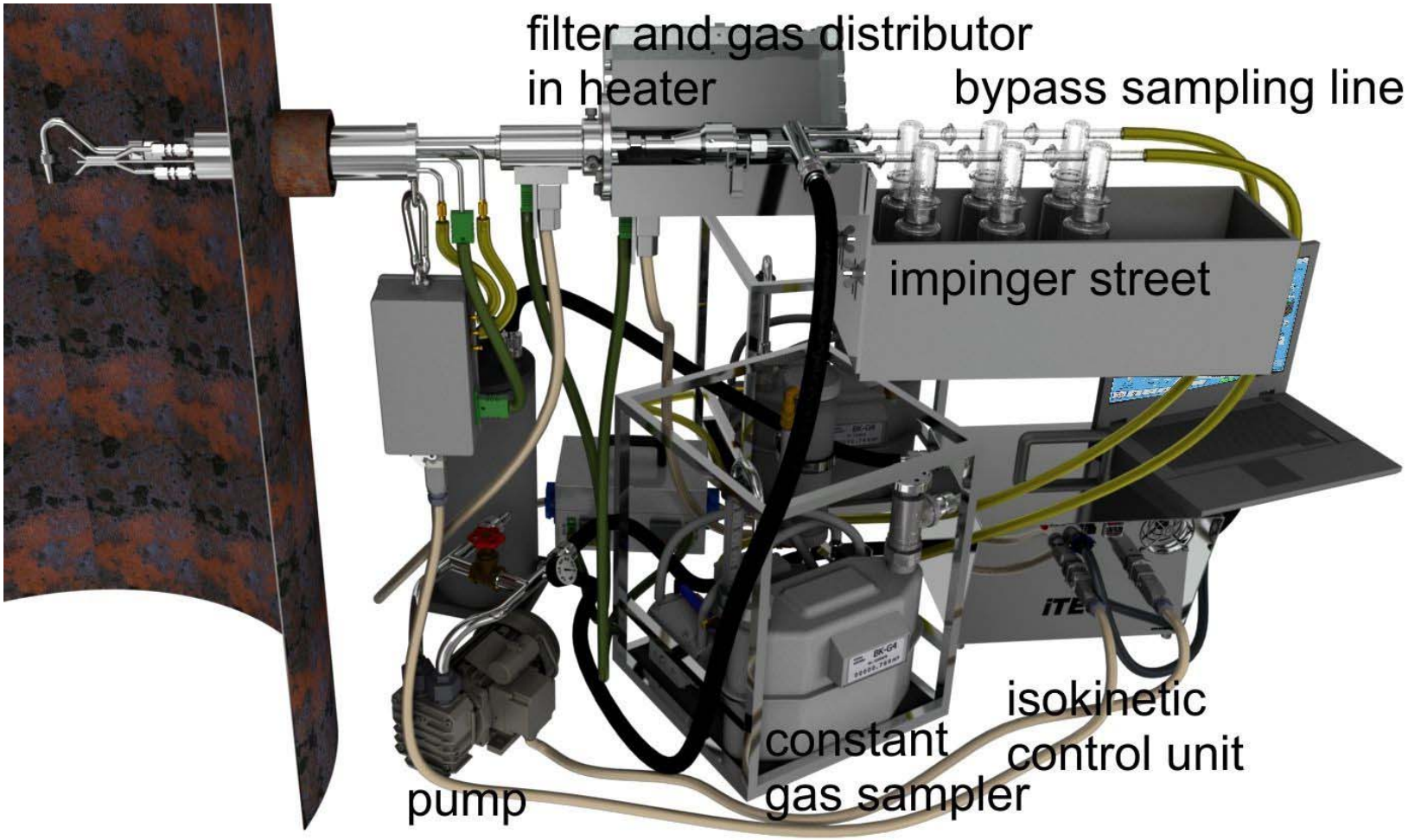
filter and gas distributor
in heater
bypass sampling line
impinger street
isokinetic
control unit
constant
gas sampler
pump

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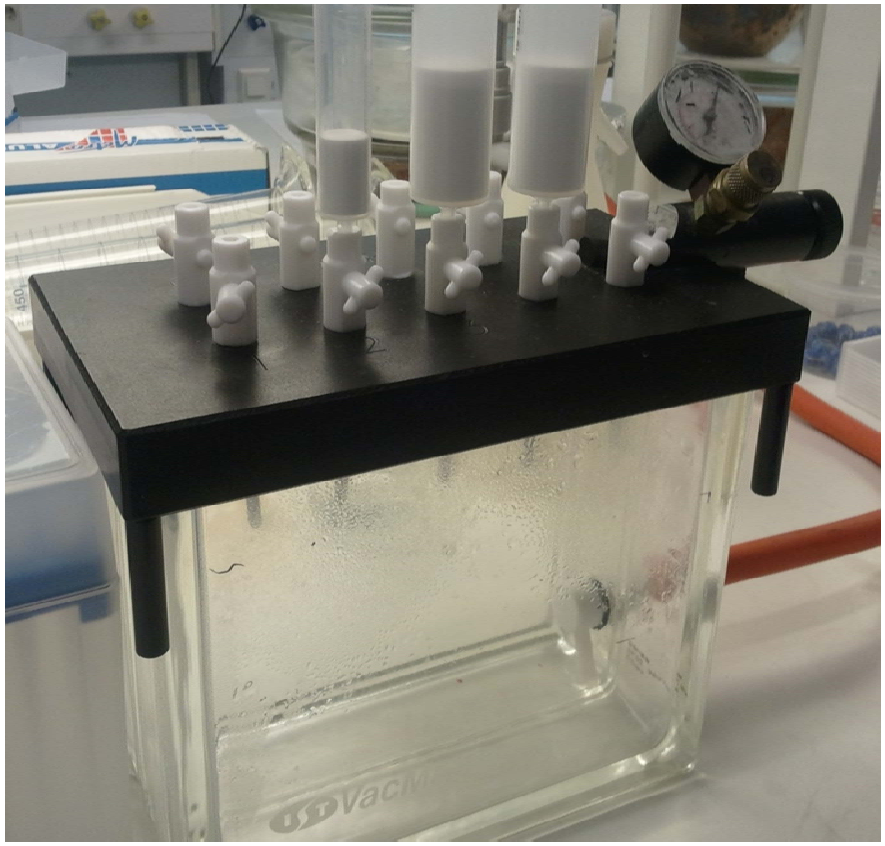
Obviously: mistakes

Invention of foam



Concentration method which actually does dilution x 1000

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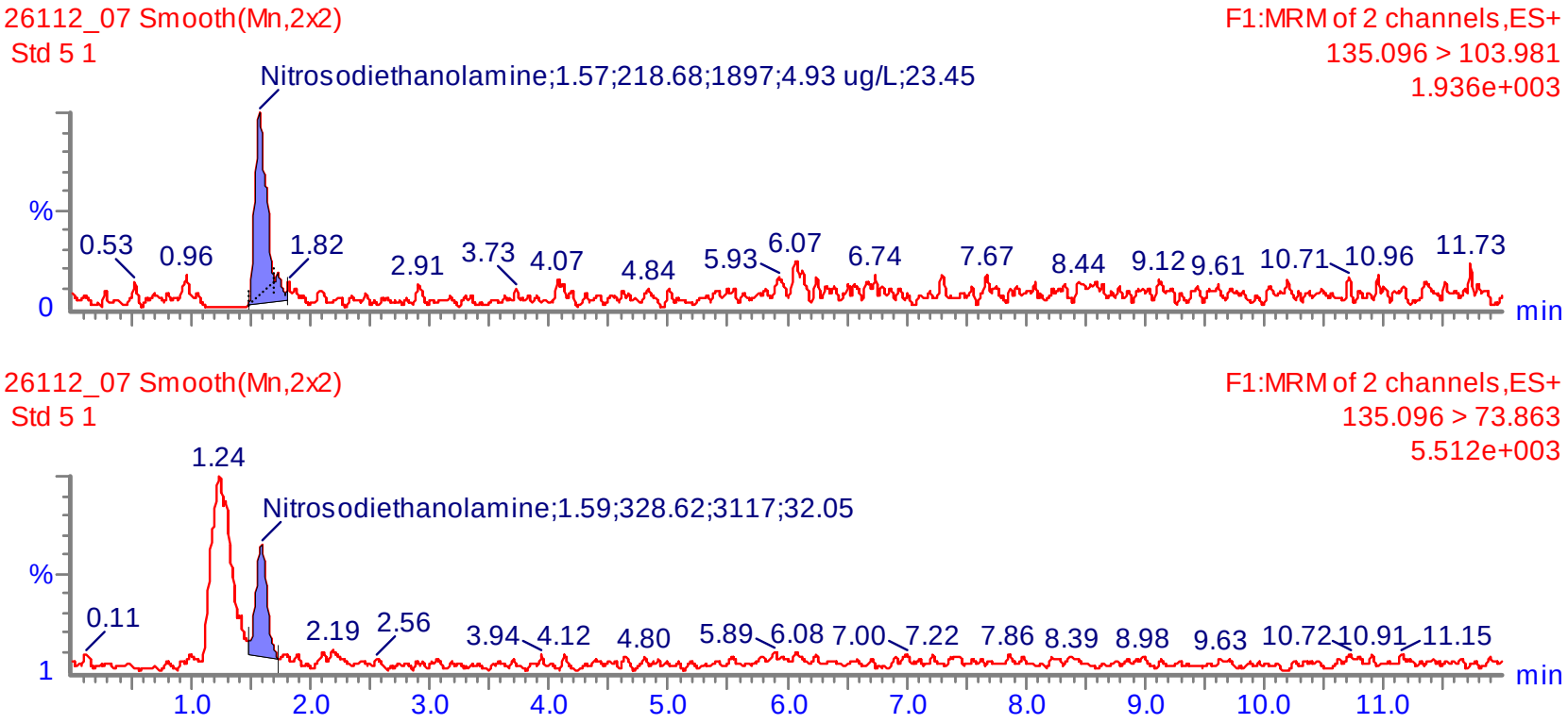
Analysis…


26112_07 Smooth(Mn,2x2)
Std 5 1
F1:MRM of 2 channels,ES+
135.096 > 103.981
1.936e+003
Nitrosodiethanolamine;1.57;218.68;1897;4.93 ug/L;23.45
%
0
0.53
0.96
1.82
2.91
3.73
4.07
4.84
5.93
6.07
6.74
7.67
8.44
9.12
9.61
10.71
10.96
11.73
min
26112_07 Smooth(Mn,2x2)
Std 5 1
F1:MRM of 2 channels,ES+
135.096 > 73.863
5.512e+003
1.24
Nitrosodiethanolamine;1.59;328.62;3117;32.05
%
1
0.11
2.19
2.56
3.94
4.12
4.80
5.89
6.08
7.00
7.22
7.86
8.39
8.98
9.63
10.72
10.91
11.15
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
min

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Laboratoriopalvelut
Laboratory Services

Vaatimus/*Requirement* SFS-EN ISO/IEC 17025:2005
02.09.2016 Liitteen päiväys / *Date of the Appendix*
17.07.2019 Päätöksen viimeinen voimassaolopäivä / *Date of expiry*
www.finas.fi Voimassaoleva pätevyysalue / *Current scope of accreditation*

PÄTEVYYSALUE
SCOPE OF ACCREDITATION

Testattava materiaali / tuote *Material / product tested*	**Testityyppi, mittausalue** *Type of test, measured range*	**Testausmenetelmä** *Test method*
Vesi *Water*	ETU (etyleenitiourea) *ETU (ethylenetiourea)*	Sisäinen menetelmä RA4009, UPLC-MS/MS-tekniikka *In-house method RA4009, UPLC-MS/MS-technique*
Vesi *Water*	MBT (Bentsotiatsoli-2-tioli) *MBT (Benzothiazole-2-thiol)*	Sisäinen menetelmä RA4034, LC-MS/MS-tekniikka *In-house method RA4013, LC-MS/MS-technique*
Vesi *Water*	NDELA (N-Nitrosodietanoliamiini) *NDELA (N-Nitrosodiethanolamine)*	Sisäinen menetelmä RA4080, UPLC-MS/MS *In-house method RA4080, UPLC-MS/MS*

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PÄTEVYYSALUE ***SCOPE OF ACCREDITATION***		
Testattava materiaali / tuote ***Material / product tested***	**Testityyppi, mittausalue** ***Type of test, measured range***	**Testausmenetelmä** ***Test method***
Prosessinäytteet *Process samples*	Nitrosoamiinit *Nitrosoamines*	Sisäiset matriisikohtaiset menetelmät mm . RA4074, GC/HRMS, perustuu EPA 521 ja OSHA 27 *In-house methods by sample to be tested e.g. RA4074, GC/HRMS, based on EPA 521 and OSHA 27*

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Emissions to air, three reasons to measure, carbon capture process:

1. Health and environment
2. Monitoring of CO_2
3. Status of the process

So what is new?

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Analogue baseline from history:

Waste incineration

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DIRECTIVE 2000/76/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL
of 4 December 2000
on the incineration of waste

Emission limits set for:

Total dust
NOx
SO2
CO
TOC
HCl
HF
Metals + Hg
PCDD/F compounds (0,1 ng/m³n I-TEQ)

Kyläsaari Waste incineration plant
1960-1983

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In practise, PCDD/F are not released any more…

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20.9.2016 Hakkila, Vantaa, Finland

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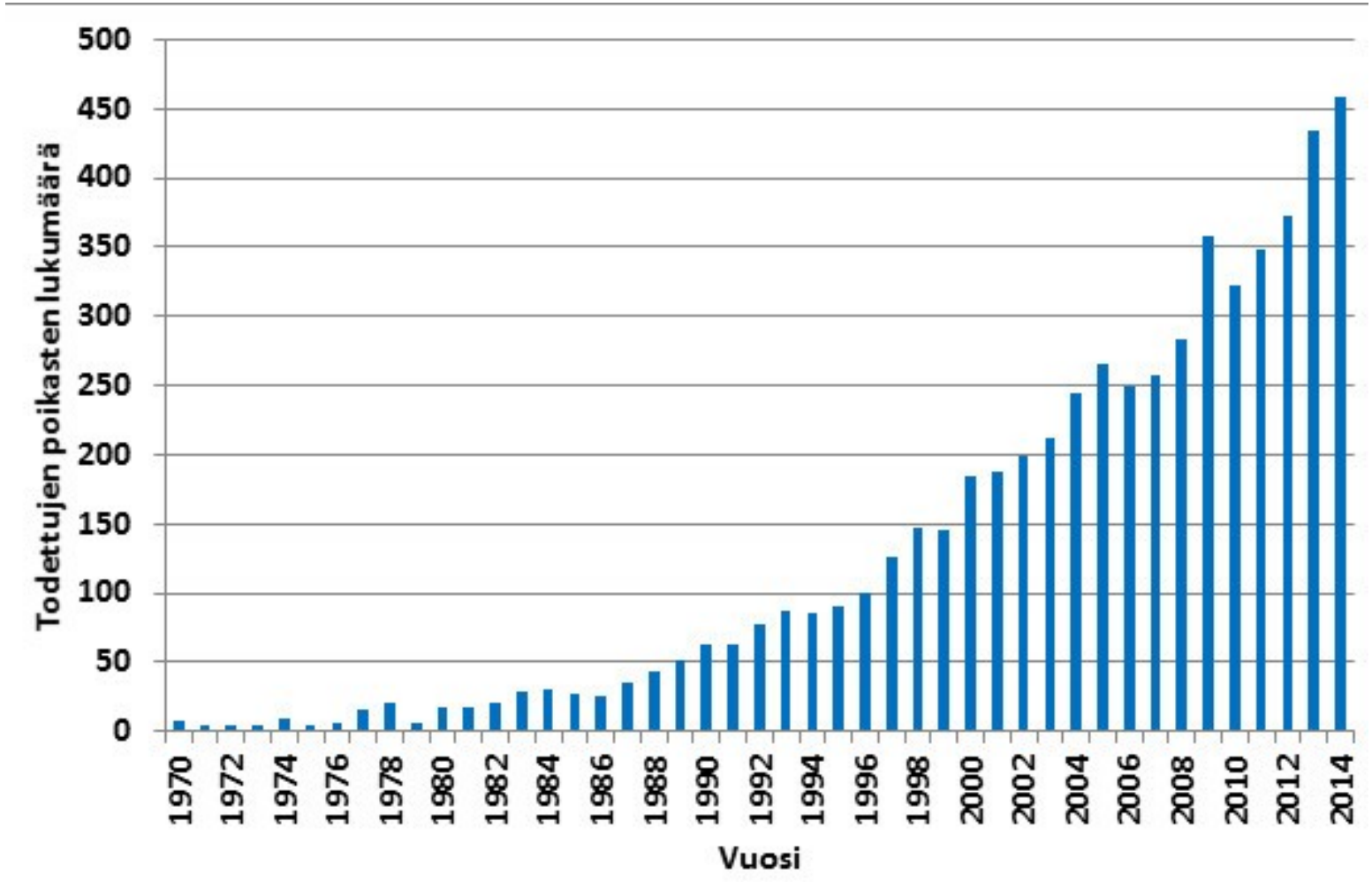
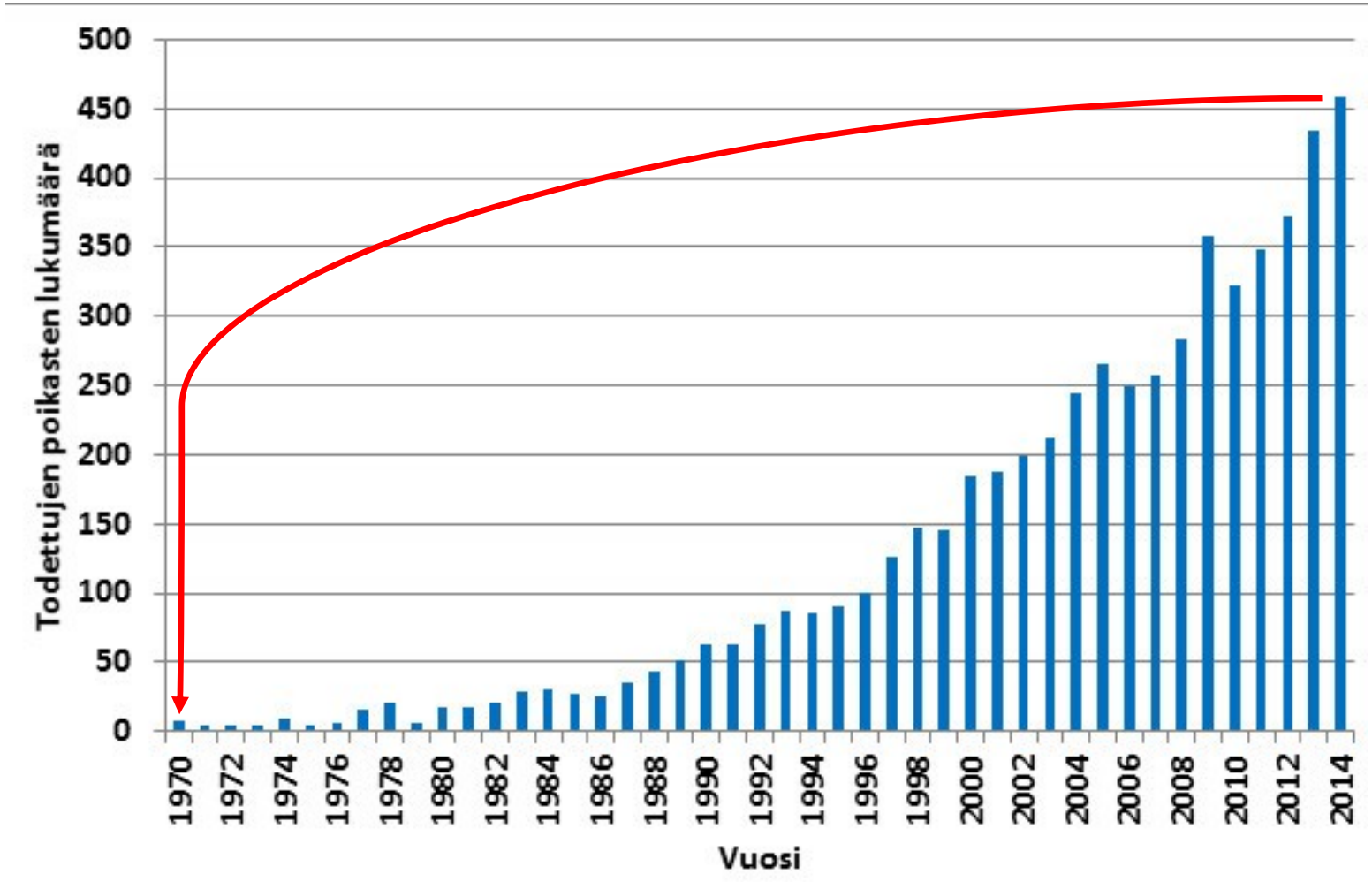
White-tailed eagle (Picture: WWF Finland)



Source: WWF Finland



Source: WWF Finland

Total number of:

- PCDD congeners: 75
- PCDF isomers: 135

total 210 pcs

7,6 % of PCDD/F has selected to represent the overall concentration of compound group.

PCB's, PAH, oxy-PAH, phenols etc…

Equivalence factors for dibenzo-p-dioxins and dibenzofurans

For the determination of the total concentration (TE) of dioxins and furans, the mass concentrations of the following dibenzo-p-dioxins and dibenzofurans shall be multiplied by the following equivalence factors before summing:

		Toxic equivalence factor
2,3,7,8	— Tetrachlorodibenzodioxin (TCDD)	1
1,2,3,7,8	— Pentachlorodibenzodioxin (PeCDD)	0,5
1,2,3,4,7,8	— Hexachlorodibenzodioxin (HxCDD)	0,1
1,2,3,6,7,8	— Hexachlorodibenzodioxin (HxCDD)	0,1
1,2,3,7,8,9	— Hexachlorodibenzodioxin (HxCDD)	0,1
1,2,3,4,6,7,8	— Heptachlorodibenzodioxin (HpCDD)	0,01
	— Octachlorodibenzodioxin (OCDD)	0,001
2,3,7,8	— Tetrachlorodibenzofuran (TCDF)	0,1
2,3,4,7,8	— Pentachlorodibenzofuran (PeCDF)	0,5
1,2,3,7,8	— Pentachlorodibenzofuran (PeCDF)	0,05
1,2,3,4,7,8	— Hexachlorodibenzofuran (HxCDF)	0,1
1,2,3,6,7,8	— Hexachlorodibenzofuran (HxCDF)	0,1
1,2,3,7,8,9	— Hexachlorodibenzofuran (HxCDF)	0,1
2,3,4,6,7,8	— Hexachlorodibenzofuran (HxCDF)	0,1
1,2,3,4,6,7,8	— Heptachlorodibenzofuran (HpCDF)	0,01
1,2,3,4,7,8,9	— Heptachlorodibenzofuran (HpCDF)	0,01
	— Octachlorodibenzofuran (OCDF)	0,001

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16 pcs. total

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Measurement of WI flue gas:

- Standards available globally
- *Routine* analysis in the lab with suitable mass spectometer

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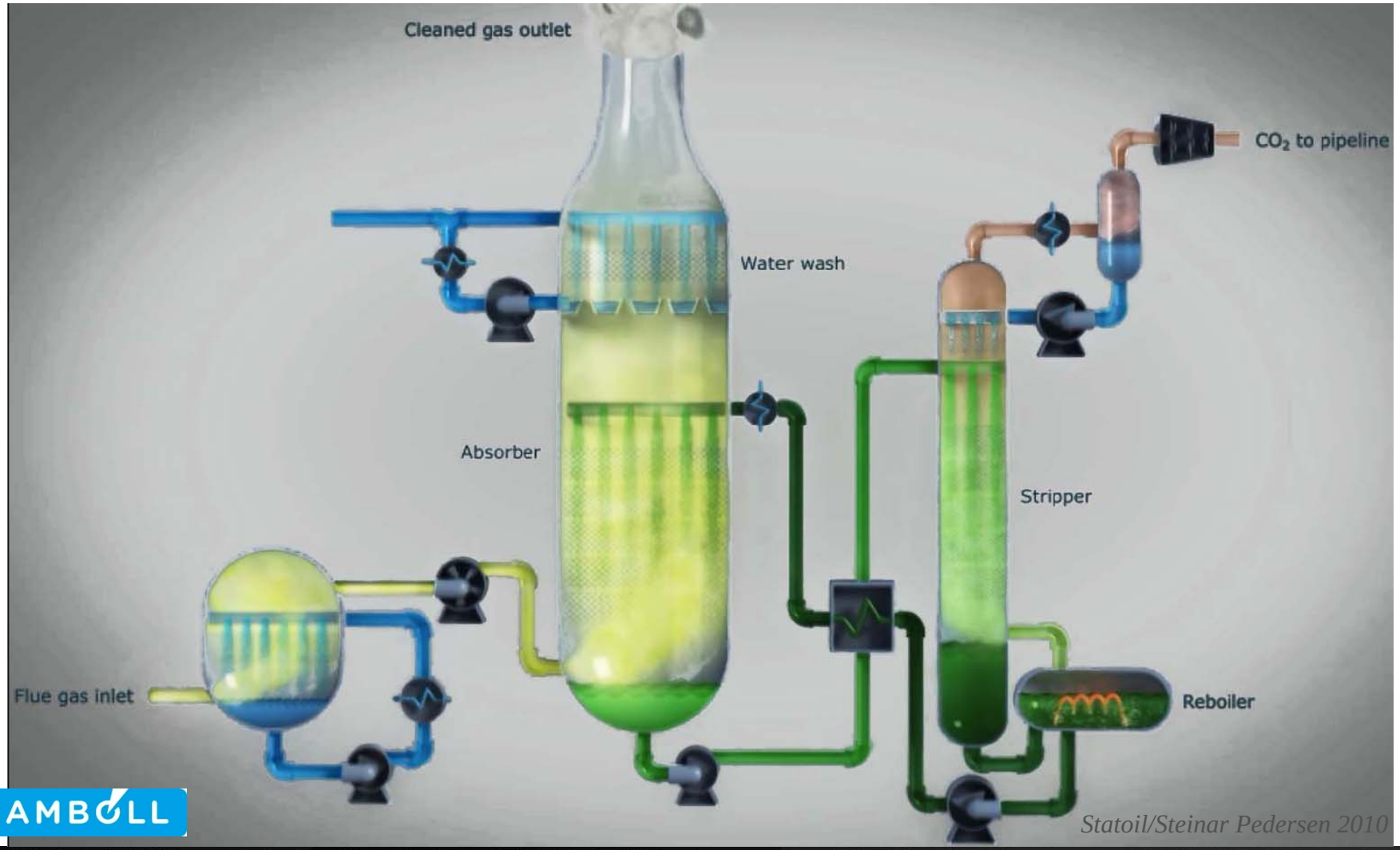
Post combustion carbon capture process



Statoil/Steinar Pedersen 2010

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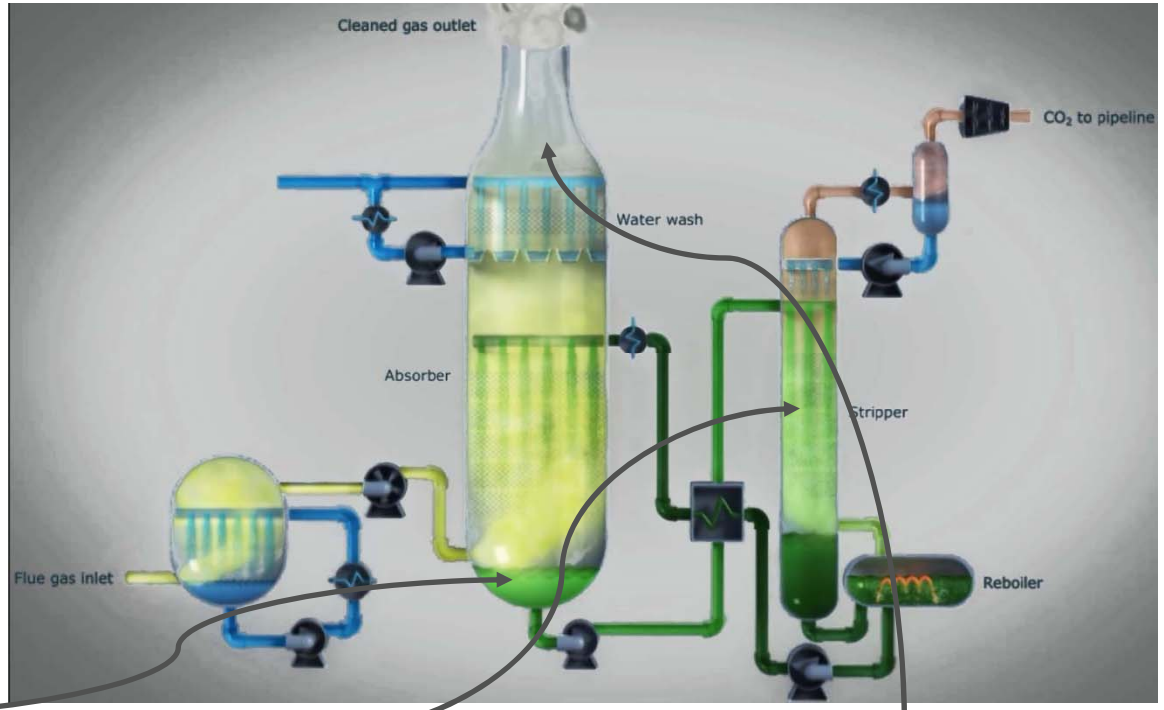
Formation of impurities



Solvent

- Absorption liquid
- Impurities in raw material

Primary degradation

- “Small compounds”
- Aldehydes
- Ammonia

Secondary degradation

- N-Nitrosamines
- Nitramines
  - Solvent specific
  - ”generic”

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generic” N-nitrosamines, EPA-521”

Analyte	Chemical Abstract Services (CAS) Registry Number
N-Nitrosodimethylamine (NDMA)	62-75-9
N-Nitrosomethylethylamine (NMEA)	10595-95-6
N-Nitrosodiethylamine (NDEA)	55-18-5
N-Nitrosodi-n-propylamine (NDPA)	621-64-7
N-Nitrosodi-n-butylamine (NDBA)	924-16-3
N-Nitrosopyrollidine (NPYR)	930-55-2
N-Nitrosopiperidine (NPIP)	100-75-4

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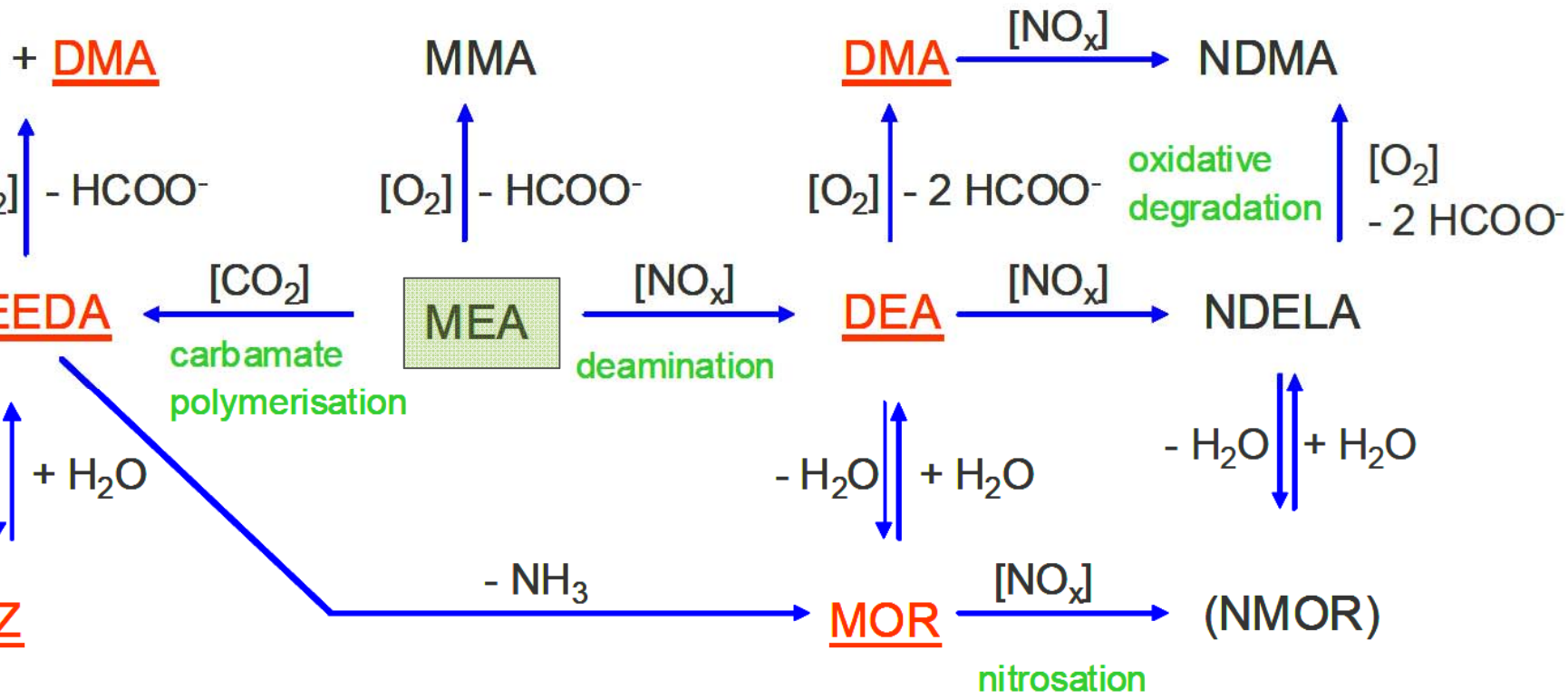

Compounds in red can directly form a stable nitrosamine

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. Challenge

Number of nitrosamines is enormous
Nitrosamine composition depends on solvent
-> representative list is not available
Composition of solvents is non-disclosed information
Solvent specific N-NO’s are not necessarily easily available

What should be analysed?

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*”Emissions from TCM shall not lead to calculated concentration of the sum of **nitrosoamines and nitramines** exceeds 0.3 ng/m³ for air concentrations…”*

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. Solution

Total nitrosoamine concentration (TONO)

What are the compounds and health effect?

Genereric N-NO's with additional compounds +
solvent specific N-NO's
= Total N-NO's

Nitramines?

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Comparison

Traditional	**Carbon capture**
Compounds mainly formed (or released) at high temperature	- Compounds formed even at low temperatures
Chemically stable	- N-NO formation in sampling and storage is possible
Samping and analysis: EN standards available	- No validated standards available
Samples can be sent to several accredited laboratories	- One accredited and commercial laboratory in Europe
Result intepretation set by	- No existing practise to limit values

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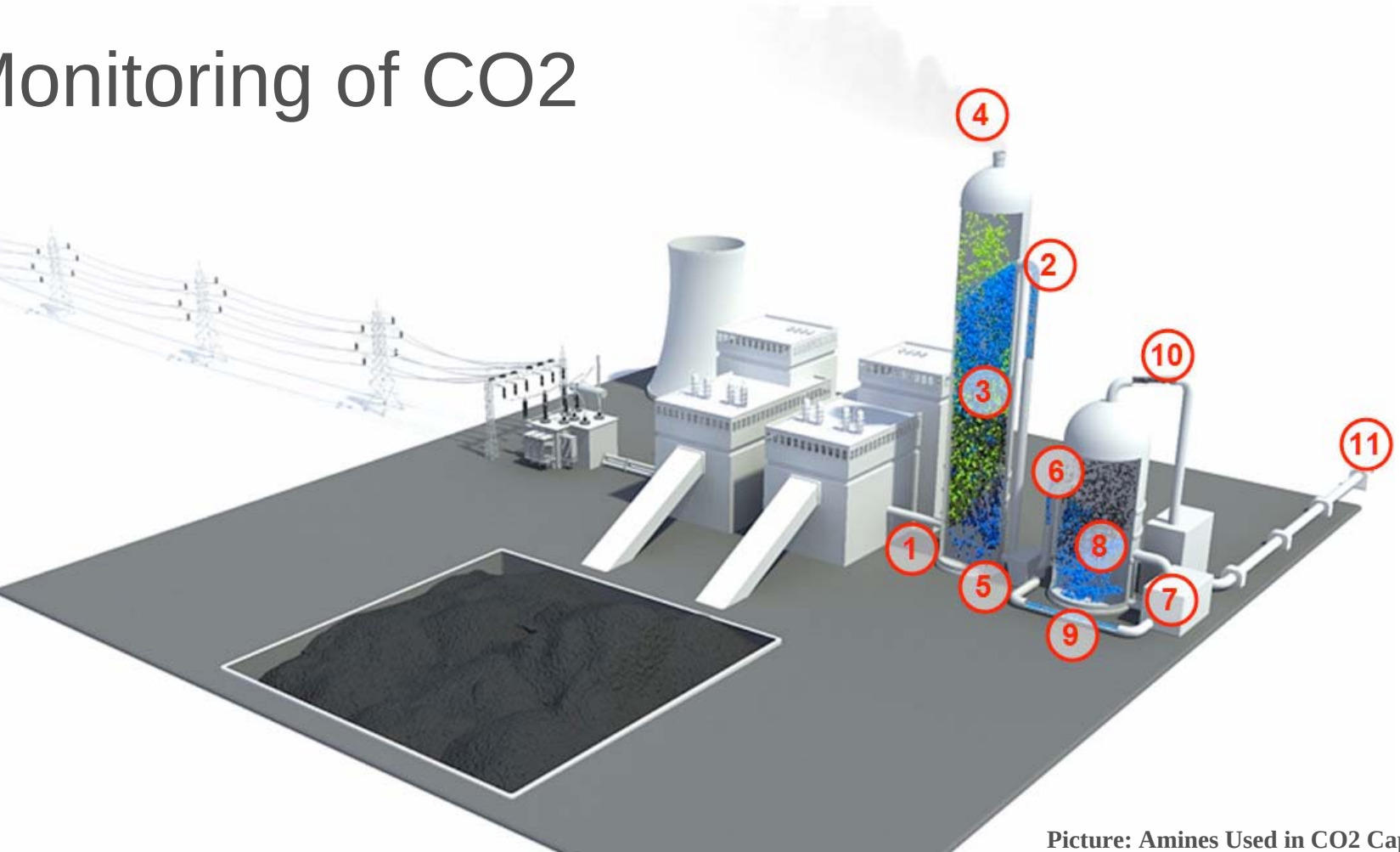
Monitoring of CO2



Picture: Amines Used in CO2 Capture

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Traditional power plant:
Burned Carbon in Fuel – carbon in ash
⇒ CO2 emission

Carbon capture plant:
Burned Carbon in Fuel – carbon in ash – captured CO2
⇒ CO2 emission

Maximum overall uncertainty to CO2 emission is 2.5 %

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emission = Flow rate (m/s) **x Area** (m^2) **x Concentration** (g/m^3)

rtainties in EN or ISO standard methods:

ow rate (pitot):	≈ 3 %
ea (1 point laser)	≈ 1 % (no shape error in the duct!)
O_2 concentration (IR-absorption)	≈ 5 %

> 2.5 %

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Thank you for your attention
and co-operation!

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