Method comparison for sampling and analysing syngas pollutants

Study carried out in collaboration with CEA Grenoble

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Projet Gaya

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ÊTRE UTILE AUX HOMMES

Agenda

- GAYA project : to produce biomethane from biomass gasification
- Sampling and analysis : key stages and many challenges to overcome
- Results of preliminary experimental campaigns
- Summary and future work

GAYA project : to produce biomethane from biomass gasification

Heat

Heat

Biomasse (wood, straw, …)

Gasification 850 °C

Clean-up

Catalytic Methanation

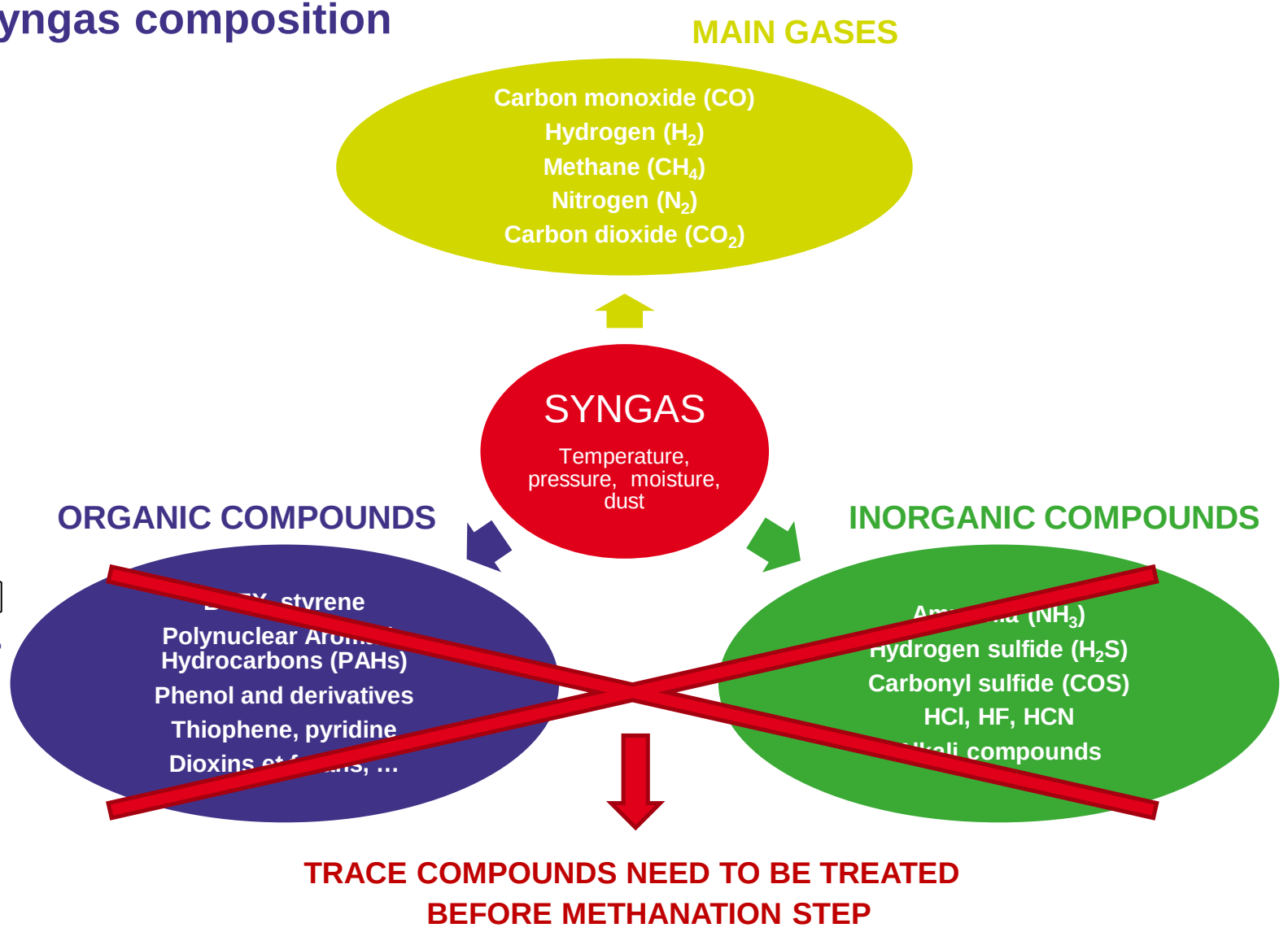
Upgrading for injection into the natural gas grid

Biomethane (Fuel)

$CO + 3H_2 \rightarrow CH_4 + H_2O$

- **2G biomethane technology**
  - A ‘green’substitute for natural gas obtained by gasification of biomass and methanation
  - 1T of wood could lead to ~600 Nm^3 of biomethane
- **A 7-year R&D program involving 11 partners, till 2017**
  - A technology platform located in France integrating industrial demonstrators
  - Goal is to demonstrate the technical relevance of the 2G biomethane pathway

Syngas composition

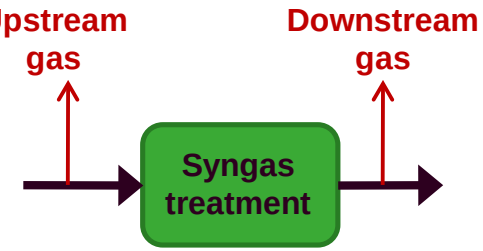


TRACE COMPOUNDS NEED TO BE TREATED BEFORE METHANATION STEP

Syngas sampling and analysis: developments achieved to overcome different challenges

Syngas sampling and analysis: key stages

- Control and adjust the process parameters
- Assess the gas treatment performance (cleaning, adsorption on C*, ZnO, …)
- Reach natural gas specifications



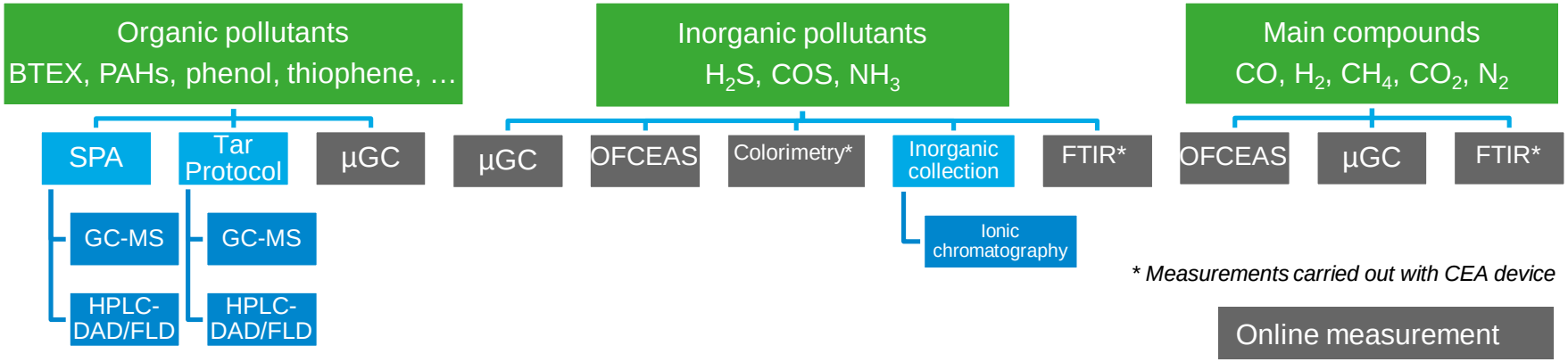
New development / innovative techniques on syngas pollutants analysis

- Optimization of tars sampling by SPA and analytical methods by GC-MS and HPLC-DAD/FLD
- Thiophene quantification by TDS-GC-MS
- Inorganics quantitation by OFCEAS

2 Measurement campaigns on relevant syngas (CEA fluidized bed) in 2013

Gasification of wood (beech) at 950°C with syngas and a heated nitrogen dilution	Gasification of agricultural waste at 800°C
• **Focus on low concentrations of tars and inorganics**	• **Focus on sulfurs measurements (thiophene, …) and syngas characterization**

Focus on experimental campaigns (July, 2013): Comparison between several analytical techniques

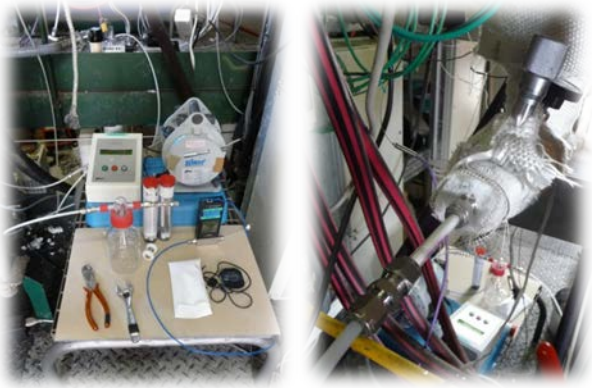


** Measurements carried out with CEA device*

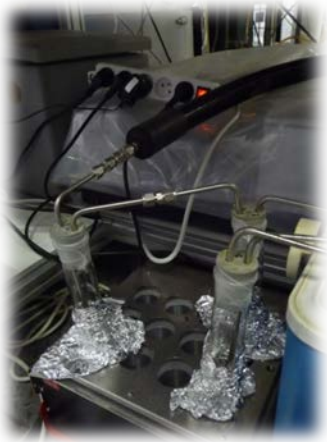
Online measurement

Offline measurement

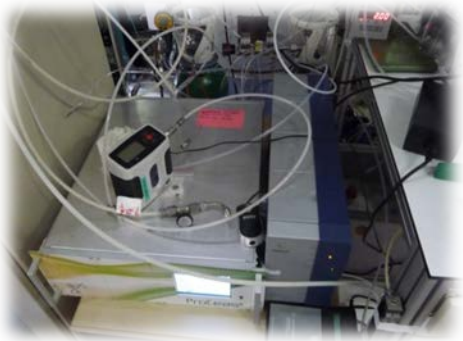
And complementary study to investigate GC x GC



SPA sampling

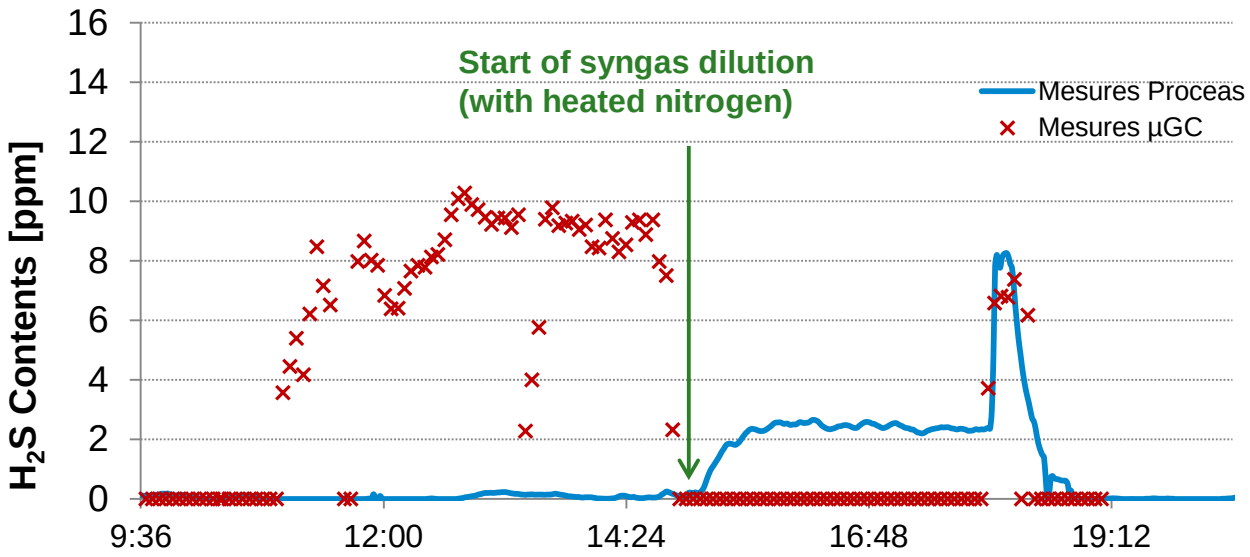


Tar Protocol sampling



OFCEAS and µGC online measurements

Hydrogen sulfide (H_2S) quantitation by OFCEAS: a challenge overcomed to quantify ppm level



Proceas – AP2E
OFCEAS technology

Technique	Micro-GC	OFCEAS	Colorimeter
H_2S contents in diluted syngas	nq	2,5 ppm	2,8 ppm
H_2S contents in syngas	8,7 ppm	10 ppm*	11,3 ppm*

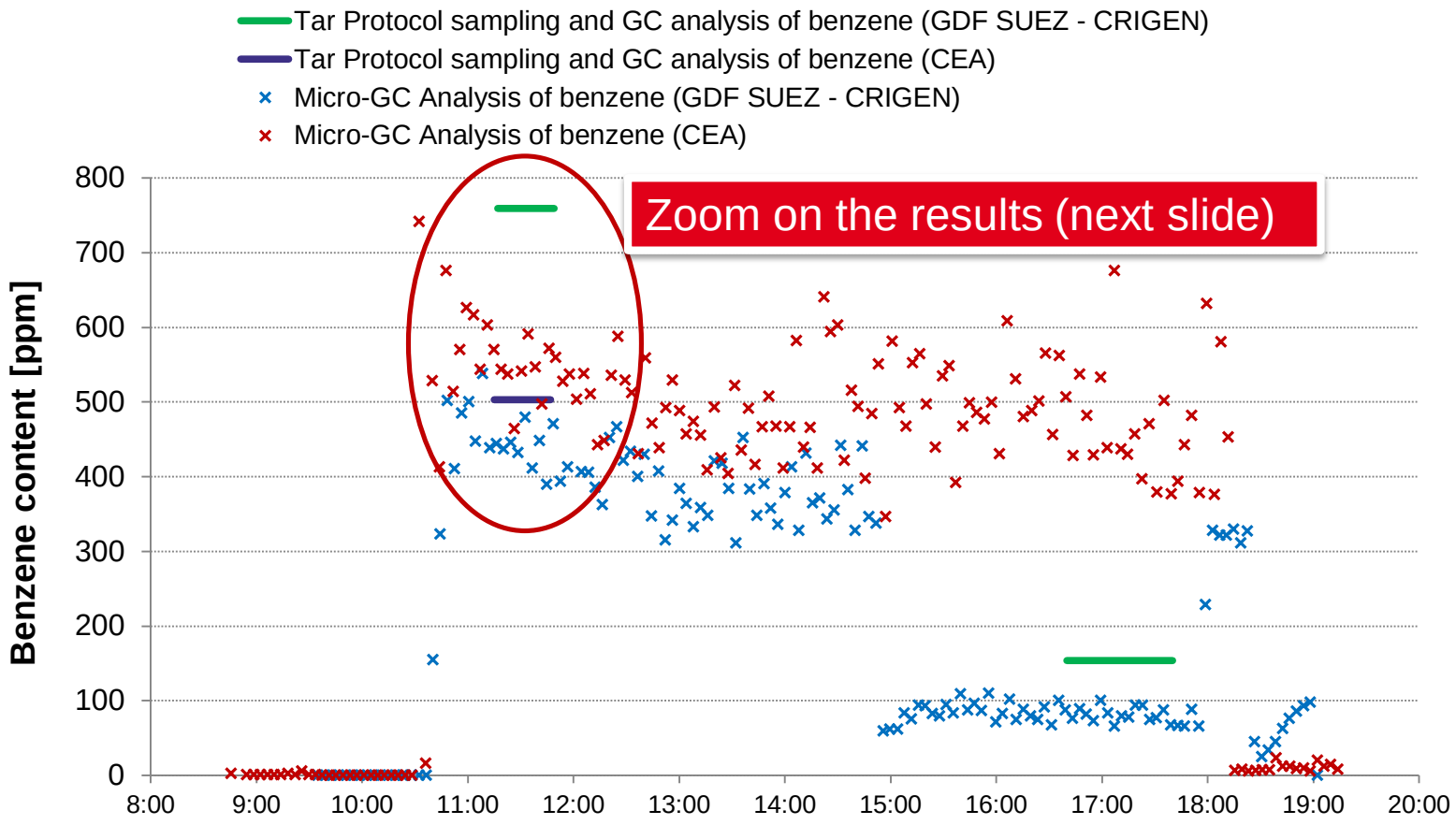
**measurements corrected with the dilution factor*

- Good correlation between the different H_2S measurements
- First experiment for quantifying syngas pollutants with OFCEAS technology
- Access to others compounds (e.g. ammonia)

- Experiments carried out on diluted syngas only
- No experiment on very low content of H_2S (below than 2 ppm)

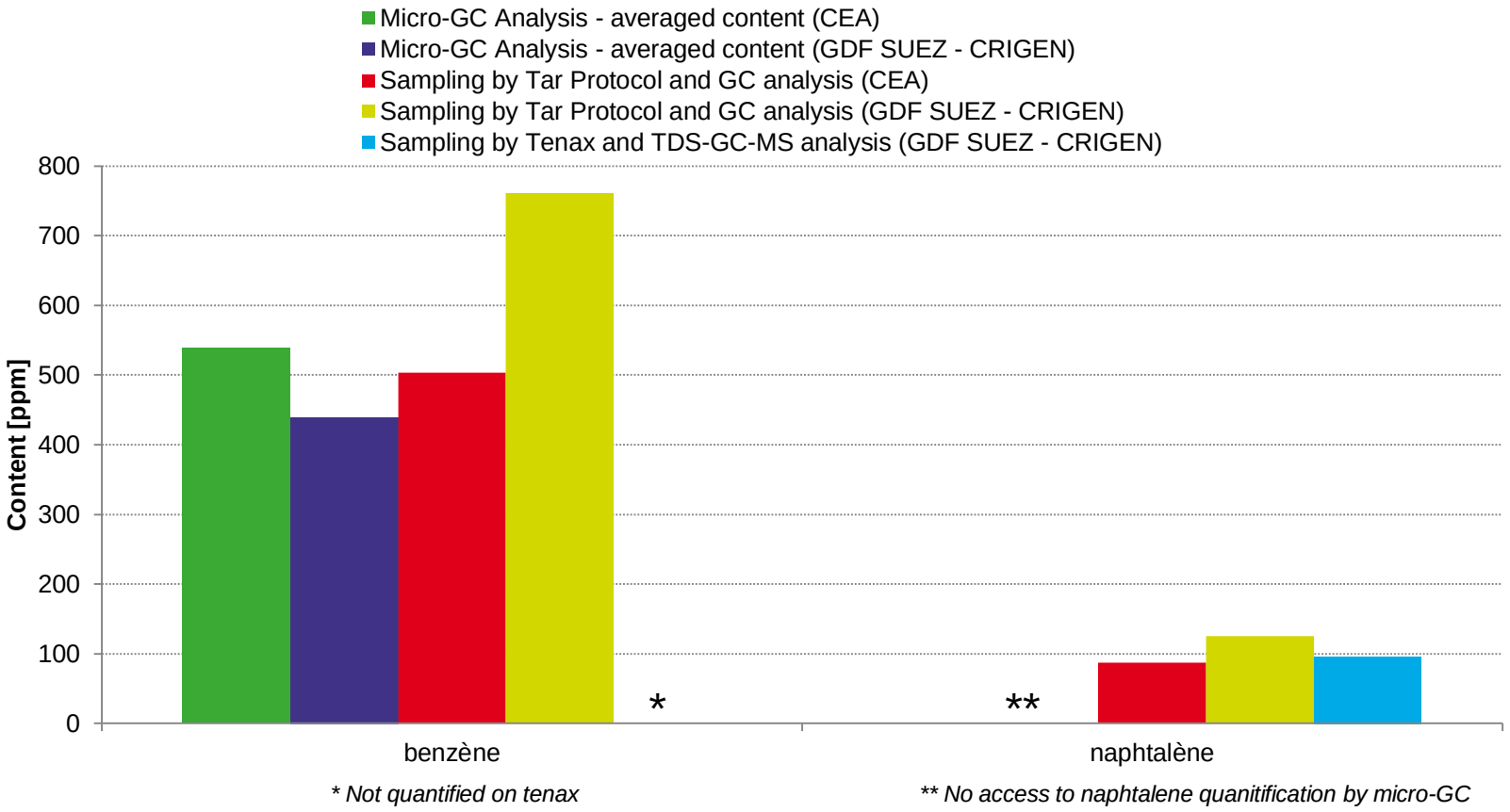
→ Need to use an heated probe

BTEX analysis: online quantitation by microGC vs tar protocol measurements – beech wood gasification at 950 °C



- Online BTEX measurements by micro-GC is very powerful
- Satisfying correlation between measurements for benzene (first TP experiment for CRIGEN)

Method comparison for benzene and naphtalene analysis

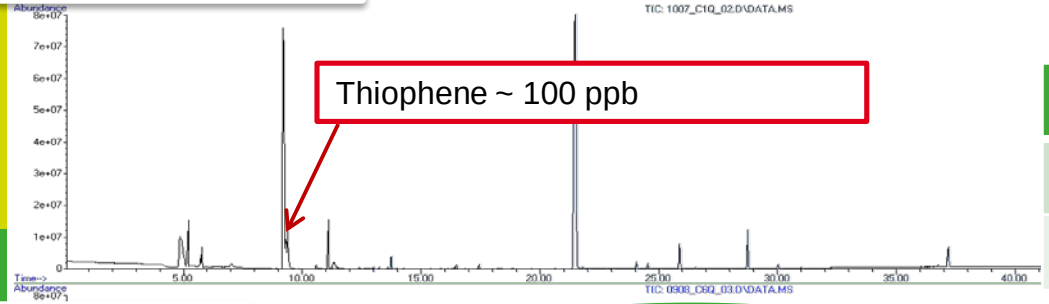


- First Tar Protocol experiment for GDF SUEZ – CRIGEN
- Satisfying correlation between micro-GC and Tar protocol for benzene
- Tar Protocol enable to access all the tar compounds

- No access to online measurement for « heavy tars » (e.g. naphtalene) with micro-GC
- GDF SUEZ Tar protocol sampling to improve
- No experiment carried out on very low content for main tar (below than 50 ppm)

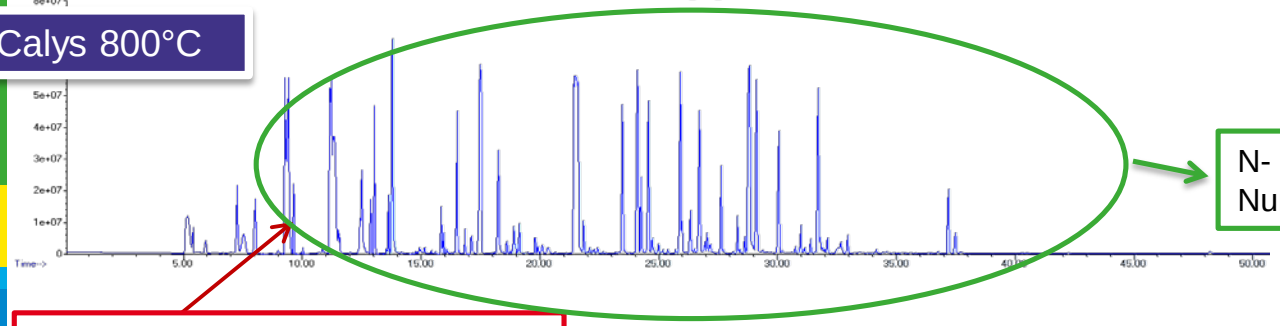
Thiophene quantification: Sampling by SPA (Carbotrap) and GC-MS analysis

Beech wood 950°C



Thiophene ~ 100 ppb

Calys 800°C



Thiophene ~ 3 ppm

N- and O-organic compounds
Numerous coeluted compounds

Thiophene content in syngas

	Beech wood	Calys
Syngas	**0,1 ppm**	**3,2 ppm**
Diluted syngas	**Not detected**	**0,1 – 0,4 ppm**

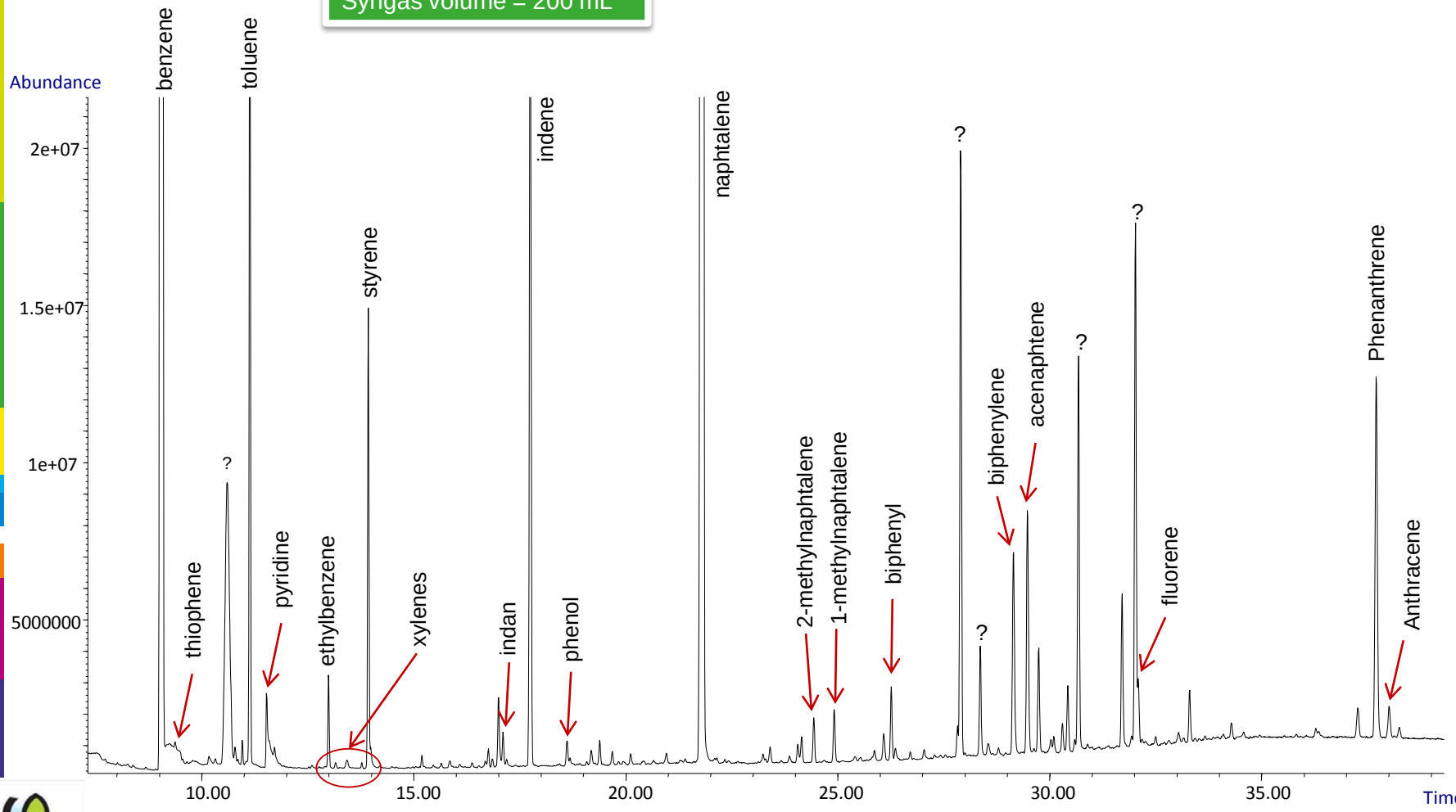
- **Thiophene quantification in syngas**
- **Numerous N- and O-organic compounds identified in syngas during second experiment = impact on process !**

- **Not online measurement**
- **Difficulty to make comparison (round robin ?**

Experiment on compact GC (Interscience) ?, IMR-MS (Airsense, VF) ?, PTR-MS (IONICON) ?, …

Preconcentration of a wood syngas sample on Tenax® TA and analysis by TDS-GC-MS: more than 50 organic compounds identified

Gasification at 950°C
Syngas volume = 200 mL



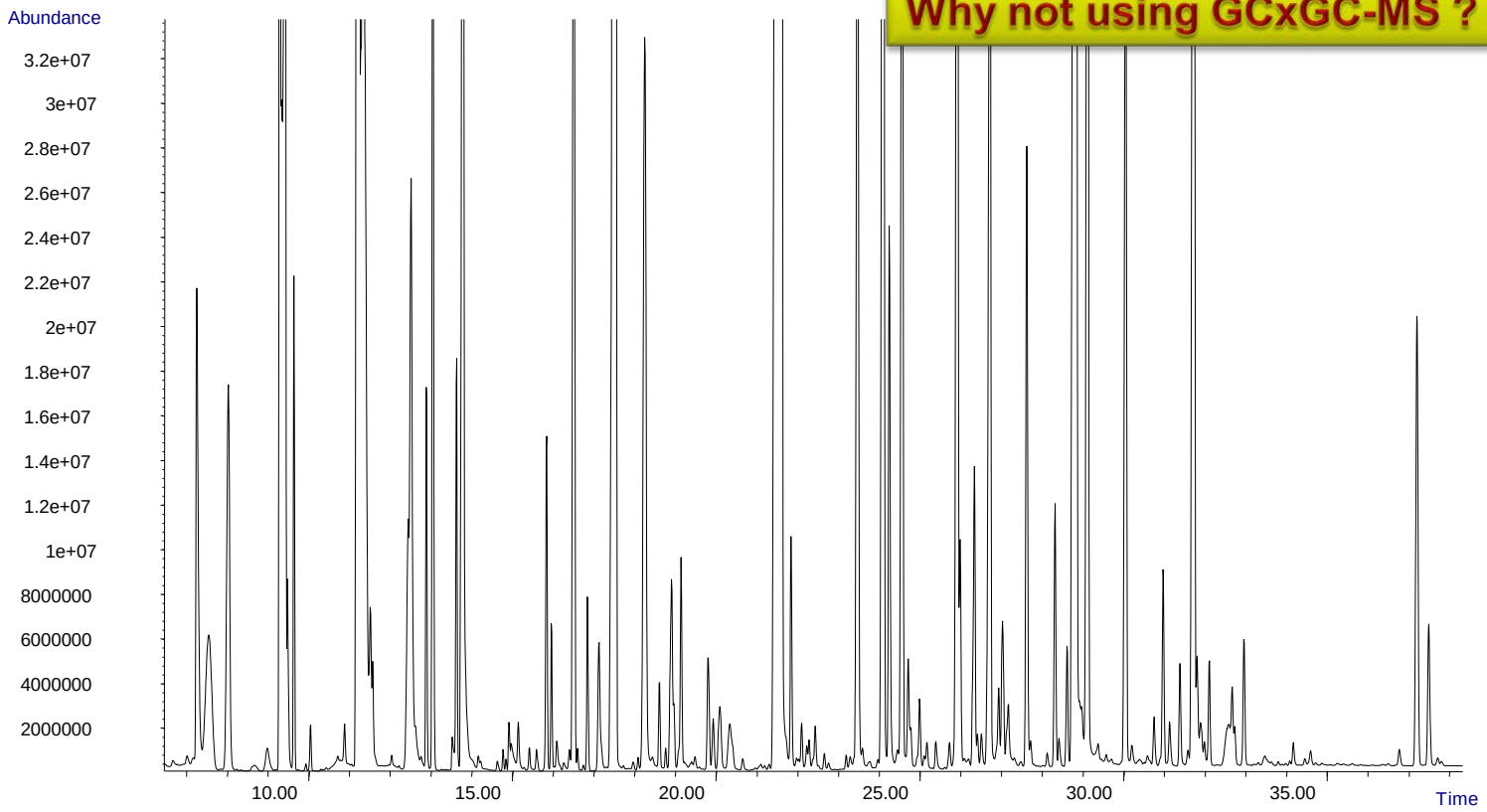
Column: DB1701 - dimensions : 60m*250µm*1µm (14% cyanopropylphényle – 86% diméthylsiloxane)

Oven : 40°C (1 min) to 150°C (0,1 min) @ 5°C/min then 260°C (26 min) @ 10°C/min

And now for a agricultural waste syngas sample…

Gasification at 800°C
Syngas volume = 300 mL

Complex samples !
Why not using GCxGC-MS ?

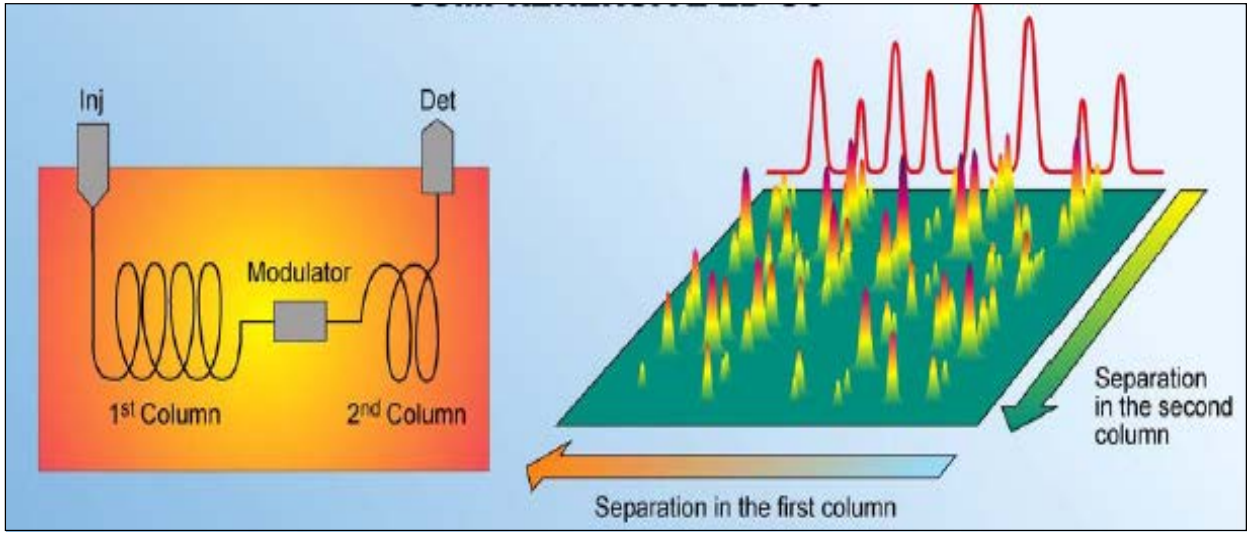


Column: DB1701 - dimensions : 60m*250µm*1µm (14% cyanopropylphényle – 86% diméthylsiloxane)

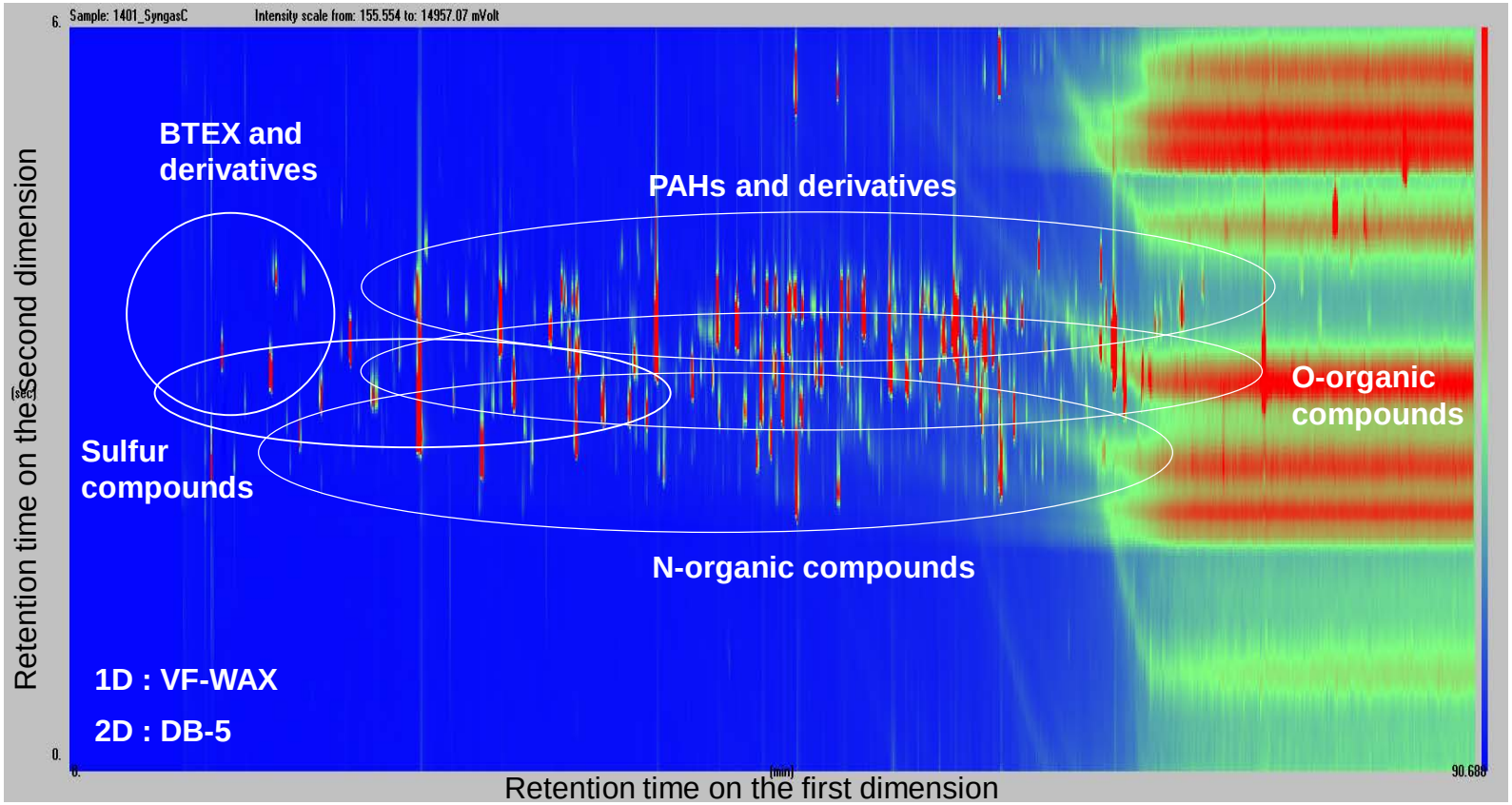
Oven : 40°C (1 min) to 150°C (0,1 min) @ 5°C/min then 260°C (26 min) @ 10°C/min

What is GC xGC ?

- A pair of GC columns, with different properties, connected in series through a modulator (e.g. DB-5 non polar combined with BPX-50 semi-polar)
- **First column** is similar than GC (e.g. 30 meter long) and the **second column** is shorter (only 1 or 2 meter)
- **Modulator** is the “milestone” that enables the transfer of the sample from the first to the second column (e.g. cryogenic trap with CO_2)



Using GC x GC for the characterization of complexe samples (syngas from agricultural waste) – in collaboration with ESPCI, Paris



- Fingerprint of a complex sample is possible : gas quality monitoring, impact on the process
- GC x GC offers a higher sensitivity and higher selectivity : more than 250 compounds
- Access to quantification

Results: a very interesting experimental background on two different biomasses

Measurement of sulfur compounds

- Use of Proceas to quantify H_2S below than 3 ppm
- Quantification of thiophene in syngas is possible by TDS-GC-MS
- Measurement of thiophene content more than 3 ppm in agricultural biomass (800°C) : an online quantitation would be very useful

Proceas – AP2E OFCEAS technology

Tars quantification

- Online monitoring of BTEX by micro-GC is checked
- Use of SPA and GC-MS is very promising to quantify but just for very low concentration of tars
- Tar Protocol sampling results are promising but has to be optimized

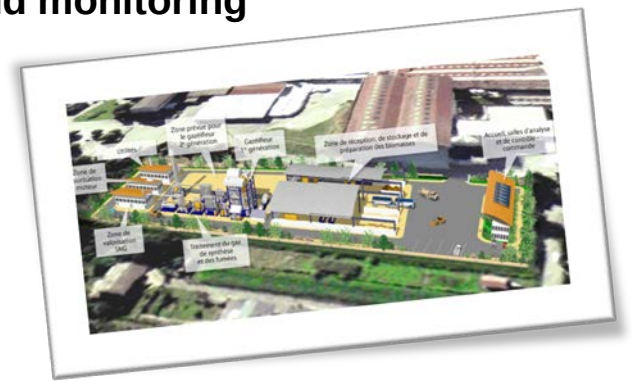
Informations from agricultural waste gasification

- Important variability of pollutant syngas composition according to the employed biomass (and the process parameters)
- Impact on plateform operational monitoring

GCxGC could be a strategic diagnostic tool for complex samples (syngas or condensates)

Summary and future works
Goal : to be ready for the R&D experiments on the platform

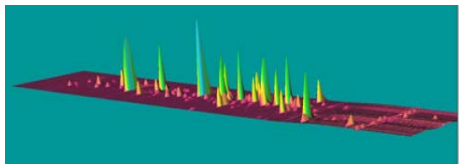
- **Background for preparation of platform exploitation and monitoring**
  - Great impact of the biomass on the syngas quality !
  - Preparation of sampling and analysis protocols
  - Integration of analytical steps within the design of experiments



- **Online measurements have to be fostered…**

…but offline performant measurements are still needed

- **New analytical solutions are promising**
  - Could online measurements of thiophene or heavy tars in syngas be possible ?
    e.g. : compact GC (Interscience), online mass spectrometer, …
  - GCxGC-MS could be a diagnostic tool for complex samples



- **New experimental campaign in 2014**
  - Determine the limits of quantification for each technique
  - Participation to focused round robins

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Study carried ou in collaboration with CEA Grenoble – Françoise DEFOORT, Sébastien THIERY

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