Tar analysis by Solid Phase Adsorption (SPA) associated with Thermal Desorption (TD) and Gas Chromatography (GC) analysis

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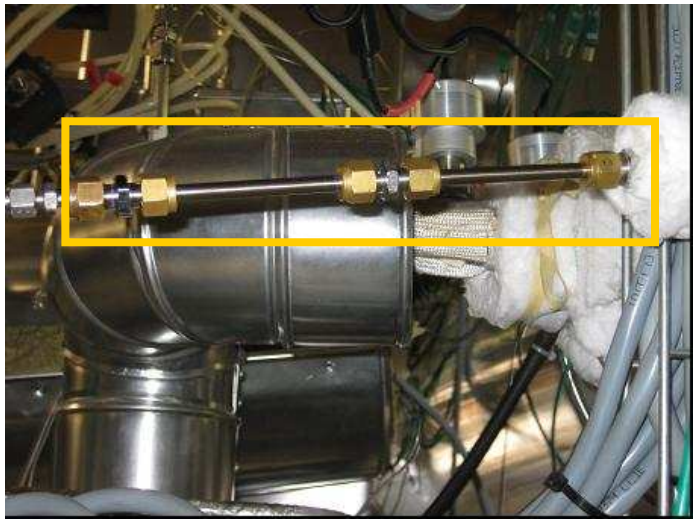
Tar Measurement Standard (TMS) guideline is very reliable but has some limits

Difficult to implement: solvent, cooling, etc.

Require a long sampling time for low concentrations

Not adapted for very low concentration (<1 mg/Nm^3)

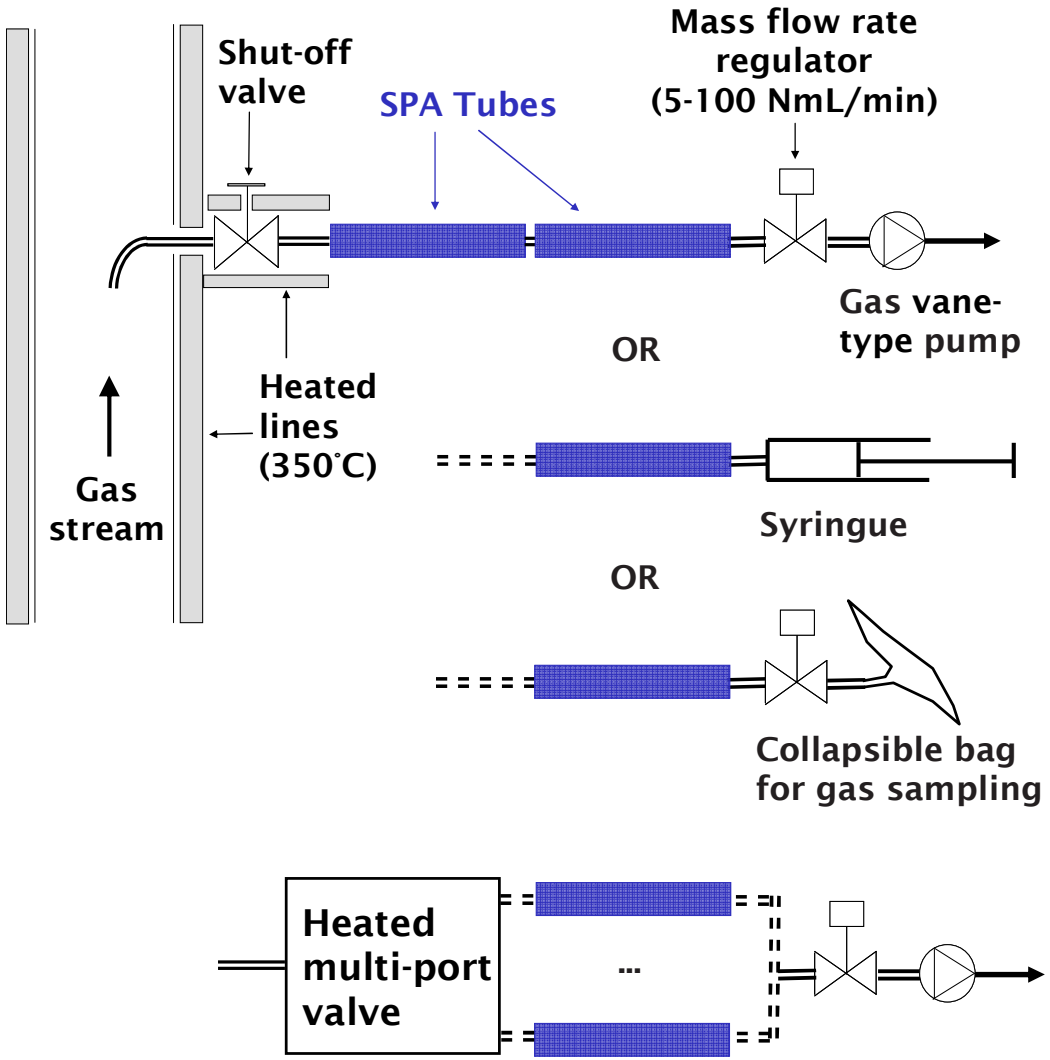
⇨ SPA-TD method developed to quantify tar (class 2-5) at low concentration



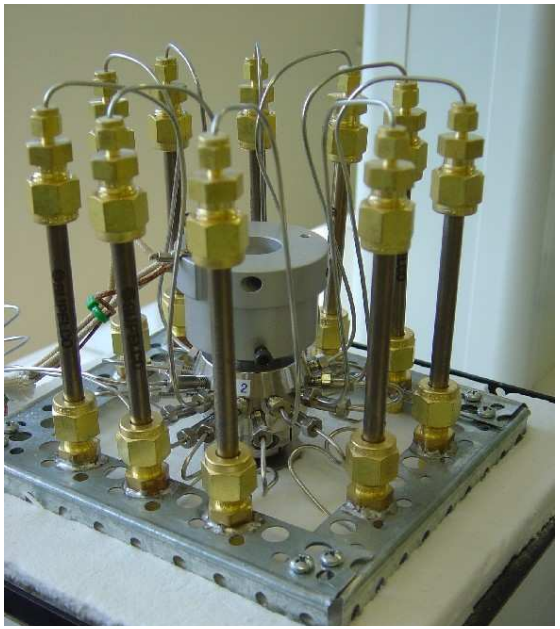
SPA sampling on CEA pilot

TMS sampling on CEA pilot

Different sampling lines could be used for SPA-TD

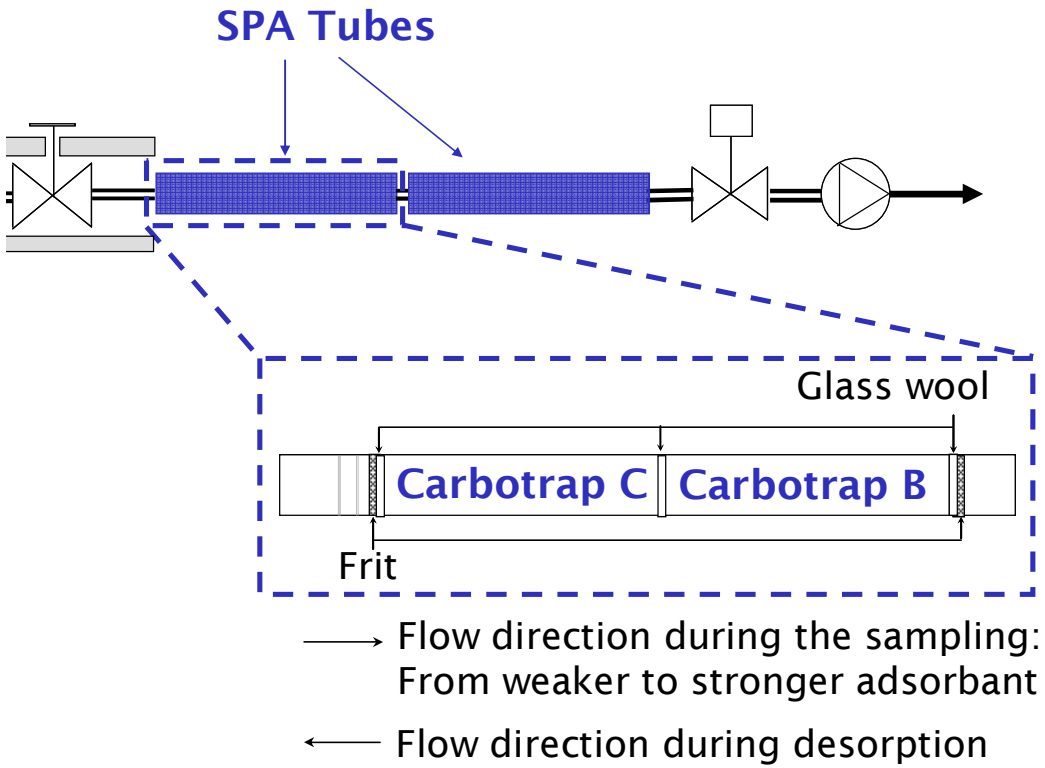


Sampling time (seconds to minutes): depending on expected concentration and adsorption breakthrough volume of adsorbent for each tar



SPA tubes coupled to a multiport valve for fast sampling (> 2 sec.)

How to choose the adsorbent?



See Supelco, Technical report
"Tool for selecting an adsorbent…"

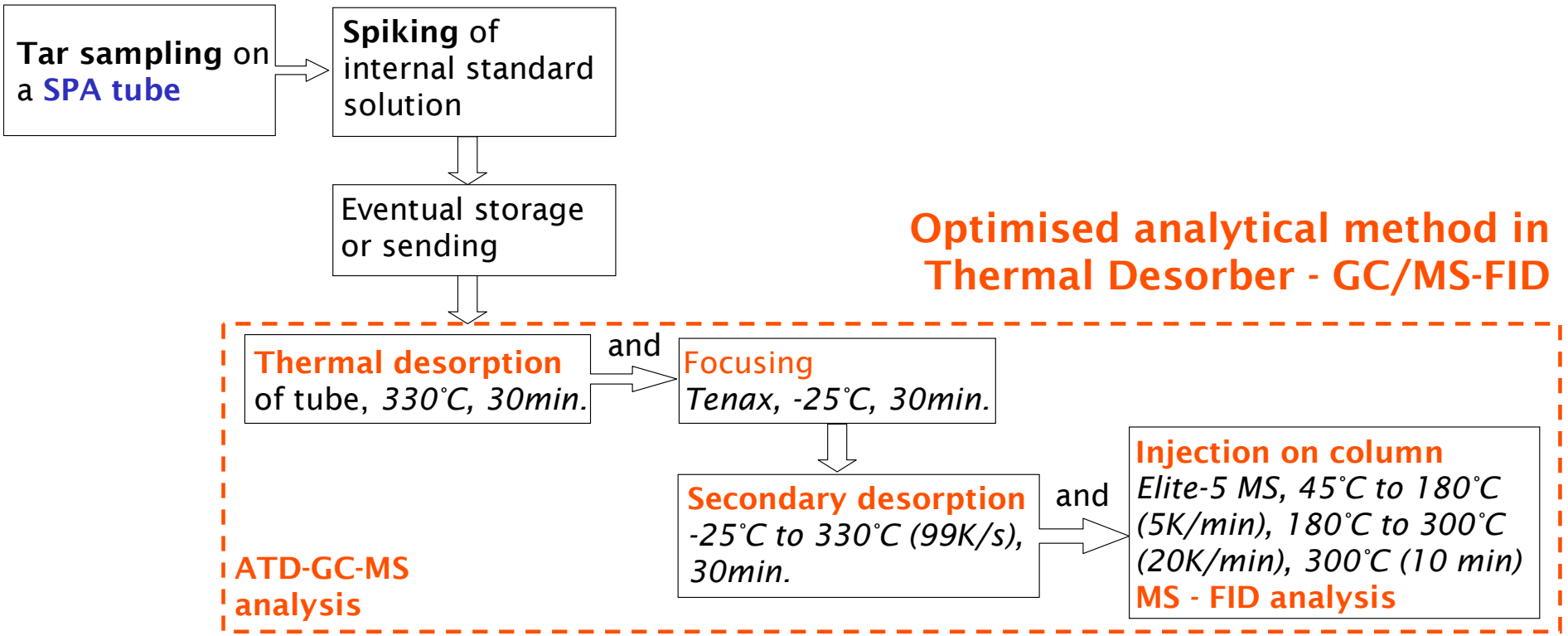
Check breakthrough for each compound with 2 tubes in serial, eventually with different adsorbent

Take care of solvent used for standards (DCM dissolved Tenax, etc.)

Selected adsorbent for benzene to 3 arom. rings : Carbotrap™ C + B
or Tenax® TA or Carbotrap™ X

Heavier compounds possible with new TD system and high temp. GC

After sampling, tar are analysed by TD-GC/MS-FID



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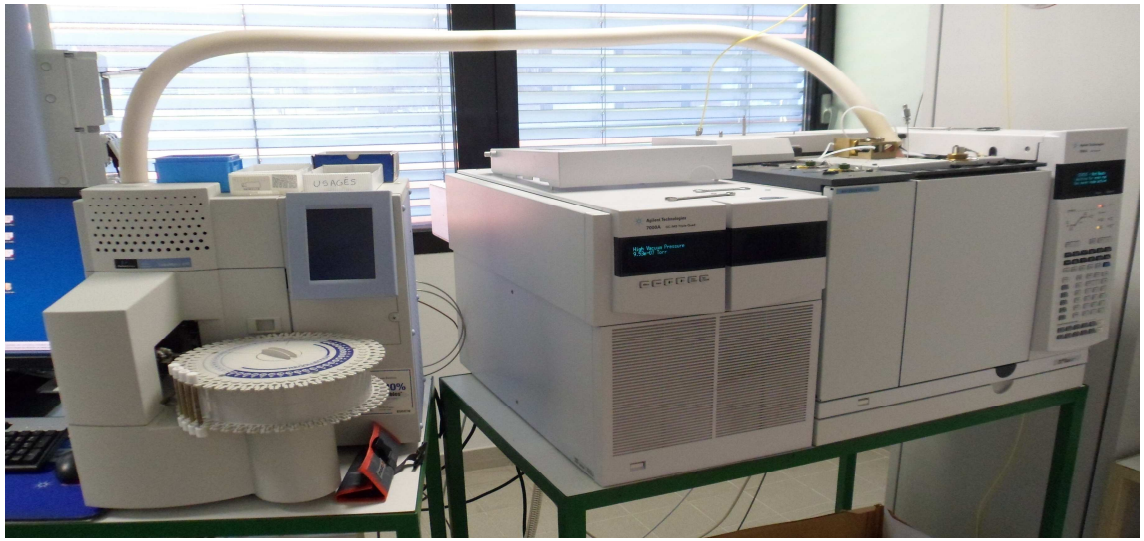
2 automatic thermal desorbers (ATD, Perkin Elmer) are available



ATD coupled to Agilent GC/MS*MS -FID

ATD coupled to Perkin Elmer GC/MS-FID

Deuterated internal standards are prefered for calibration

External calibration (not recommended)

Internal calibration with deuterated standards **if** a MS detector is used

If use of FID, need to find GC-separated internal standards

On MS: single ion monitoring (SIM), 1 major ion for quantification and 2 ions for qualification (to ensure that it is the goal compound)

Heated injection glassware ("ATIS" Supelco)

Calibration with deuterated internal standards gives good linearity and reproducibility

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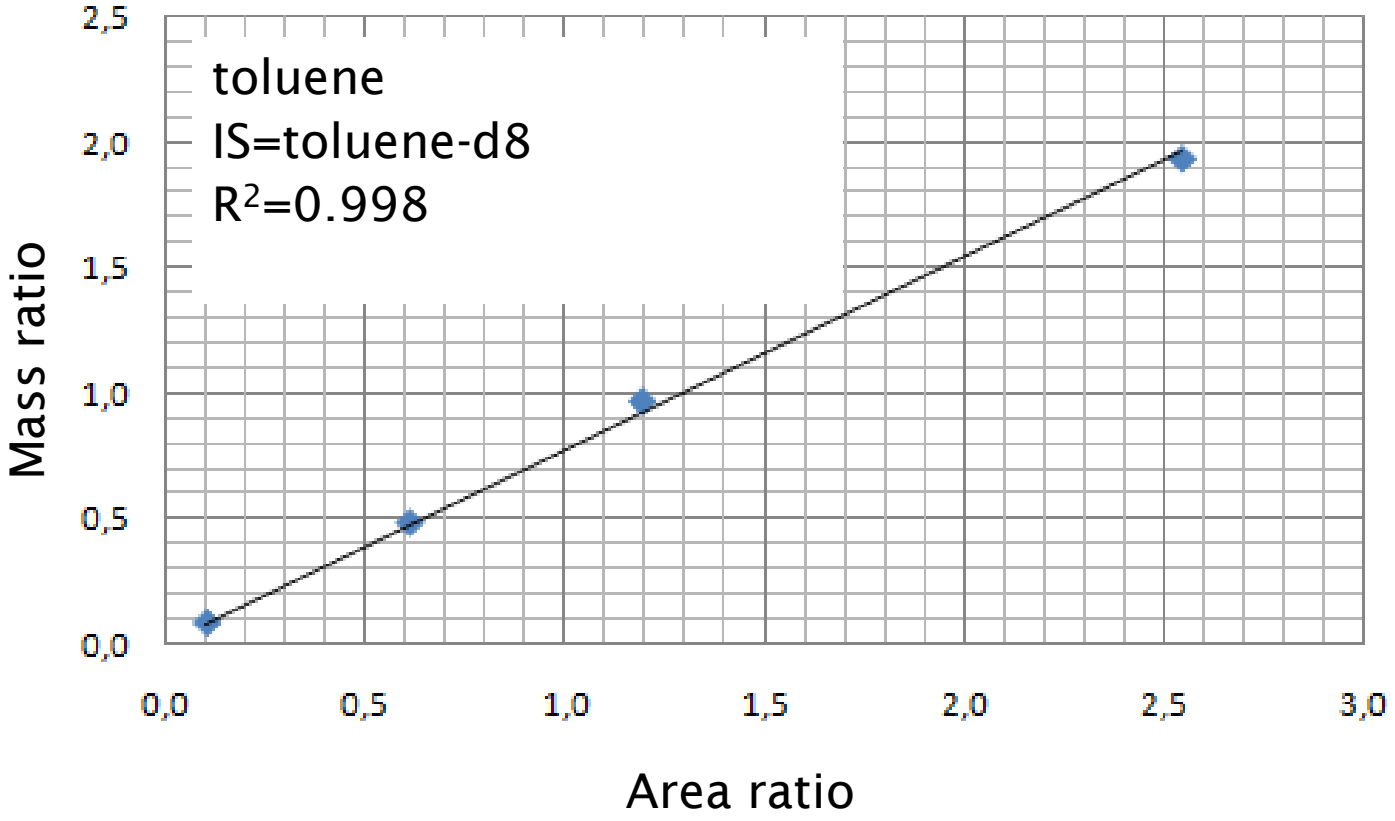


Recommendations for calibration method

Spiking with one solution of compounds to be analysed then with one solution of internal standards (variation of area ratio by keeping the same solution of IS)

The same solution of IS used for quantification of unknown sample

One calibration method for a mass ratio of max. 50 to keep good linearity

Adjust split ratio to keep ~1-100ng of compound on the detector (FID or MS)

Analytical parameters for some selected compounds

Tar	Range (ng)	R^2	LoD (ng)	LoQ (ng)	Repeatability standard deviation
Benzene[(1)]	3.6 - 108	0.997	8.8	26.6	0.65
Toluene[(1)]	3.3 - 99	0.999	3.7	11.4	0.52
Ethylbenzene[(2)]	3.2 - 96	0.998	4.6	13.9	0.43
Indene[(2)]	3.2 - 96	0.998	5.3	15.9	0.68
Naphthalene[(2)]	2.6 - 75	0.999	3.4	10.2	0.38

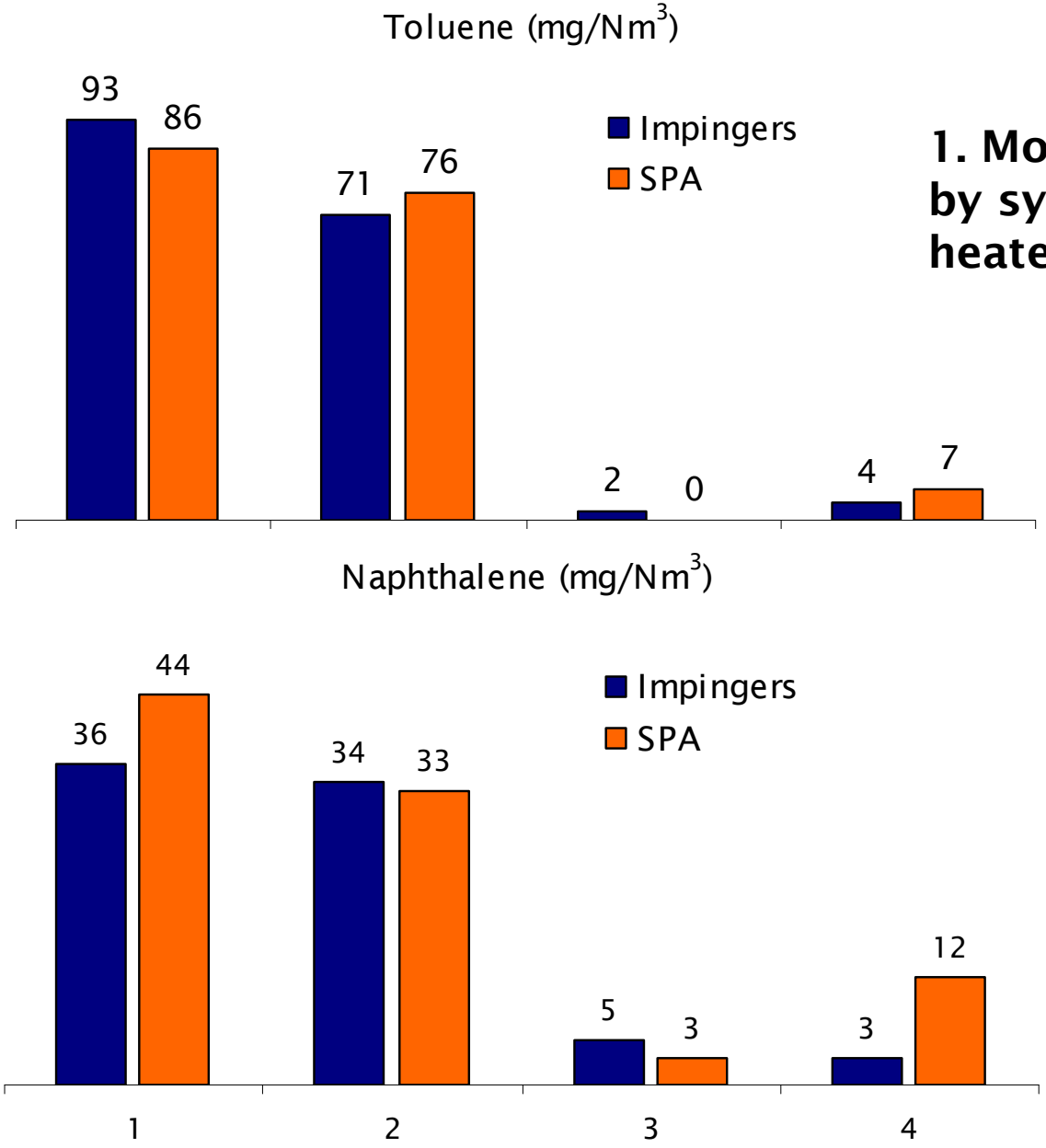
Internal standard : [(1)] toluene-d8 / [(2)] naphthalene-d8

12 compounds calibrated with 5 internal deuterated standards

Sampling time to achieve limit of quant. of SPA much lower than impingers: no dilution by solvent

Tar concentration (mg/Nm^3, on benzene basis)	1000	10	0.1
TMS (Impingers) Sampling flow rate 1NL/min, 1.25L of solvent	1 min	10^2 min	10^5 min
SPA/TD Sampling flow rate 100NmL/min	10^{-5} min	10^{-3} min	10^{-1} min

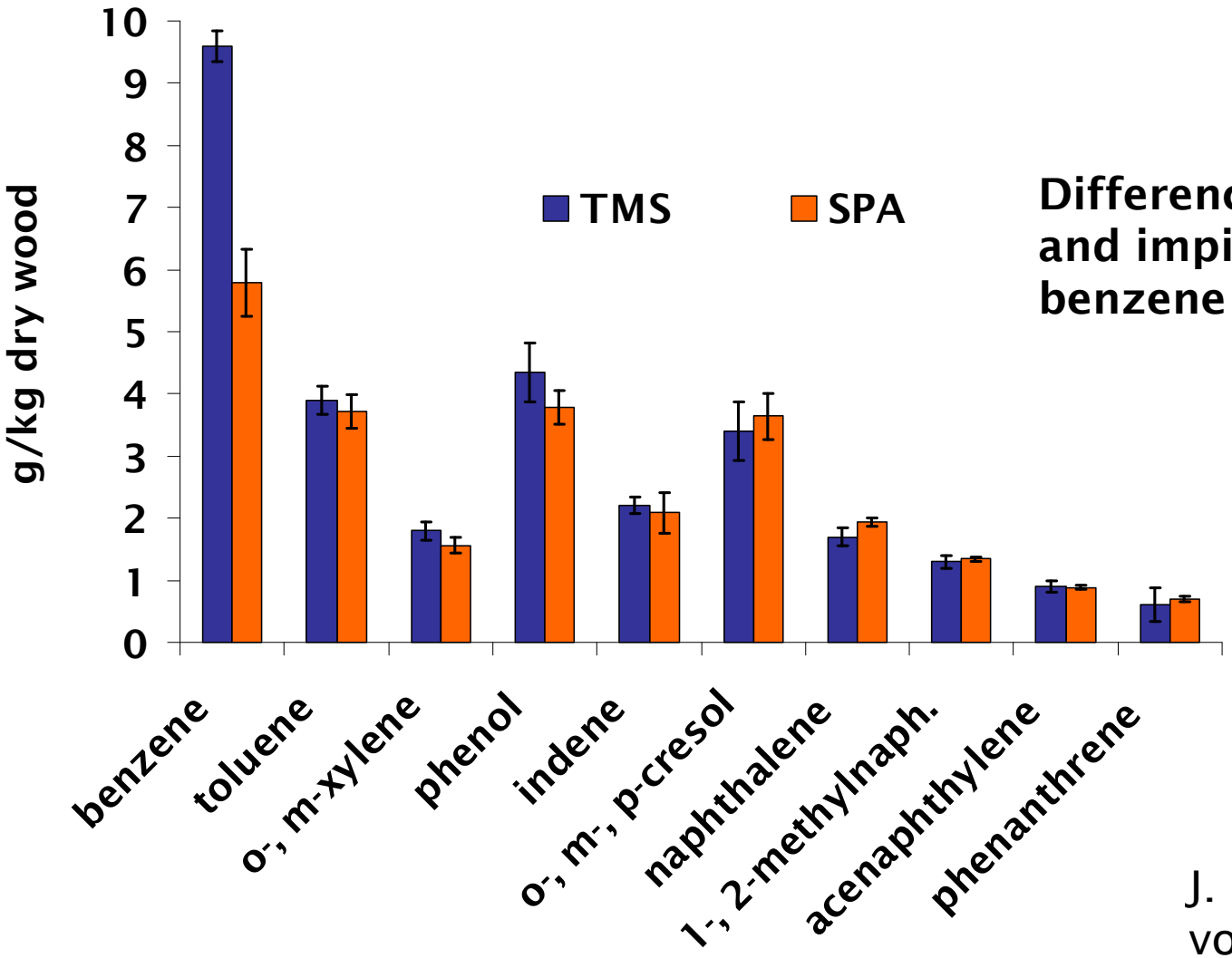
Comparison between SPA and impingers sampling



1. Model tar gas stream produced by syringe spiking through a heated lab-scale reactor

Comparison between SPA and impingers sampling

2. Real tar produced from biomass pyrolysis at 700°C



Difference between SPA and impingers for benzene not explained

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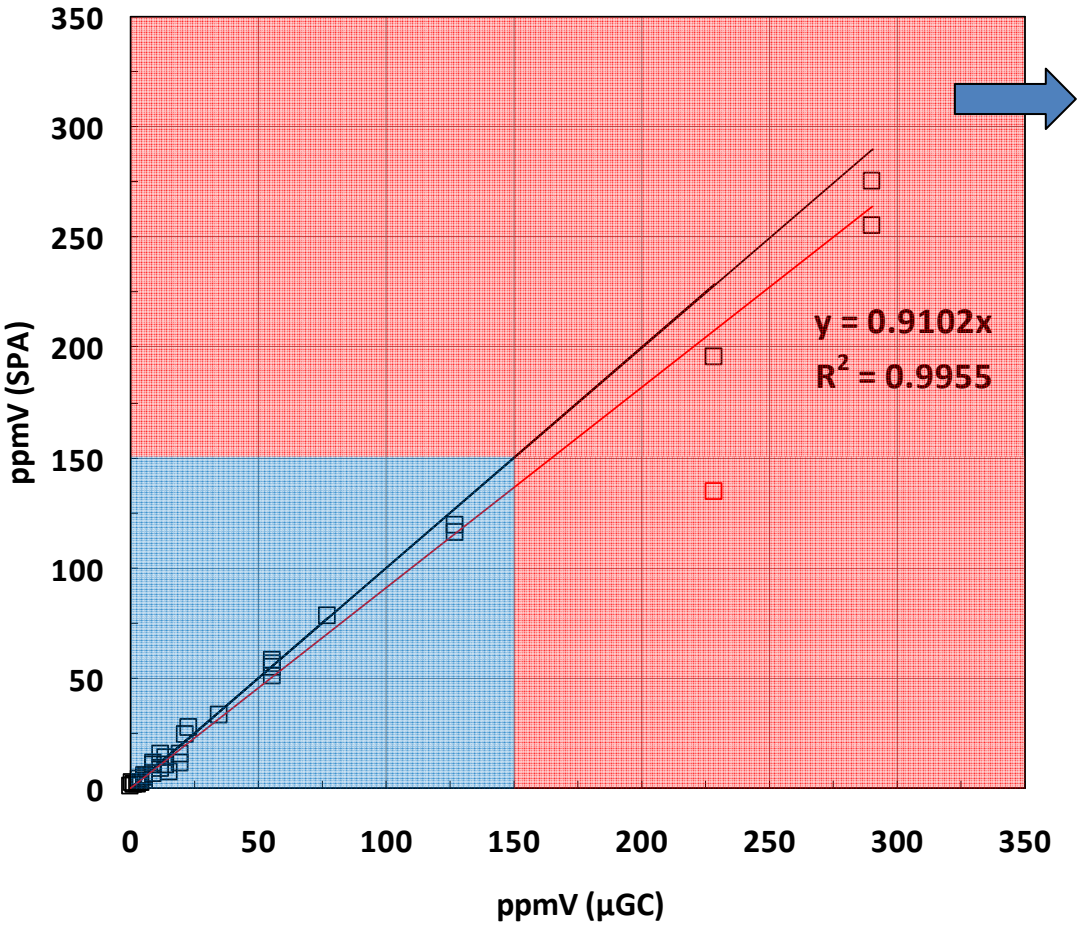
Comparison between SPA and µGC analysis for benzene

3. Real gases, pilot scale on CEA pilot plant (S. Ravel, S. Thiery)



Zone of too high benzene concentrations for SPA

+ Comparison of SPA tubes analysis between Critt and CEA on the same gases (not shown)

SPA method used on gasification and combustion pilot plants

Tar concentration (mg/Nm^3 at 10%O_2)		
Compounds	**Wet wood**	**Dry wood**
Benzene	2.103	0.733
Naphthalene	0.527	0.385
Toluene	0.271	0.084
Fluoranthene	0.135	0.057
Pyrene	0.105	0.047
Acenaphtylene	0.054	0.042
Indene	0.007	0.010
Acenaphthene	Not detected	0.006

Quantification by SPA of tar emission (low concentration) on a biomass combustion pilot plant

Key points for implementing the method

Avoid condensation of tar and water in sampling pipe (heat tracing) as for impingers

Prevent contamination of SPA tubes from dirty pipes

Attention must be paid to the sampling conditions (adsorption **breakthrough**)

Attention must be paid to the **TD step** (temperature / split / duration / **no cold zone in thermal desorber**)

SPA-TD-GC/MS-FID is a convenient method for tar analysis at low concentrations

Validated at lab and pilot plant scales (1 - 500 mg/Nm^3)

More accurate than TMS at low concentrations (< 10 mg/Nm^3)

Sampling line **simplified**

Sampling **time shortened** and limits of quantification improved

More convenient method regarding **operators' health** (no solvent on sampling train), sample **storage, sending**, etc.

➡ **Need other methods to validate SPA at very low concentrations**

SPA could be extended to higher concentrations if a small sampling volume is well controlled to avoid breakthrough

Thank you for your attention

Open to any collaborations

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