

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

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Measurement, Analysis and Monitoring of Condensable Gas Components (especially Tar)
in Product-Gases from Biomass Gasification and Pyrolysis

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■ Advanced syngas applications (SNG, FT Diesel, H₂ ...)

- Need of very low tar content (metal-based catalysts are prone to deactivation)
- Behaviour of tar content is a key parameter for processes

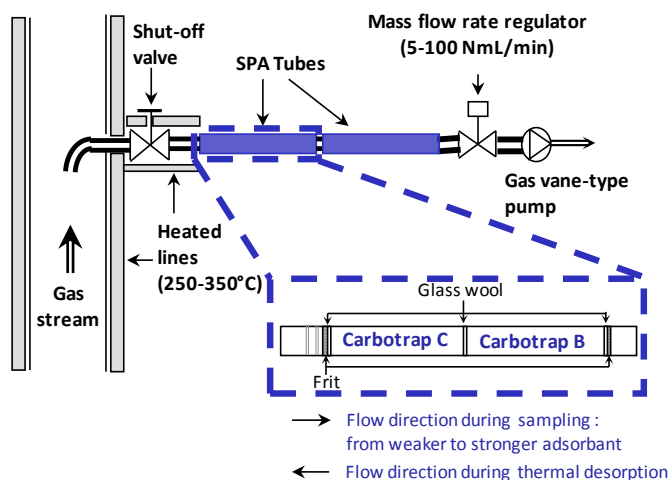
■ Tar Measurement Standard (TMS) guideline [CEN BT/TF 143]

- Reliable method for a more effective comparison of tar concentrations
- Difficult to implement / Use of solvent
- Require a long sampling time to quantify tar at low concentration ranges
- Not adapted for very low concentration (<1 mg/Nm³)

➔ **Development of an analytical method by Solid Phase Adsorption (SPA) associated with Thermal Desorption (TD) and Gas Chromatography (GC) analysis to quantify tar (class 2 – 5) at low concentration**

This method provides an optimization of the syngas purification process step and a better control of the gasification process (for laboratory and plant operations)

SPA sampling

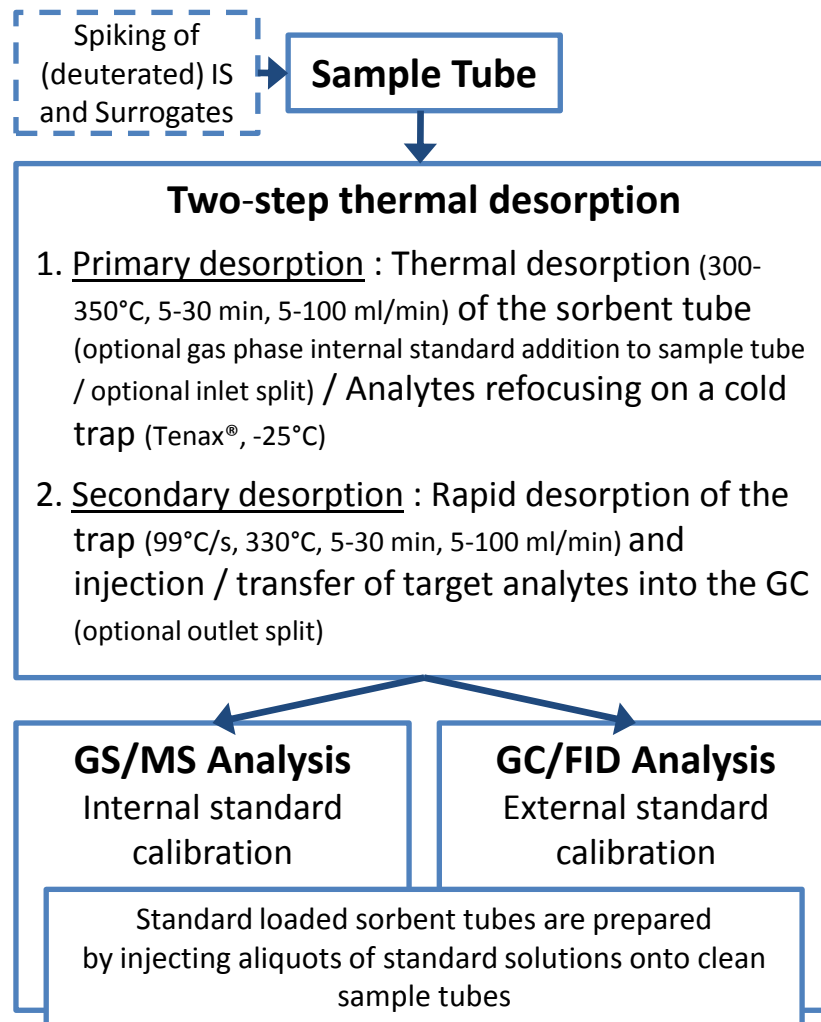


- **Adsorbent** : Carbotrap™ C + B or Tenax® TA or Carbotrap™ X

- **Sampling flow (5 - 100 NmL/min) and time (a few second to several minutes)** : depending on the tar concentration expected and the adsorption breakthrough volume of adsorbent for each tar

- **Sampling line** : shut-off valve / heated pipes / one or two SPA tubes / mass flow regulator / gas pump

TD - GC analysis



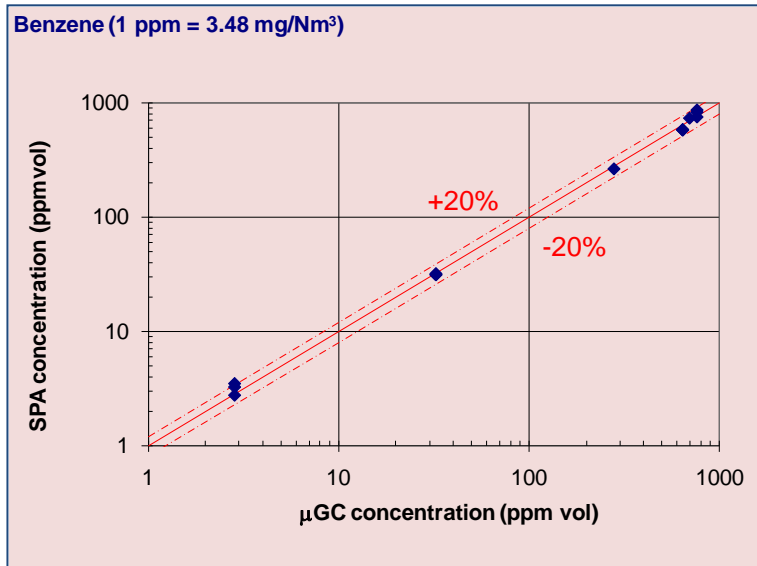
Analytical parameters

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

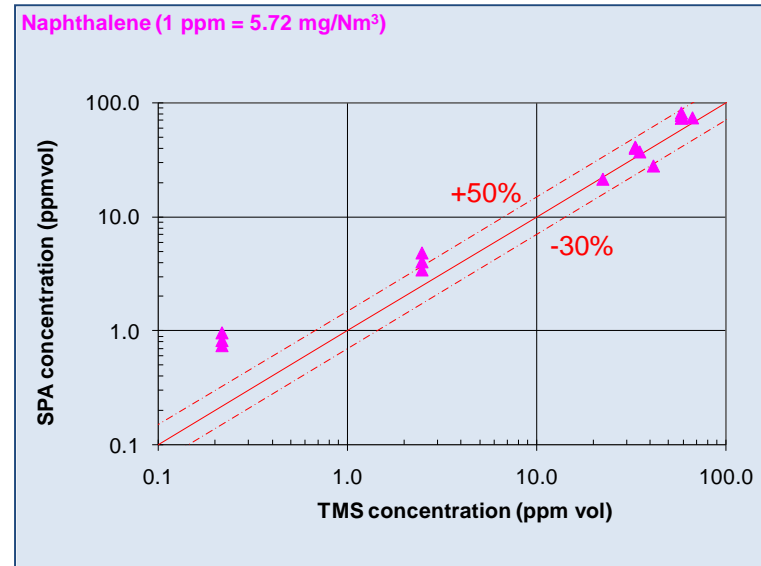
Internal standard : ⁽¹⁾ toluene-d8 / ⁽²⁾ naphthalene-d8

Theoretical sampling time for SPA and TMS to achieve limit of quantification

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 of SPA and μ GC measurements for benzene +/-20%



Comparison of SPA and TMS measurements for naphthalene +50%/-30%

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

- A simple and rapid method convenient for measurement of tar traces in product-gases from biomass gasification and pyrolysis
 - Validated at lab and pilot-plant scales (between 1 and 500 mg/Nm³)
 - More accurate method than TMS at low tar concentrations (< 10 mg/Nm³)
 - Sampling line simplified
 - Sampling time shortened and limits of quantification improved
 - More convenient method regarding operators' health, sample storage...

■ Key points of the method :

■ Sampling and analysis protocols

- Avoid condensation of tar and water in sampling pipe (heat tracing)
- 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)



Future work : full scale plant testing