Measurement and Characterization of Tars using the SPA Method

On-going Developments on Tar Analysis

Klas Engvall
Royal Institute of Technology (KTH)
Stockholm, Sweden

Kevin Whitty
University of Utah
Salt Lake City, Utah, USA

Outline

- Biomass gasification tars
- “Conventional” tar sampling and analysis
- Solid Phase Absorption (SPA) sampling and analysis
- Modifications to the SPA method
- Conclusions

Biomass Gasification Tars

- Production of condensable polyaromatic “tars” is inherent in most biomass gasification processes
- Tars foul and can plug equipment downstream of the gasifier
- Challenging to remove from syngas
- Reduce energy efficiency of gasification process
- Reports of as much as 10% of biomass carbon ending up in the form of tars

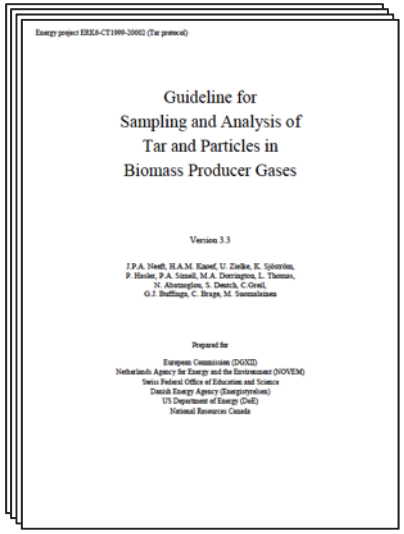
Tar Analysis

A few common steps:

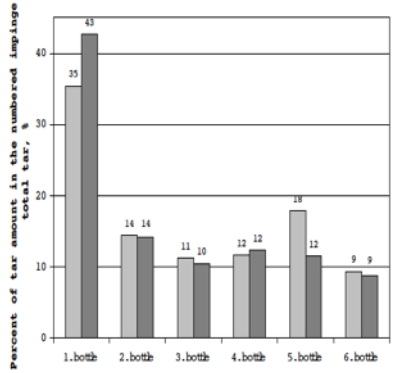
1. Sampling of the tar: Generally collected from a side stream, including more or less complicated sampling equipment to attain a representative sample.
2. Storage of sample: Only valid for offline methods.
3. Pre-preparation/conditioning of the sample:
   - Offline methods: The collected tars are extracted to or dissolved in an appropriate solvent for further chemical analysis.
   - Online measurements: Conditioning such as drying of gas removal of particulates etc. may be required depending on the analytical technique.
4. Analysis of sample: Chemical analysis of pre-prepared/conditioned tar sample. Most common analytical techniques are based on gas chromatography (GC) or high pressure liquid chromatography (HPLC).

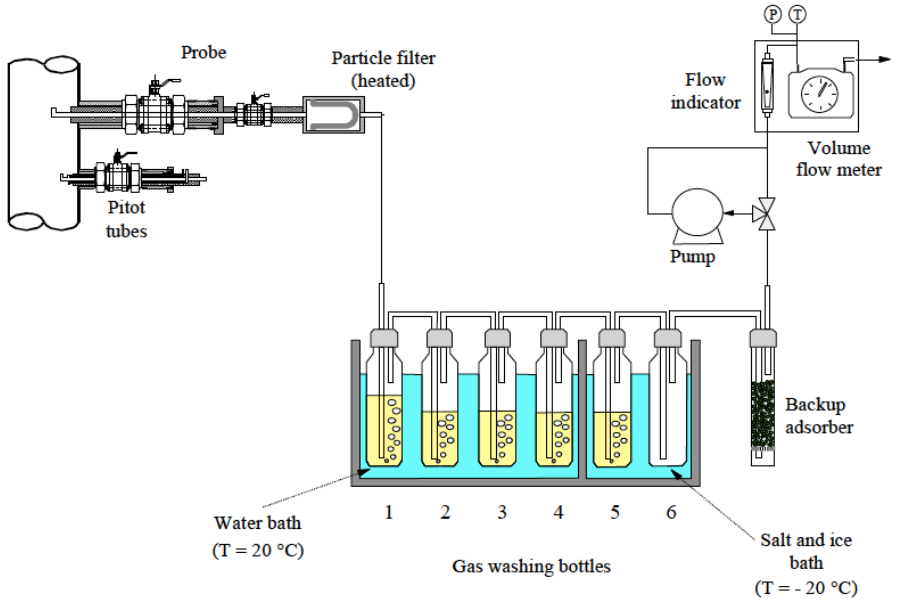
“Conventional” Tar Analysis

- Tar protocol developed over several projects supported by IEA Bioenergy Task 33, US DOE and European Commission 1998-2005
  - Significant contributions by ECN, VTT, KTH, DTI, BTG, NREL
- Adopted as CEN standard for tar sampling
- Procedure
  - Draw specific volume of process gas through filter then series of cold impingers to collect tar
  - Evaporate solvent to measure gravimetric (total) tars
  - Analyze tars by GC-MS to evaluate composition
- Quantitative, but very laborious


Guideline for
Sampling and Analysis of
Tar and Particles in
Biomass Producer Gases

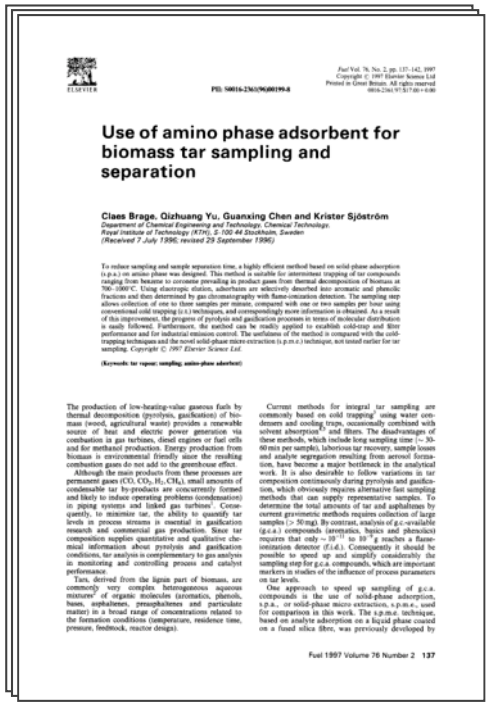
Version 3.3





Solid Phase Absorption (SPA) for Analysis of Biomass Gasification Char

- SPA sampling and analysis method was developed by KTH in the 1990's.
- SPA used for measurement of the concentration (mass) of individual light aromatic hydrocarbons and phenols.
- The SPA-method is restricted to GC-available (GA) compounds only.
- These compounds are, however, significant process markers that provide good measures of reactor performance and gas quality.
- At 900° C the GA-compounds roughly correspond to the total tar amount.

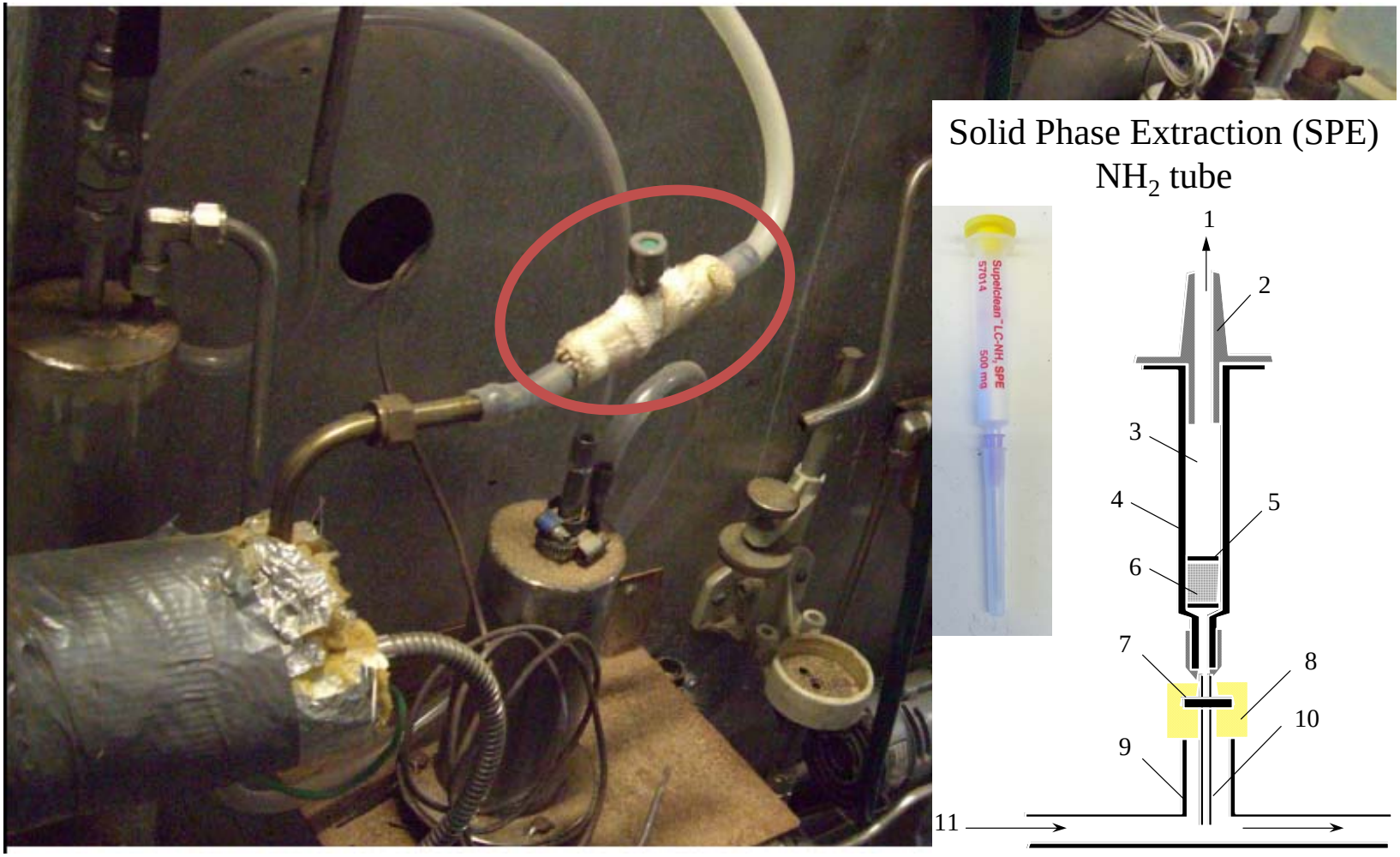


Use of amino phase adsorbent for biomass tar sampling and separation

Claes Brage, Qizhuang Yu, Guanxing Chen and Krister Sjöström

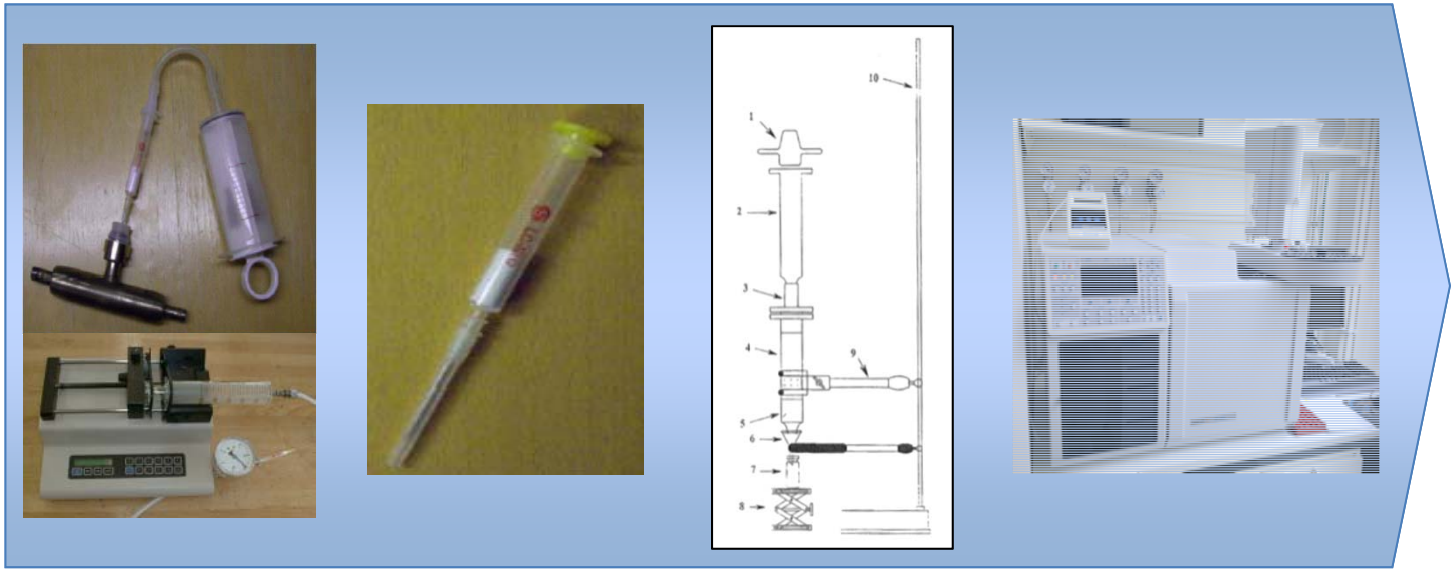
Claes Brage, Qizhuang Yu, Guanxing Chen, Krister Sjöström
"Use of amino phase adsorbent for biomass tar sampling and separation"
Fuel Vol.76, No. 2, pp. 137-142, 1997.

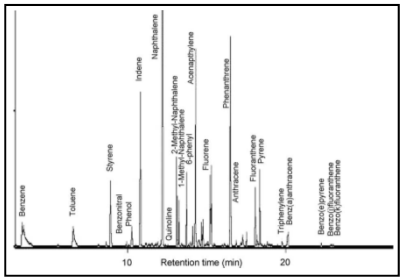
Solid Phase Absorption (SPA) Sampling



1 = to syringe or electrical pump; 2 = adapter (polypropylene); 3 = sample reservoir; 4 = sorbent tube (PP, 1.3 OD x 7.5 cm); 5 = fritted disc (20µm polyethylene); 6 = amino-phase sorbent (40 µm, 60 Å); 7 = rubber/silicone septum; 8 = septum retainer (polypropene); 9 = "Tee"-adapter (glass); 10 = syringe needle (stainless steel); 11 = producer gas.

Solid Phase Absorption (SPA) Analysis





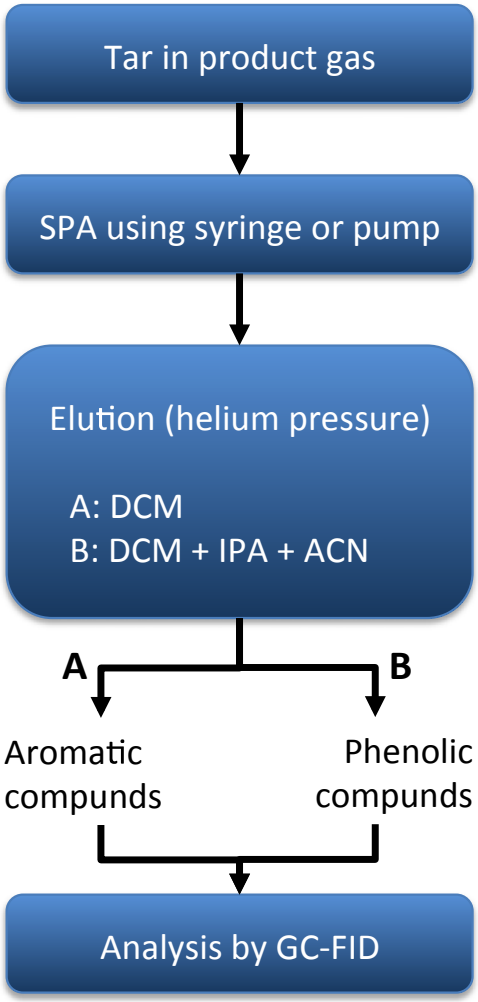
Sampling	Sample storage	Sample preparation	Chemical analysis	Results
"T", needle, SPE-NH_2 tube and 100ml syringe. Custom made reversible SPE tube.	The SPE tube is capped in both ends after sampling. Samples stored in a fridge/freezer	Elution for aromatic and phenolic compounds	GC-FID - Gas chromatograph with flame ionisation detection	

Solid Phase Absorption (SPA) Analysis

Sampling

Sample preparation

Chemical analysis

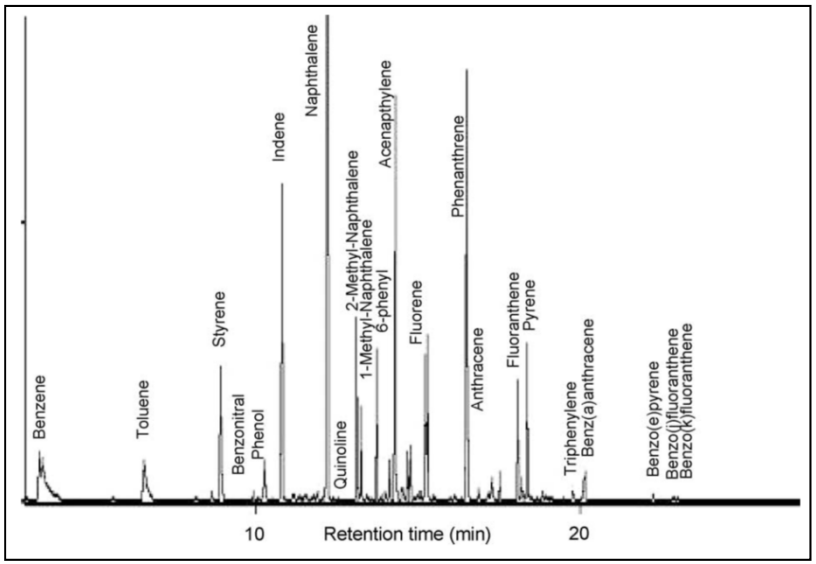


100 ml producer gas is passed through the SPA (amino phase bonded to silica).

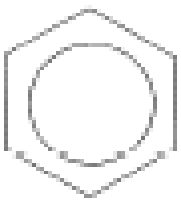
DCM: dichloromethane
IPA: isopropanol
ACN: acetonitrile

GC-FID: gas chromatograph with flame ionization detection
Internal standards: TBCH [tert-butylcyclohexane] and PEP [p-etoxyphenol]

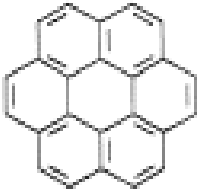
Solid Phase Absorption (SPA) Analysis



- PEP [p-etoxyphenol] allows for derivatisation of the phenolic fraction, improving the chromatographic performance.



Benzene



Coronene

- Traditional SPA may be used to determine compounds ranging in molecular weight from 78 (benzene) to 300 (coronene)

A (biased?) Comparison Between SPA and Other Tar Analysis Methods

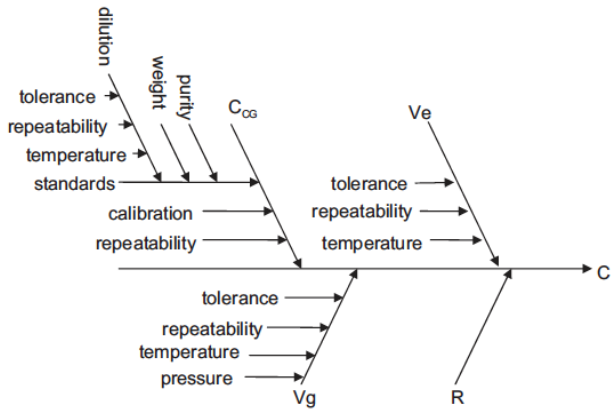
Cold solvent trapping (CST) (**"*Tar guideline*"**)	**Traditional SPA** (**"KTH"**)	**On-line analyser** (**"*GC-FID, MBMS, GC/LAMS*"**)
Advantages: -Gives total tar, heavy and light tar **Drawbacks:** -Time consuming, sampling as well as analysis -Large solvent volumes -Not suitable for (very) low tar concentrations -Low precision	**Advantages:** -Uncomplicated and fast sampling -Low cost -High accuracy and reproducibility -Sampling and analysis can be done separately **Drawbacks:** -Not suitable for heavy tars -B(TX) must be analysed within a few hours	**Advantages:** -Short to relatively short sampling and analysis time **Drawbacks:** -Expensive to very expensive. -Experienced as ungainly -Complicated and often needs an expert for operation -Generally not suitable for heavy tars

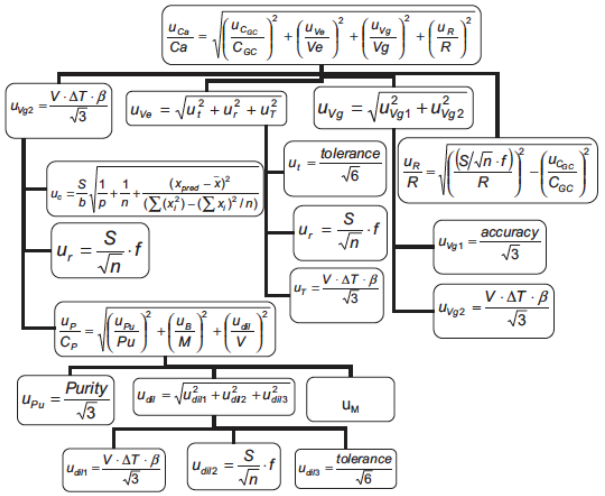
Challenges of SPA Method

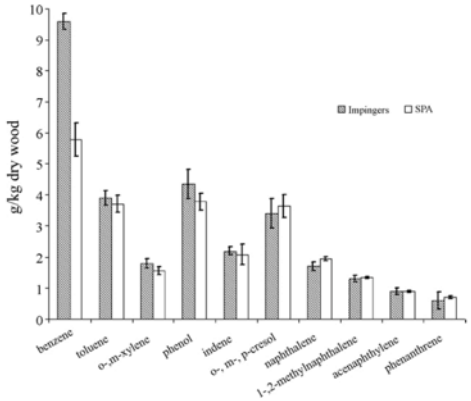
- Inleakage of air, especially for sub-atmospheric pressure systems
- Using temperature high enough to avoid tar condensation yet low enough not to melt septum
- Plugging of needle by septum material
- Condensation of tars in needle of syringe
- Undesirable heating of SPE column during sampling due to temperature, steam condensation
- Possible conversion of tars by upstream filter material or filter cake
- Breakthrough of light tars (BTX)
- Desorption of light components from SPE cartridge during storage
- Efficient elution of aromatic and phenolic compounds
- Inability to measure heaviest tars
- Consistency of procedures for sampling and analysis

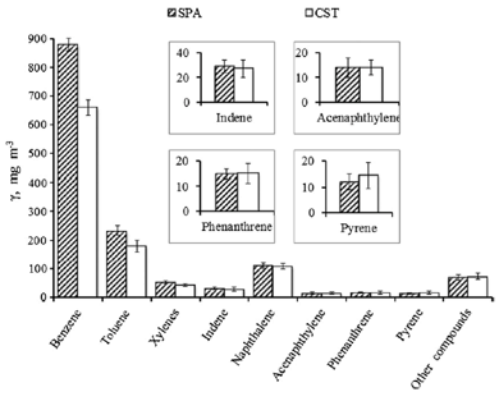
Quantitative Evaluation of SPA Method

- Several studies have compared SPA and impinger-based methods
  - Range of compounds
  - Total tar
  - Component concentrations
- Other studies have quantified uncertainty in SPA method
- Conclusion is uniformly that SPA is more repeatable and yields results at least as reliable as impinger-based analysis



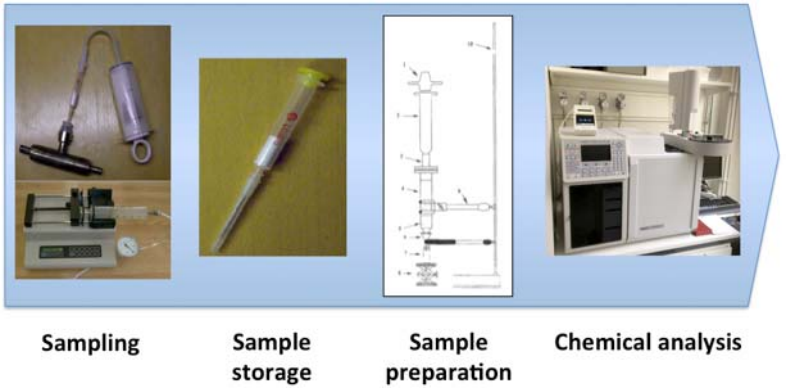


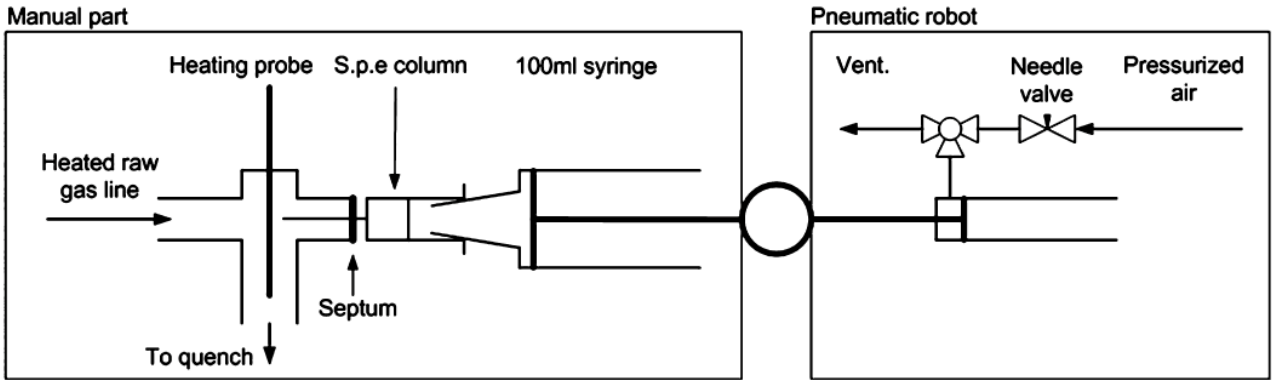




“Automatic” Tar Sampling

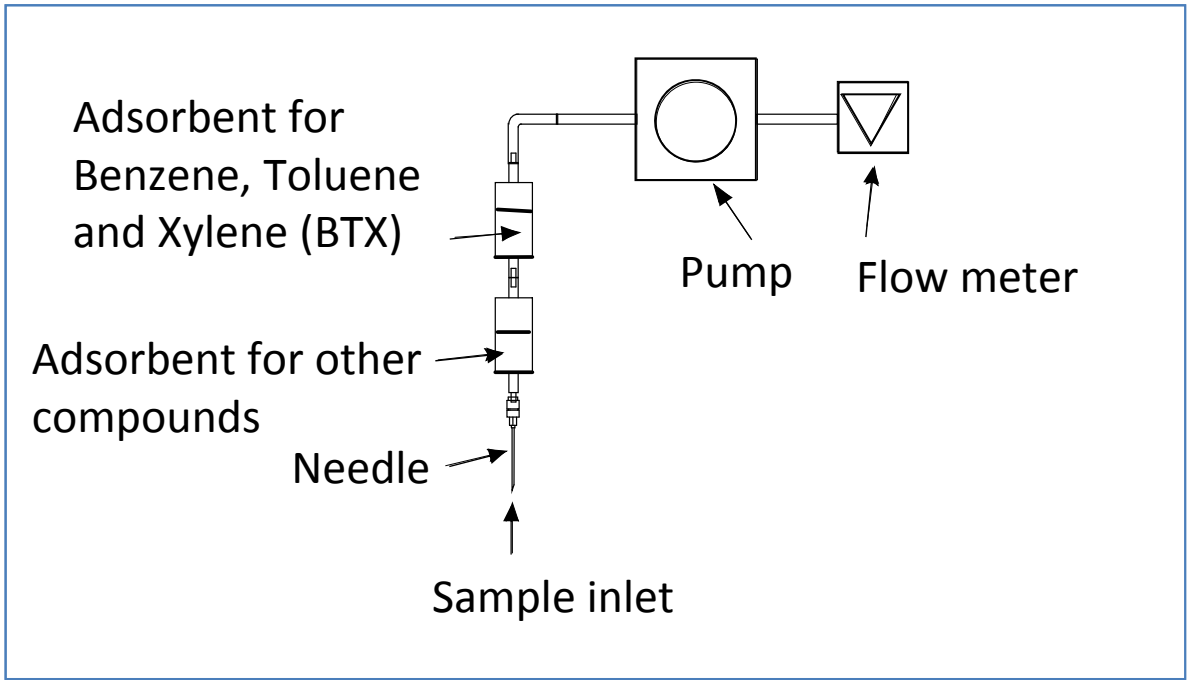
- Inconsistency in any of the SPA analysis steps may lead to variations in measured values.
- Manual operation of sampling syringe incurs variations in plunger speed, sampling time, sample volume
- Pneumatic “robot” for sampling improves consistency and reduces errors associated with sampling (Chalmers)
- Alternative is to use a syringe pump (ECN)





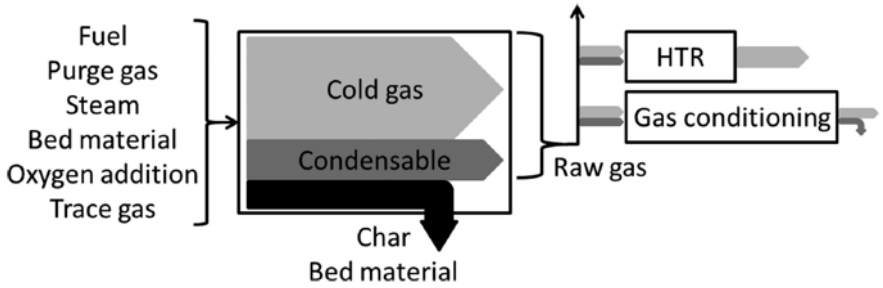
SPA Analysis at Low Tar Concentrations and Separate BTX Analysis (KTH)

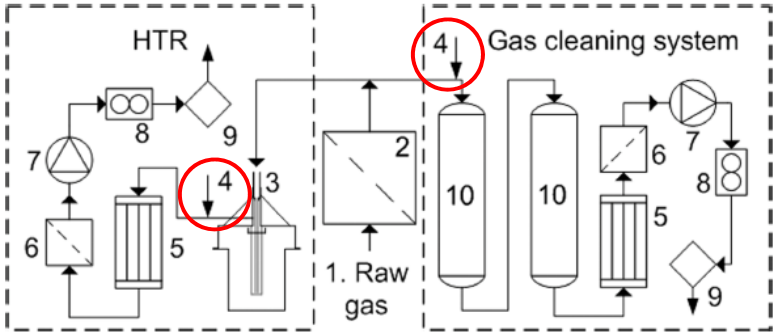
- Determination of light tar in low concentrations

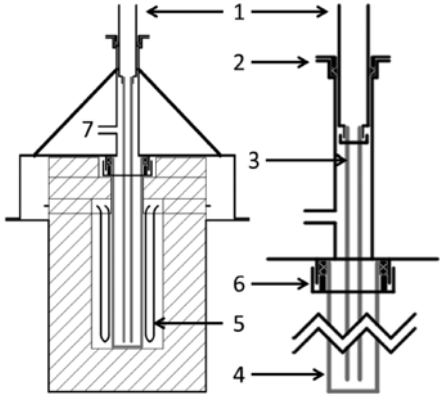


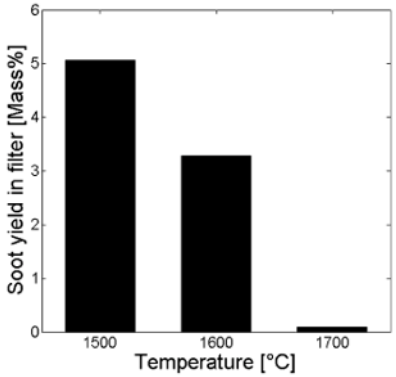
Syngas Total Elemental Analysis for Mass Balance (Chalmers)

- Uses high temperature reactor (HTR, 1700° C) to convert C3-C6 hydrocarbons and tars to light gases
- Filtered, hot syngas measured at two different locations
  - Directly after filter (standard SPA)
  - After passing through HTR to convert all gases to light gases
- Measured by GC with He tracer for mass balance
- Difference in GC analysis of streams allows quantification of tars not identified by standard SPA method



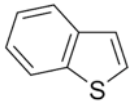




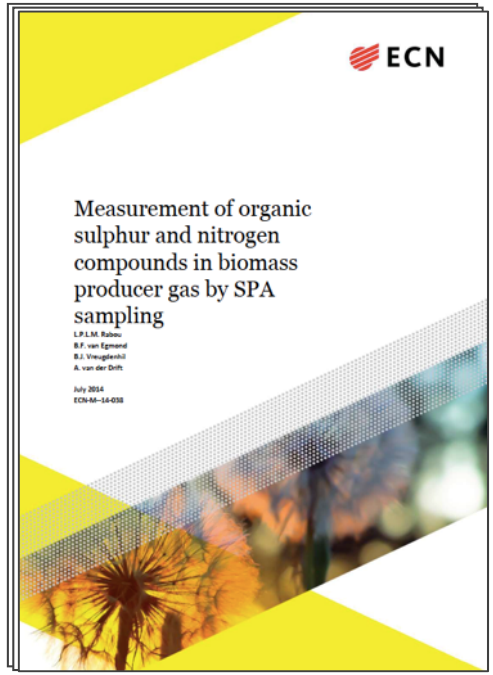


Israelsson, M., Larsson, A., Thunman, H., "Online Measurement of Elemental Yields, Oxygen Transport, Condensable Compounds, and Heating Values in Gasification Systems," Energy & Fuels 28:5892-5901 (2014).

Measurement of Sulphur- and Nitrogen-Containing Compounds (ECN)

- SPA method can be used for identification of condensable compounds containing sulphur or nitrogen
- Sub-ppm detection level
- Heavier compounds captured well
  - > Benzothiophene (S) 
  - > Pyridine (N) 

  lighter components break through
- Other sorbent materials may improve capture



Compound	1st SPA	Compound	1st SPA	Compound	1st SPA
Benzene	<15%	Thiophene	<15%	Pyridine	95%
Toluene	<15%	2-Methyl thiophene	<35%	2-Methylpyridine	>95%
Ethylbenzene	<15%	3-Methyl thiophene	<35%	3-Methylpyridine	>95%
Xylene	<25%	Benzothiophene	100%	4-Methylpyridine	>95%
Styrene	<25%	Dibenzothiophene	>95%	Quinoline	100%
Phenol	100%			Isoquinoline	100%
Indene	~70%	*Accuracy for Methylthiophene, Methylpyridine and Dibenzothiophene limited by low concentrations*			
Naphtalene	100%				

Rabou, L.P.L.M., Van Egmond, B.F., Vreugdenhil, B.J., Van der Drift, A., "Measurement of organic sulphur and nirogen compounds in biomass producer gas by SPA sampling," ECN report ECN-M-14-038 (2014).

Conclusions

- Dealing with tars a significant challenge for biomass gasification systems
- Simple, low-cost, yet robust means of measuring and characterizing tars is desirable
- Impinger-based method of standard tar protocol is relatively robust but time consuming and laborious
- SPA method much simpler and equally as good for many situations, but does have drawbacks
- Variants of SPA method allow for more complete quantification or analysis of other components
- Continued development of SPA procedure will improve robustness and utility of the method