Business from technology

# GC based analysis of tar, ammonia and water

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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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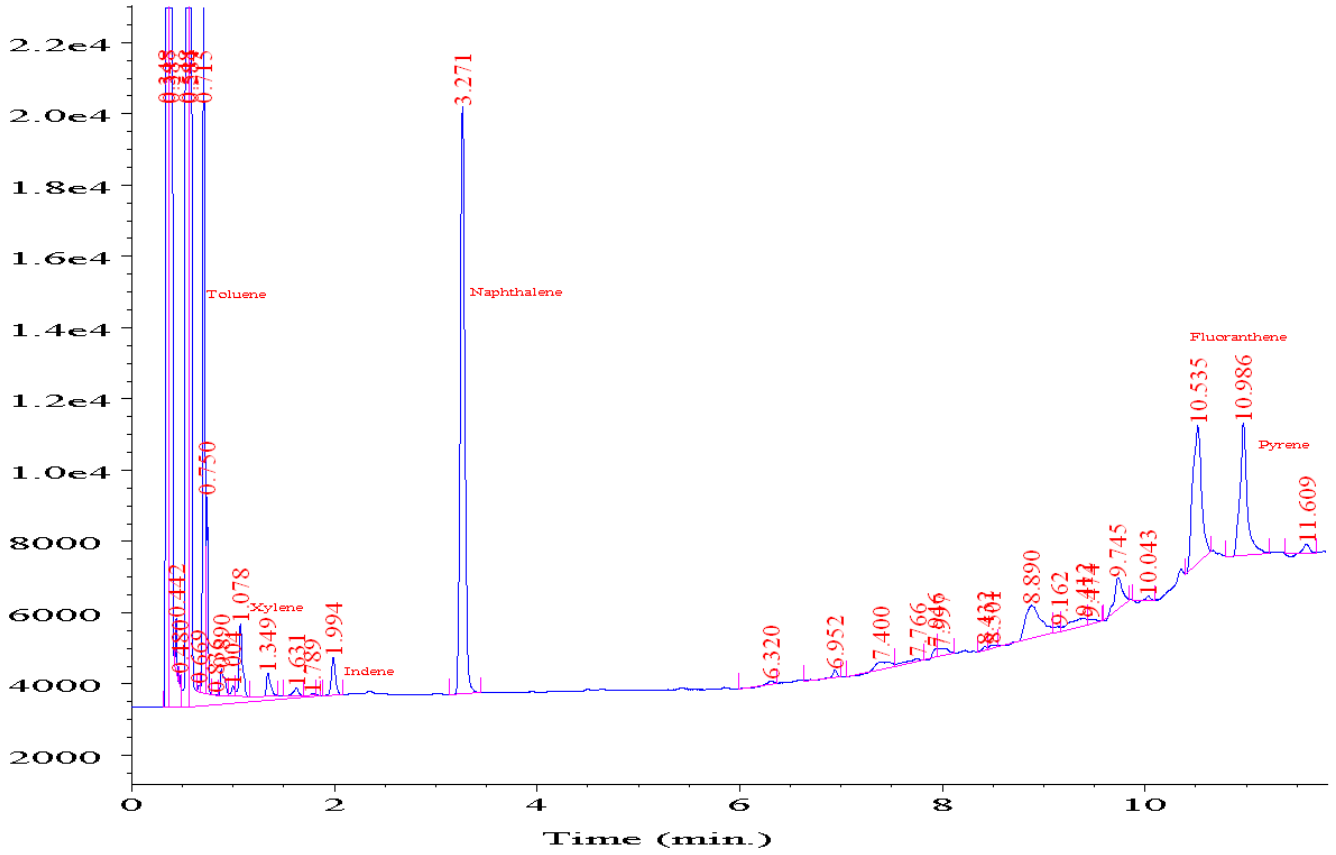
# Advanced analysis techniques for gasification gas

- The aim has been to develop better analysis methods for the impurities in biomass gasification gas
  - Shorten the analysis time, improve accuracy and reduce labor intensity
  - From off-line to on-line
- Research subjects:
  - Analysis of small concentrations of sulphur in the gasification gas
  - Improved analysis method for alkalimetals
  - Establish on-line-tar analysis for light tars
  - Improved $NH_3$- and HCN-measurement methods
- Development work in a projects with Carbona, Neste, Stora-Enso, Foster Wheeler , Metso, VAPO, UPM and Gasum

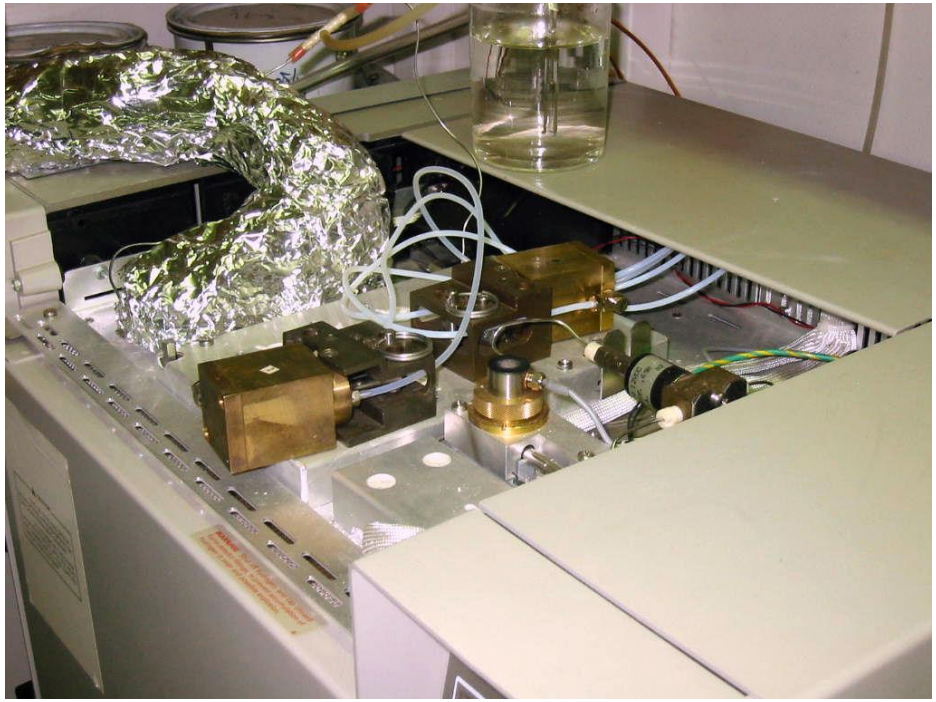
# 'Rapid' on-line tar analysis of reformed gasification gas

- Analysis time 5-20 min (several possible operation modes)
- Calibrated compounds:
  - Benzene
  - Toluene
  - Naphthalene
  - Phenanthrene
  - Anthracene
  - Fluoranthene
  - Pyrene
  - (if desired, 40 additional compounds)
- HP-1 (10 m x 0.53 mm x 0.26 µm) or HP Ultra 2 –column (25 m x 0.32 mm x 0.52 µm)
- Gas phase samples online
- Connected to the gasifier automation system
- Has been in use at VTT for more than three Years

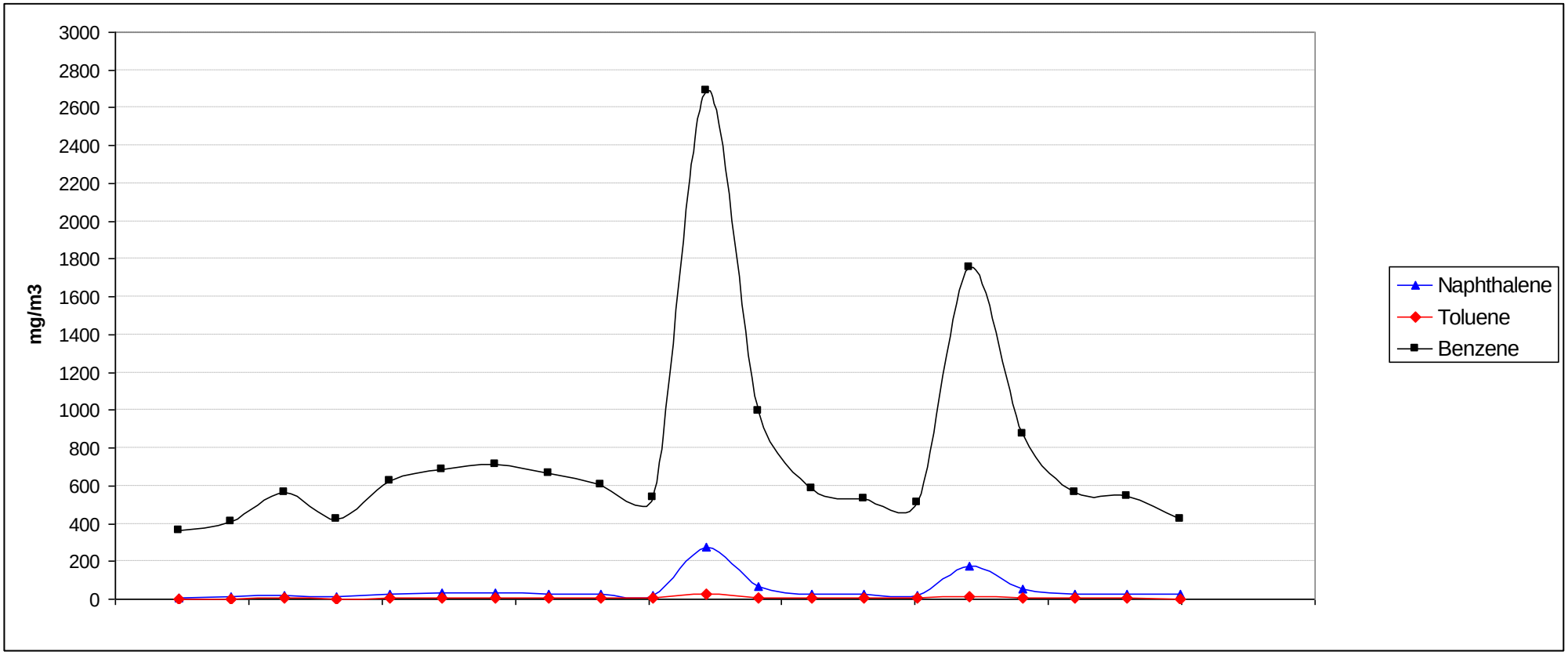


# Validation of the on-line tar measurement method

- More than 500 on- and off-line tar measurements were carried out
- Under carefully controlled conditions both the Tar Protocol and the on-line method give consistent results

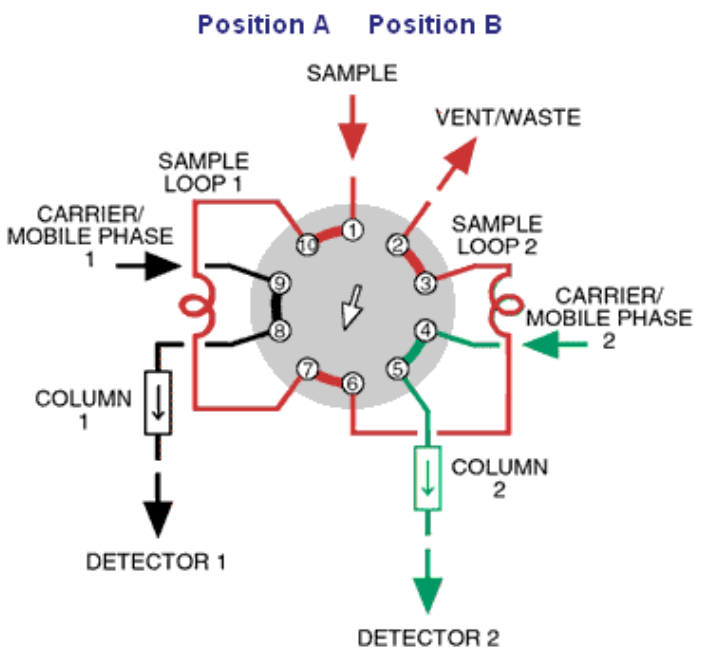


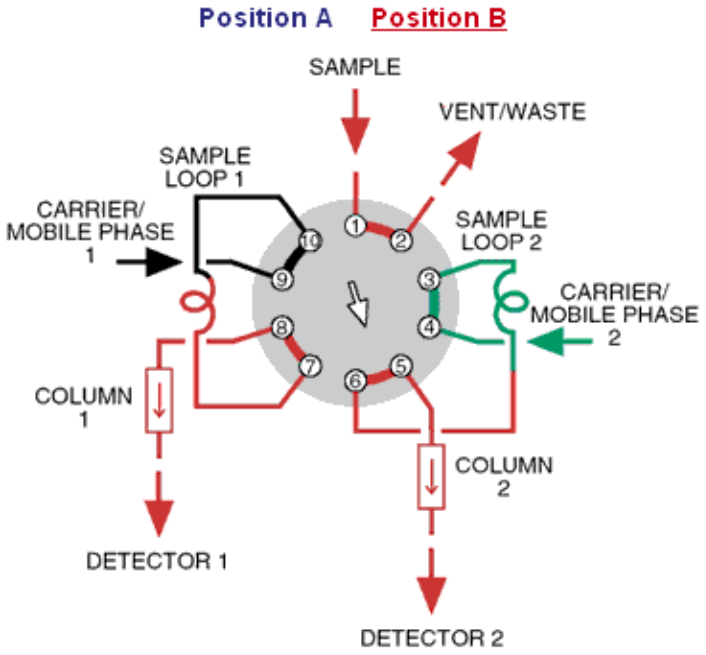
# Example of rapid tar measurement by on-line-GC




Air-blown CFB gasification followed by tar reformer

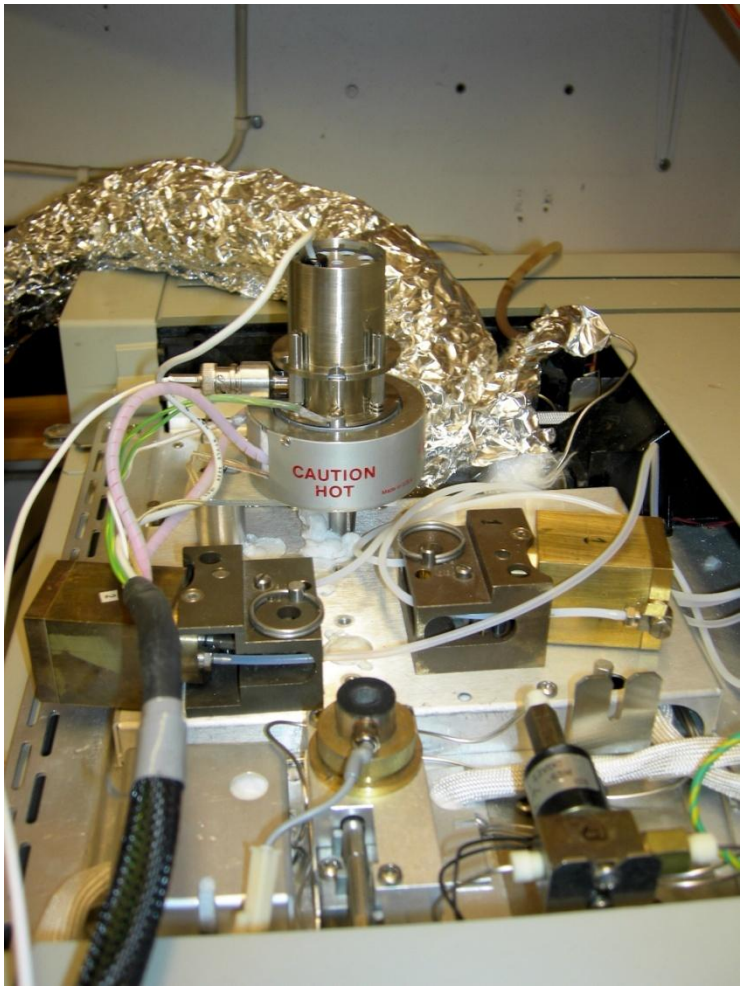
# On-line analysis of tars, water and ammonia 1/3

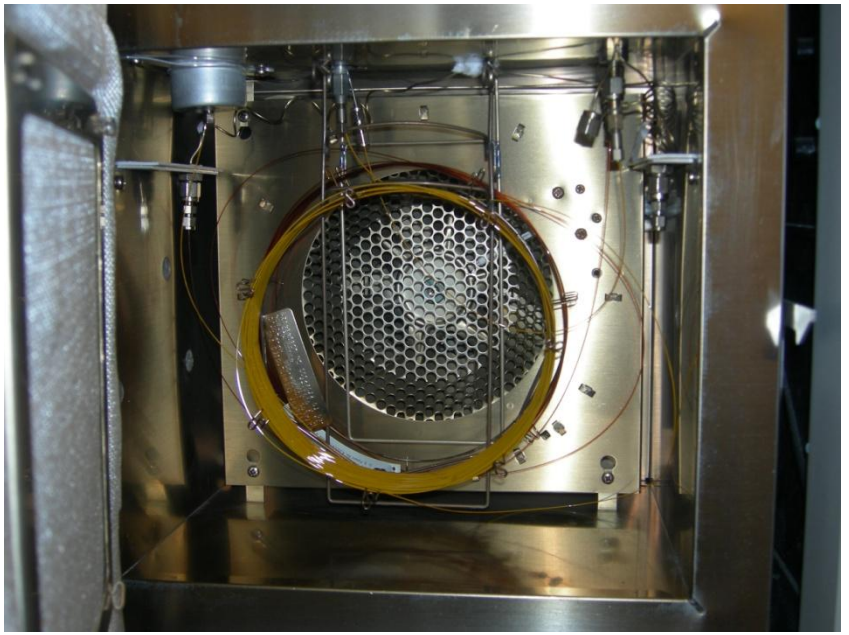



Simultaneous injection to two different columns:
Column 1: HP-1 for the analysis of hydrocarbons (FID)
Column 2: Poraplot-Q for the analysis of water (TCD) and ammonia (PID). TCD and PID in series.

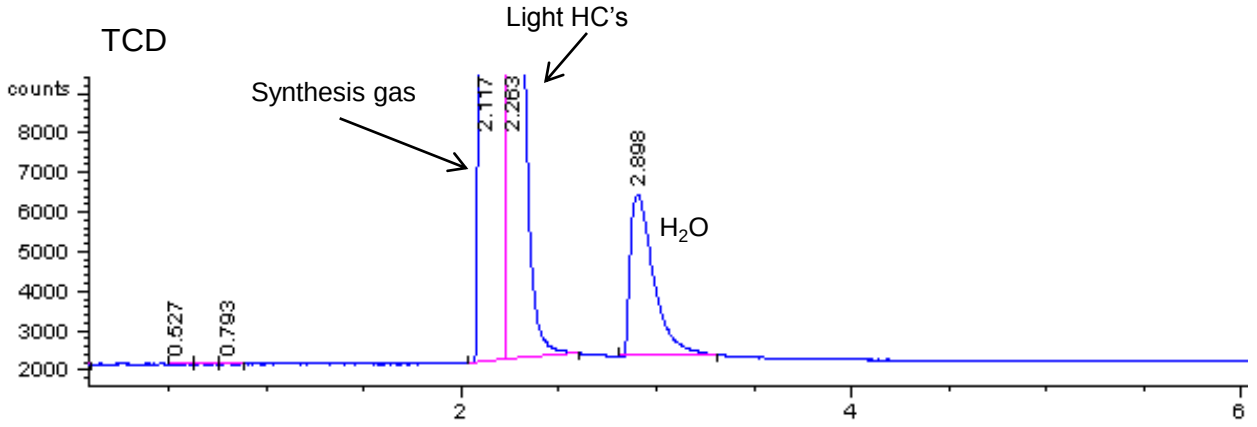
# On-line analysis of tars, water and ammonia 2/3



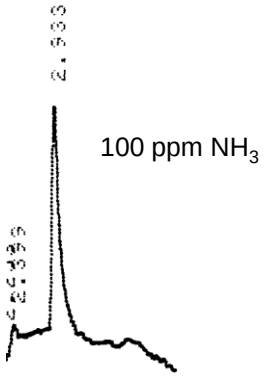



# On-line analysis of tars, water and ammonia 3/3

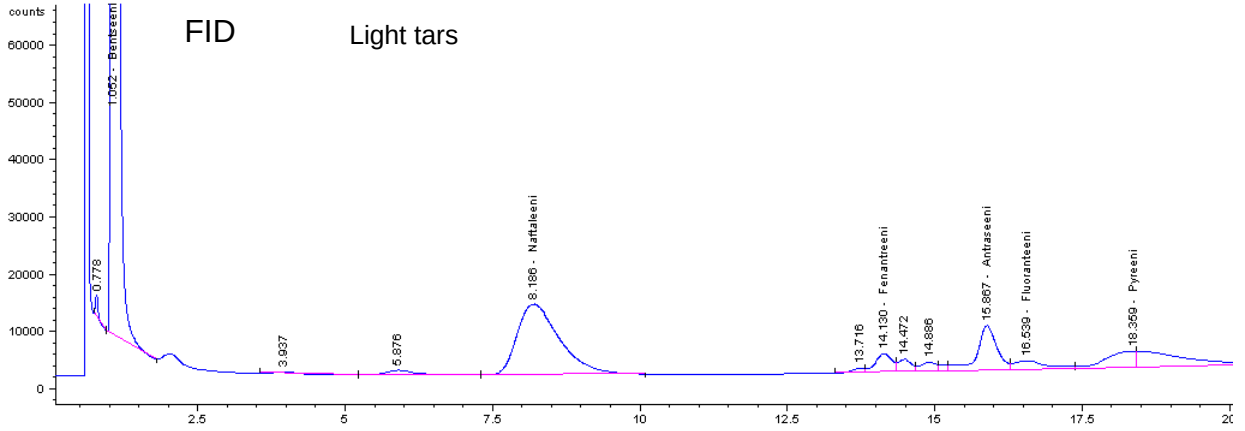
TCD




PID




FID Light tars



# Dilution sampling

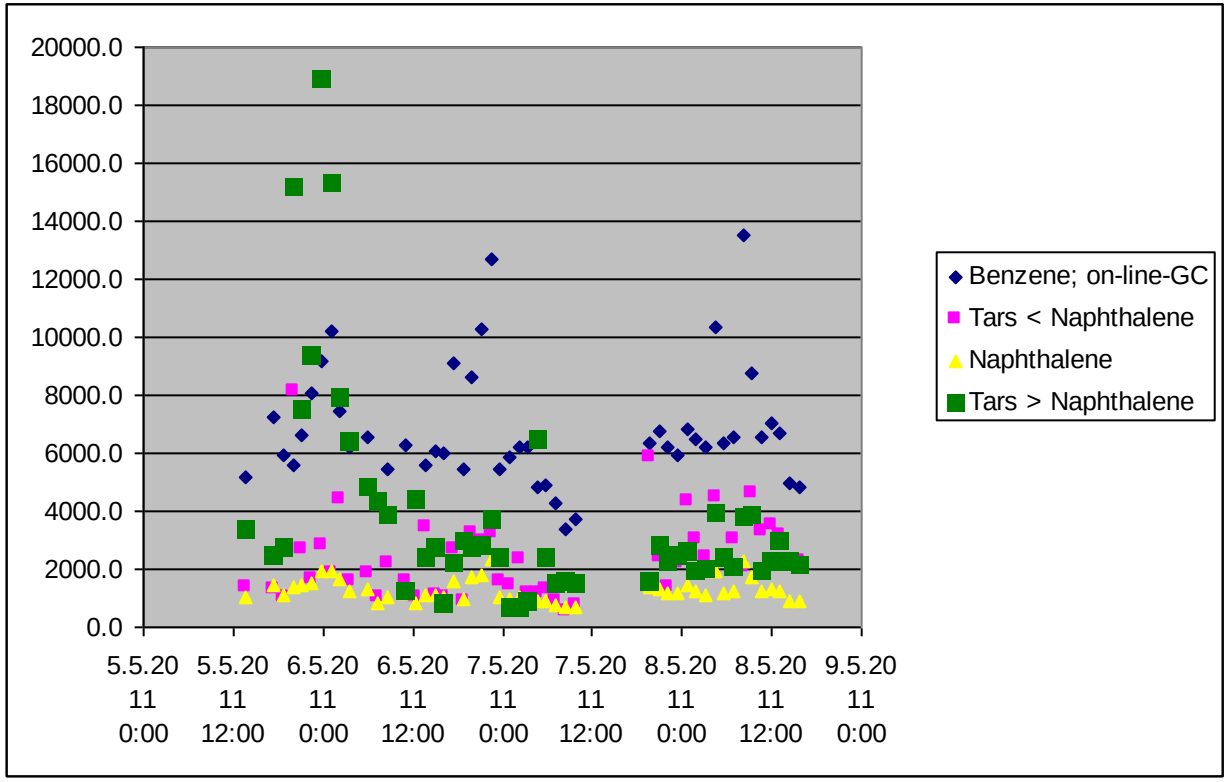
- Based on technology patented by VTT (e.g. WO/2007/080221)
- Can be applied to both atmospheric and pressurised systems
- Temperature range 280-800°C
- Dilution ratio typically 0-100
- Can be used for instance with a GC, ICP or FT-IR

- Results with tarry raw gas have been promising
  - Results consistent with controlled off-line sampling
  - No problems with condensation of tars in the sampling lines
  - Good repeatability
  - Now in regular use at one site Finland

- Under continuous development

# Dilution sampling: tar measurement of tarry gas

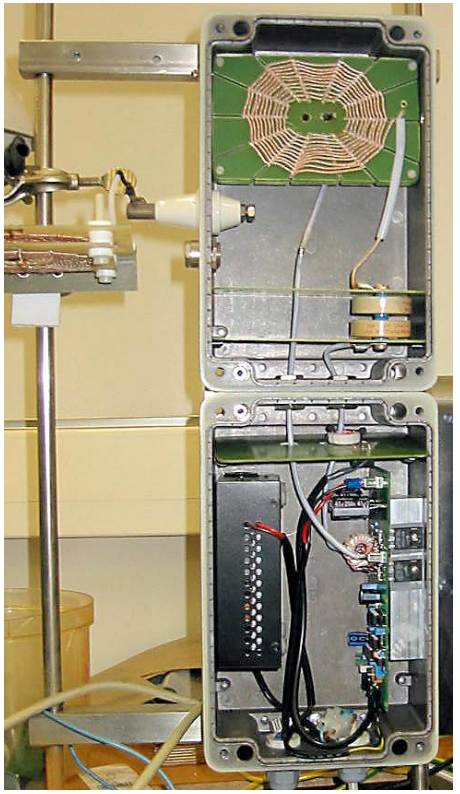
| | |
|---|---|
| Benzene | Acenaphtylene |
| Pyridine | Acenaphthene |
| Toluene | Dibenzofurane |
| Ethenylbenzene | Bibenzyl |
| m-Xylene | Fluorene |
| Ethynylbenzene | Phenanthere |
| Styrene | Anthracene |
| o-Xylene | Carbazole |
| Benzaldehyde | 1-Phenylnaphthalene |
| Phenol | 2-Methylanthracene |
| Benzonitrile | 4H-Cyclopenta(def)Phenantherene |
| 4-Methylstyrene | Fluoranthene |
| Indene | Benz(e)acenaphthylene |
| o-Cresol | Pyrene |
| m+p-Cresol | Chrysene |
| Naphthalene | 1,2 Benzanthracene |
| Quinoline | 2,3 Benzanthracene |
| Isoquinoline | Benzo(b)fluoranthene |
| Quinatsoline | Benzo(e)pyrene |
| 1H-Indole | Benzo(a)pyrene |
| 2-Methylnaphthalene | Perylene |
| 1-Methylnaphthalene | Benzo(ghi)peryle |
| Biphenyl | Anthanthrene |
| 2-Ethylnaphthalene | Coronene |
| 1.6 Dimethylnaphtalene | |



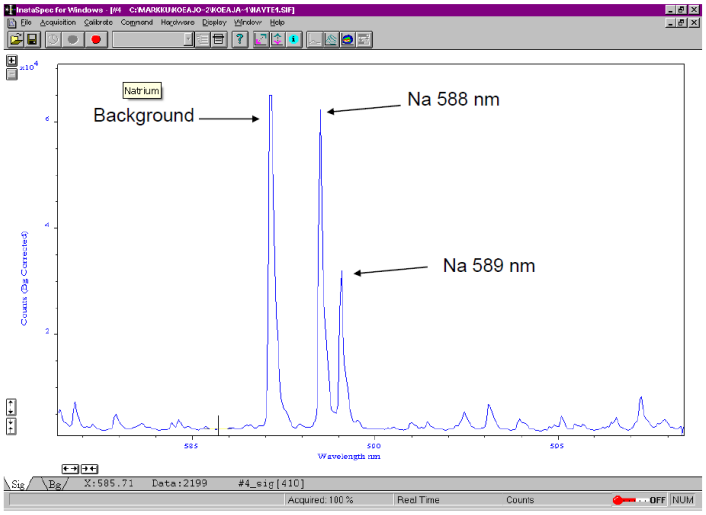
# Dilution sampling: tar measurement of tarry gas

# Development of a cheap and robust ICP-method for the on-line metal analysis

- ICP can be used for the simultaneous analysis of several metals (Na, K, Fe, Ni, Cu, Zn, Sb…)
- Plasma is generated using power transistors by ramping the freguency until resonance is achieved according to a VTT's patented method
- Typical bands of various metals can be detected not only from a dry gas but also from wet gas or liquid solutions
- Method was successfully tested with real gasification gas



**Sodium emission spectra**



# Analysis of HCN using static head space-technique (HS/GC-FID)

- 5 ml of 1:2 $H_2SO_4$ / water is injected to a gas tight 20 ml ampoule. The ampoule is sealed with a septum cap. 1 ml of sample (pH = 12) is injected through the septum on the $H_2SO_4$-solution.
- The sample ampoule is heated in the HS-apparatus at 80 °C for 5 min and then injected to GC-FID-analysis