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The actual need of a guideline for sampling and analysis of chemical matter (not tars) from product gas, pyrolysis gas and synthesis gas

Milan, 22.06.2012

Sampling conditions

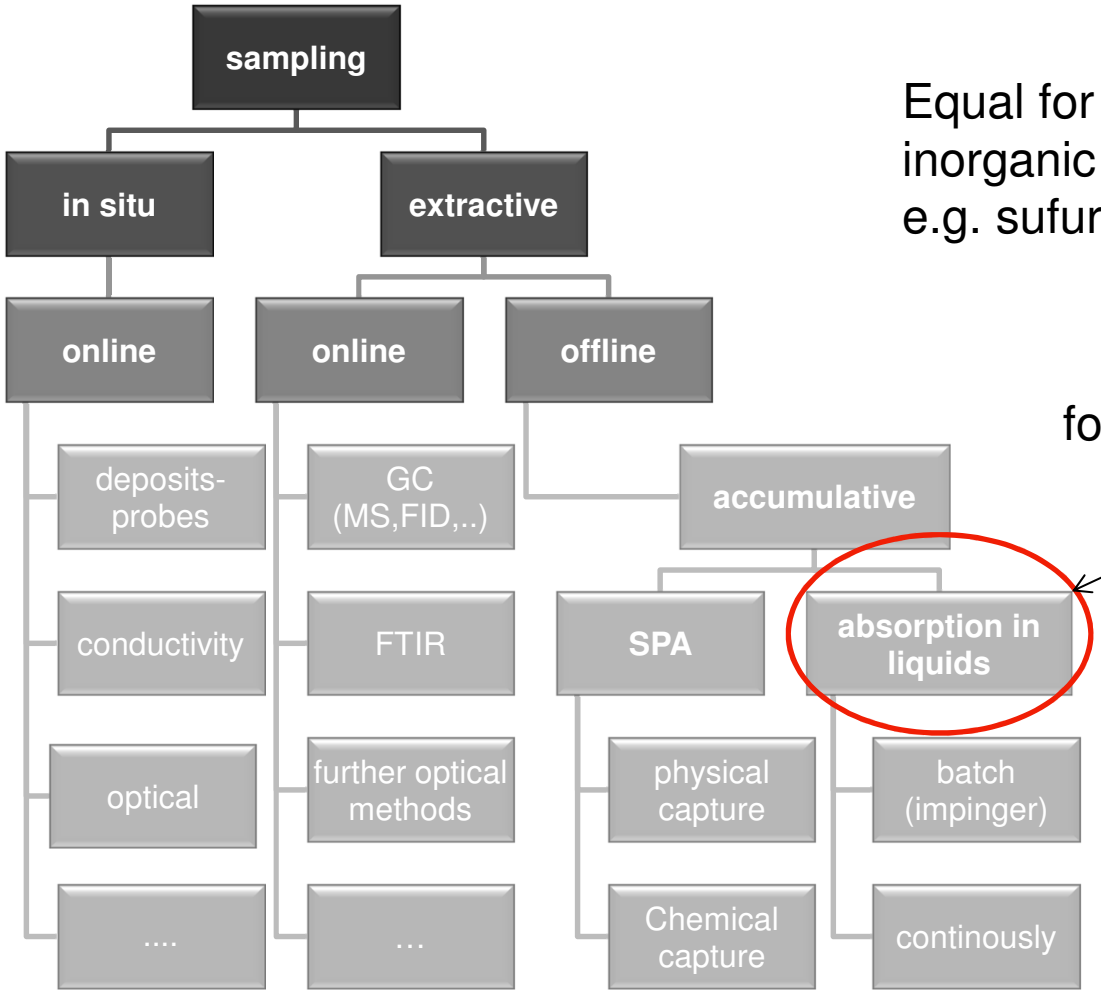
Sampling-conditions at measurement point:

- temperature: 50 – 1500 °C
- pressure: -2 – 60 bar
- concentrations: < 1 mg/m³ to 30 g/m³
- water-content: 0 – 0.1 $kg/kg_{gas,dry}$
- dust: <50 mg/m³ - 30 g/m³
- tar: < 1mg/m³ - 300 g/m³

Settings of equipment:

- valves for pressure reduction?
- condenser?
- heating?
- filtering?
- fittings?
- …

Sampling, detection, analysis methods



Equal for organic and inorganic components
e.g. sufur containing tar

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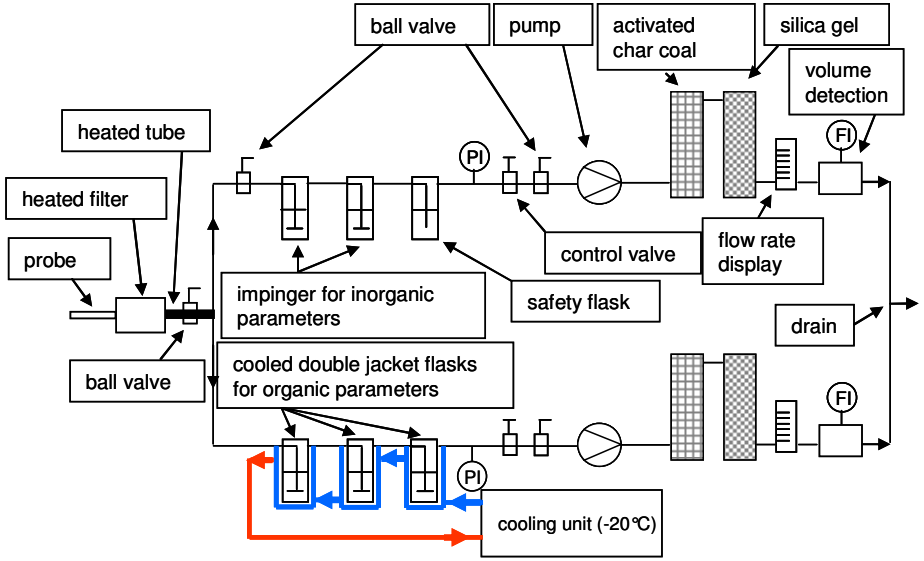
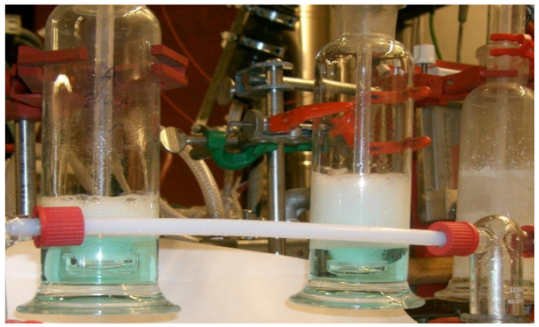
Equipment at Bioenergy2020+ (extractive, accumulative method)

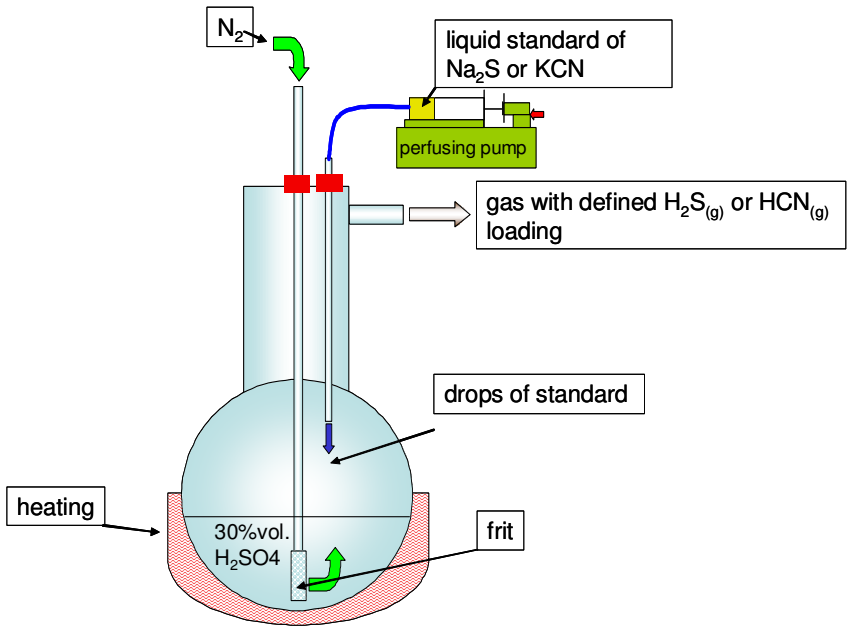


- probe: stainless steel, PTFE, glass
- heated filters: planar or depth
- absorption: impingers (250 ml)
- pump: membrane pump
- gas drying/cleaning: silica, activated carbon
- volume detection: diaphragm gas-meter
- water-content: from solvent-sample



Quality measures – gas-generating unit

Gas-generating unit:



Settings:

- gas flow: 50-500 l/h
- stripping out: $H_2SO_4 + N_2$
- gas preheating: 120 °C
- dosage of liquid standard: 0.1 to 50 ml/h
- absorption units: 1 -2 impingers
- tested components:
  - **H_2S**: $Na_2S_{(aq)} + H_2SO_4 \rightarrow H_2S_{(g)} + SO4^{2-} + 2Na^+$
  - **HCN**: $2KCN_{(aq)} + H_2SO_4 \rightarrow 2HCN_{(g)} + SO4^{2-} + 2K^+$

Results- validation of H_2S-measurement

- H_2S causes:

  Damage to catalyst, increases emissions, corrosion

- Main reactions of sampling procedure

$$Zn(CH_3COO)_2 + H_2O \rightarrow Zn^{2+} + 2CH_3COO^- + H_2O$$

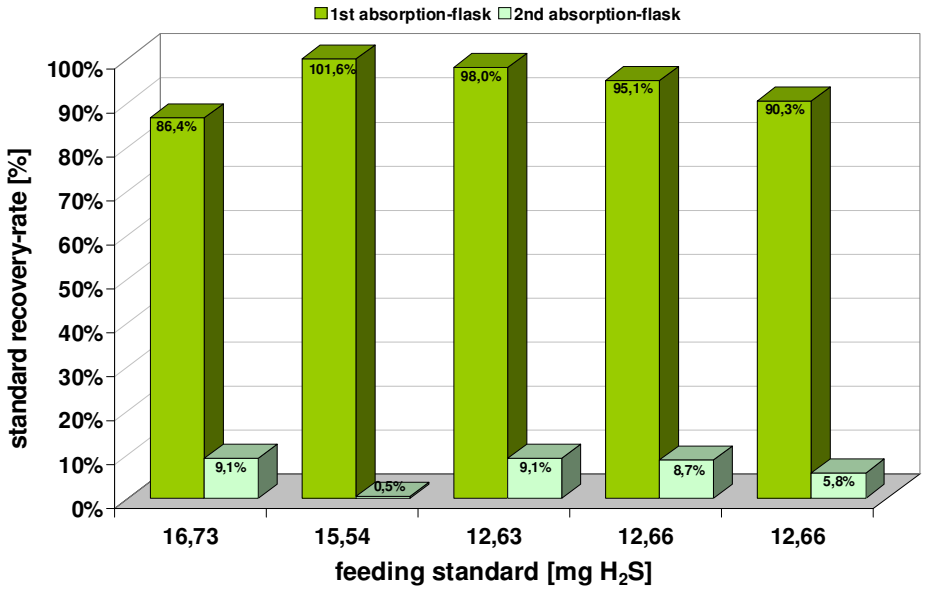
$$H_2S_{(aq)} + H_2O \rightarrow HS^- + H_3O^+$$

$$HS^- + H_2O \rightarrow S^{2-} + H_3O^+$$

$$Zn^{2+} + S^{2-} \rightarrow ZnS_{(s)\downarrow}$$

$$Pb^{2+} + S^{2-} \rightarrow PbS_{(s)(black)}$$

- Advantanges
  - ➢ good retention rates
  - ➢ CO_2 has no influence
  - ➢ Direct photometric analysis possible
  - ➢ Optical check-up with PbAc
- Disadvantages
  - ➢ Solid precipitation



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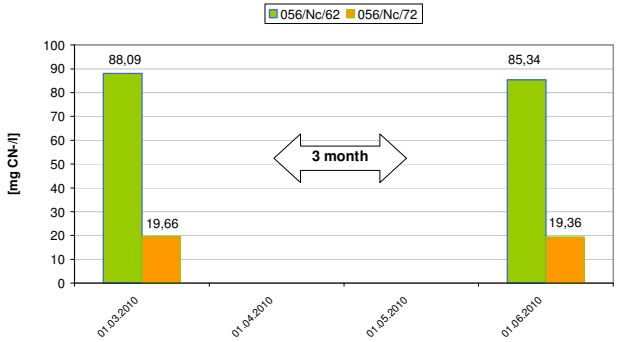
Development of special method for HCN-sampling

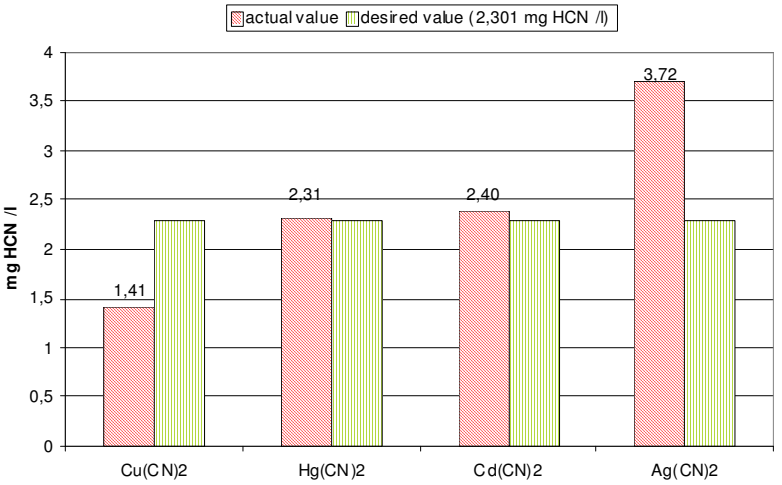
- Main reactions

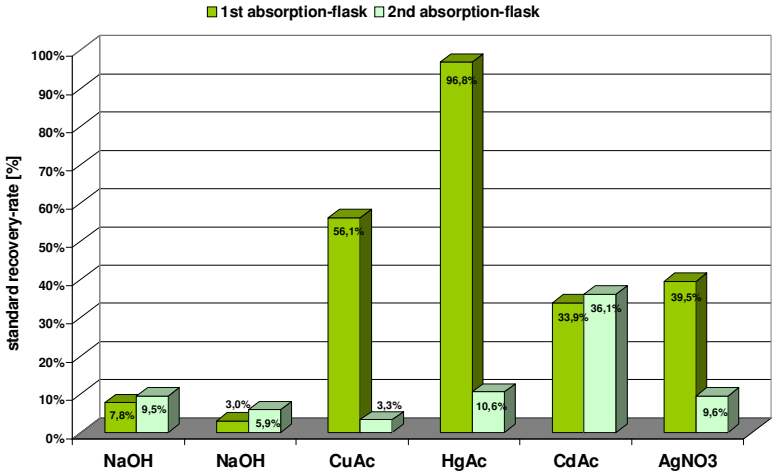
$$Hg(CH_3COO)_2 + H_2O \rightarrow Hg^{2+} + 2CH_3COO^- + H_2O$$

$$Hg^{2+} + 2HCN + H_2O \rightarrow [Hg(CN)_2]_{aq} + 2\,H_3O^+$$

- Advantanges
  - Efficient capture
  - CO_2 has no influence
  - Direct photometric analysis possible
  - No solid precipitation
  - Long time stabile
- Disadvantages
  - H_2S has to be removed before
  - NH_3 creates amido-mercury chains (..Hg-NH_2-Hg-NH_2..)



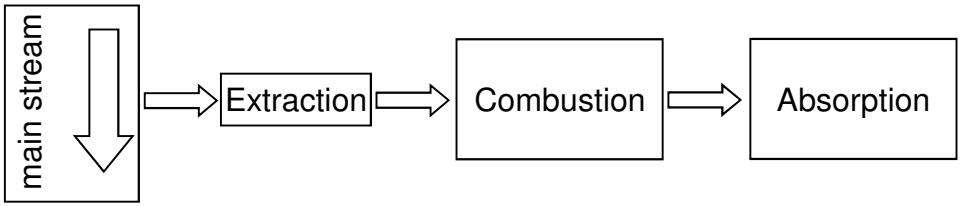




Sampling H_2S from pyrolysis-gas

Sampling total sulfur - basics

- Causes: catalyst damage, increased emissions
- Observation of traces important for SOFC
- System (principle)



- Main reactions of sampling:

Combustion:

$$R\text{-}S + H_2S + O_2 \rightarrow SO_{2(g)} + CO_2 + \ldots$$

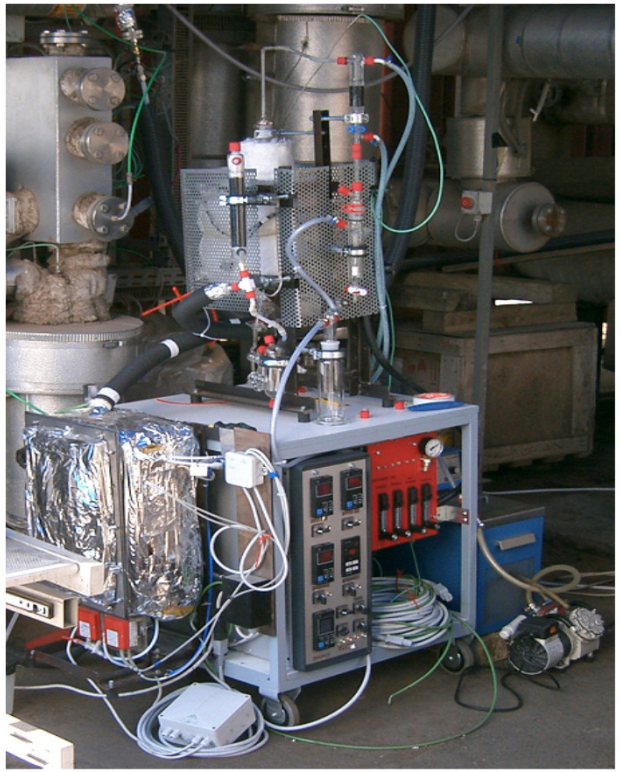
Absorption:

$$SO_{2(aq)} + 2H_2O \leftrightarrow HSO_3^- + H_3O^+$$

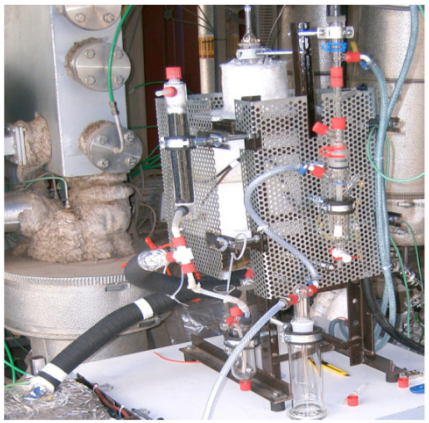
$$HSO_3^- + H_2O \leftrightarrow SO_3^{2-} + H_3O^+$$

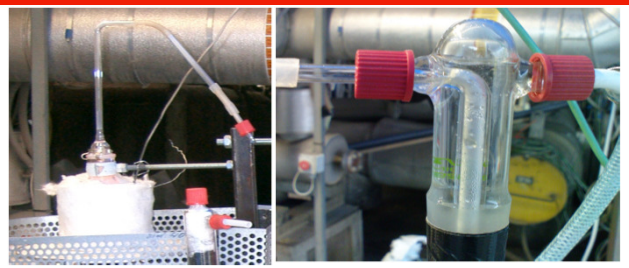
$$SO_3^{2-} + H_2O_2 \rightarrow SO_4^{2-} + H_2O$$

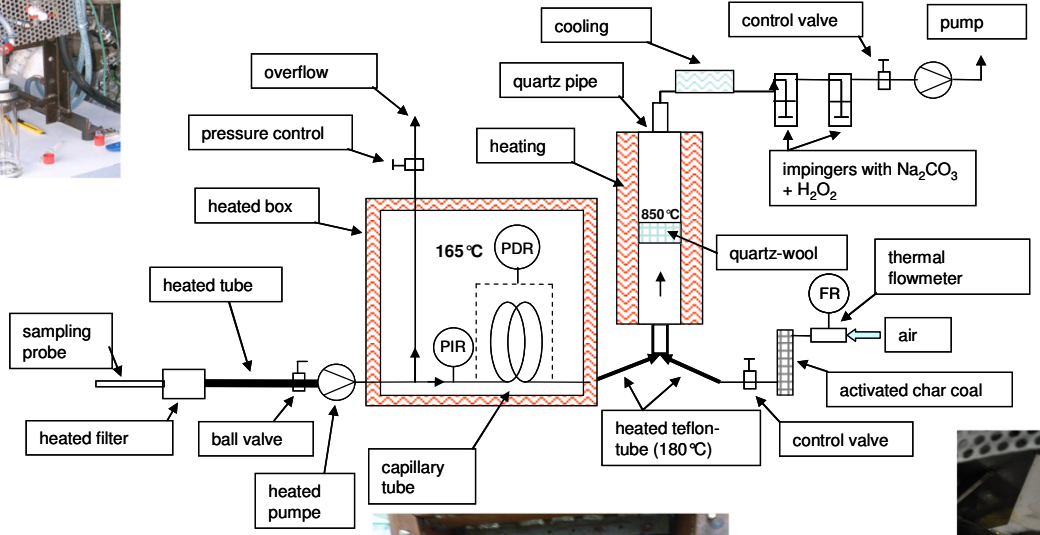
- Detection of SO_4^{2-} via IC (Ion Chromatography)

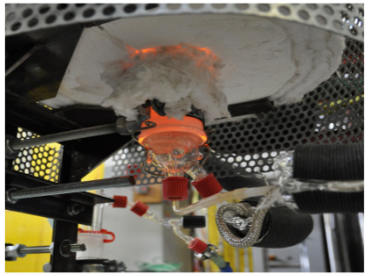


Sampling total sulfur - detail





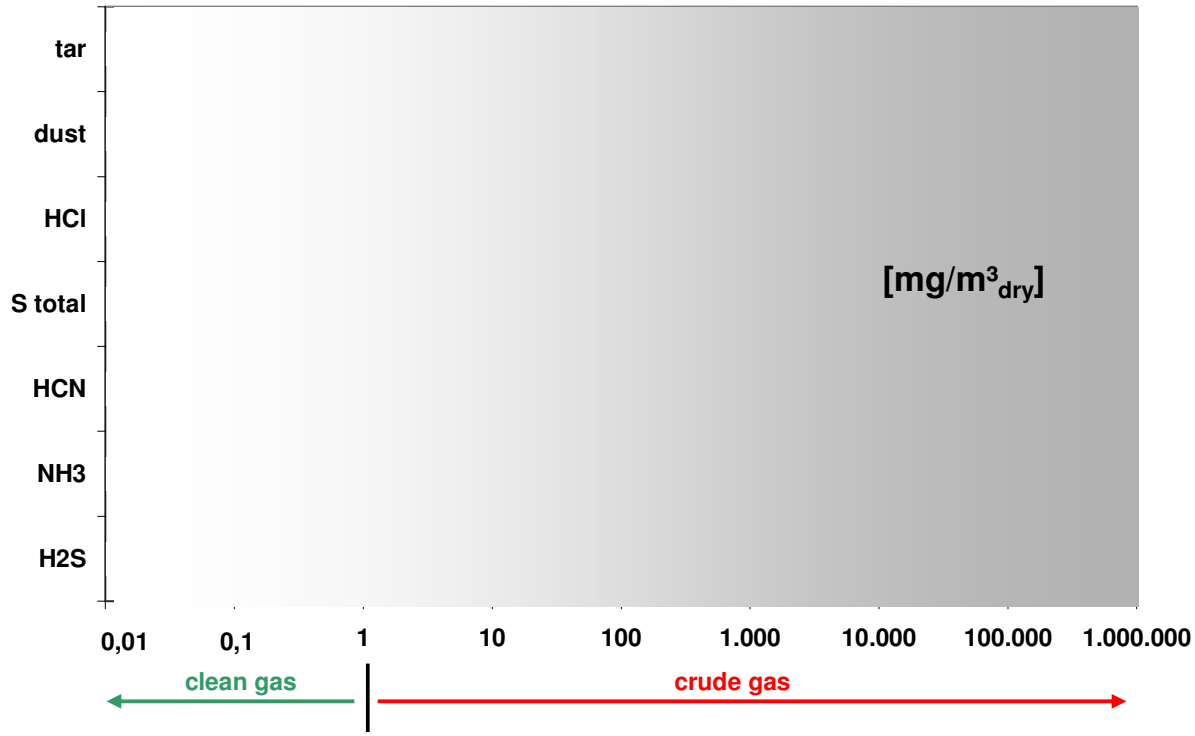




Summary

- Organic parameters
  - Gravimetric tar, BTXE, PAH, Phenols, total sulfur
- Inorganic parameters
  - H_2S, NH_3, HCN, HCl, NaCl, KCl, metals
- Gases
  - Pyrolysis-gas, crude-gas, product-gas, syngas
- Sampling ranges

(no dilution, 100l gas volume, 100ml liquid volume, 1h sampling)



Constitution of working group

...equal for organic and inorganic components

T1A: gas extraction & pre treatment	**T1B: sample transport, Volume metering**
T2A: accumulation offline solvents & SPA	**T2B: online detection-systems** basics
T3A: analytical procedure: solvent & solids: detection and quantification	**T3B: analytical procedure:** detection and quantification calibration-reference
T4: result procedures calibration & references (steps, full) quality insurance, guidelines	
T5: safety / measures gases/liquids/solvents/solids/dust samples/treatment/wastes safety relevant tips and tricks	

A guideline or method library is recommended for chemical parameters

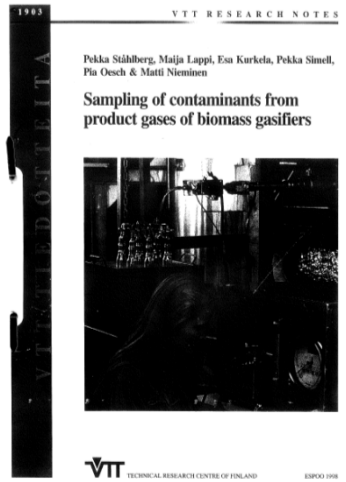
Situation:

•For different types of Gases a large number of applied procedures is already reported.

•Activities can be reported from ~1980 til now.

•As example VTT has compiled their concepts of procedures already in 1996-1998.

•2007 IEA Biom T33 has arranged a shortlist (N-param.)



Aim for the next future:

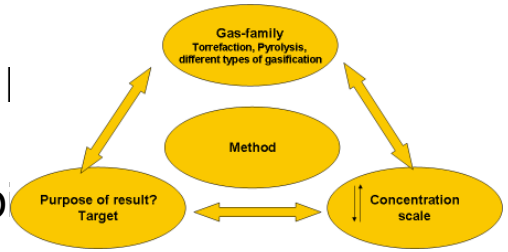
•A application matrix should be proposed.

•A Pre-review of existing methods and a draft matrix should

•Short information should be given in a Pre-Guideline.

•A program for validation of this methods, regarding: Availab

quality issues should be made.



Application Matrix chemical parameters:

parameter is looked for

type of the gas	**e.g. water**	**e.g. S as H_2S**	**e.g. S as organic bond S**
e.g. Synthesis gas complete treated		•Sub-types •techn. Needs •Conditions •constrains	
.			
.			
.			
e.g. Product gas Fluidised bed			
.			
.			
e.g. Pyrolysis gas allothermal			

Application Matrix chemical parameters: (*Detail of yellow box before*)

e.g. S as H_2S

Examples chosen freely

type of the gas

Type #

	Accumulative (T2C-A)	‚Acc. on SPA draeger'	‚online with GC/SCD' T2C-B
	Measures of sample preparation Of **GAS** = T1A/B •Temperature •Water •Particle •Tars •others	Procedure of T2, T3 Time behavior Selectivity Tested about:	***Items 1***
			Items 2
			Items 3
			Items 4

How to calibrate multicomponent?

Calibration gases

Testgas generators

- Forced dosage
- Thermodynamic dosage

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Thank you for your attention!

Further questions? Please contact:

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Milan, 22.06.2012

Als Mitglied des Fachverbandes vertreten bei

innovations kompetenz