&RQWLQXRXVQHZ7DU0RQLWRULQJ DQG 7DZLWK-)8DX RUHVFHQFH

York Neubauer

TCKON Engineering Services Dr.-Ing. York Neubauer

Berlin, Germany

IEA Bioenergy, Task 33: Thermal Gasification of Biomass and Waste
WORKSHOP “GAS CLEANING, EXPERIENCES, NEW DEVELOPMENTS, ANALYTICS AND DIAGNOSTICS”
June 6th 2019, KIT, Karlsruhe, Germany

outline

- (on-line) ‚tar'-monitoring and ‚tar'-analysis – what is needed?
- The dream of on-line tools for perfect results at neglectible operating and maintenance efforts
- Approaching the needs and wishes with UV-fluorescence
- outlook

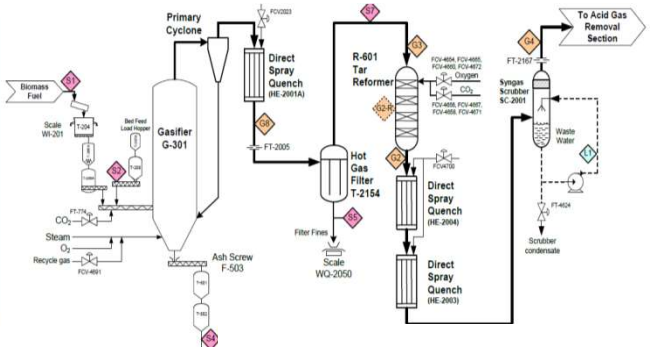
perspectives

- stable and trouble free operation
- maintenance
- working safety for operating & maintenance personnel

- ROI

- commisioning
- optimization
- product development
- general contractor

- reaction engineering (gasifier)
- material science
- catalyst development and testing
- chemical analysis
- …



- gasifier
- filter
- scrubber
- adsorber

- Standardized analytical procedures (emissions)

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- catalysts
- bed materials
- ash disposal

overall gas composition as quality measure

desired	contaminants	hydrocarbon gases C1-C5
	H_2S	
	COS	ethane
	NH_3	
N_2	HCN	propane
	HCl	propene
	…	…

steam/water

benzene
1-ring aromatics
polycyclic aromatic compounds (PAC)

Which ones are the troublemakers?

‚tar' – when condensed and in each other dissolved

Needs and wishes

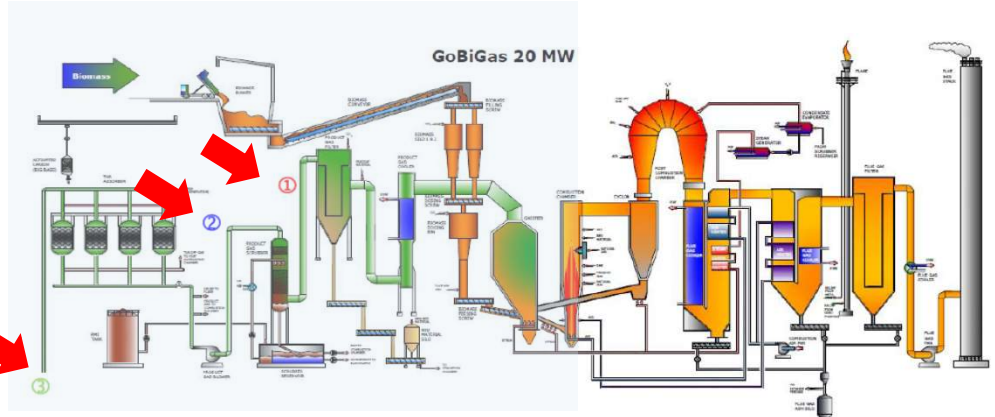
- Fast and detailed results
- Preferred L Q O L Q H P H D V X U H P H Q W V revealing reactor insights on time
- continuous monitoring
- validated, spatial resolved data for modelling and simulation

- A reliable, robust, easy to operate and to maintain measurement or monitoring instrument.
- A ‘translation’ of the physical tar species properties and amounts into a useful value, characterizing the current status of the respective plant section.
- A device that can be taken care of by a technician - rather than a scientist !
- A tool that handles tar loaded gas which stays longer in operation than the monitored part of the plant itself!

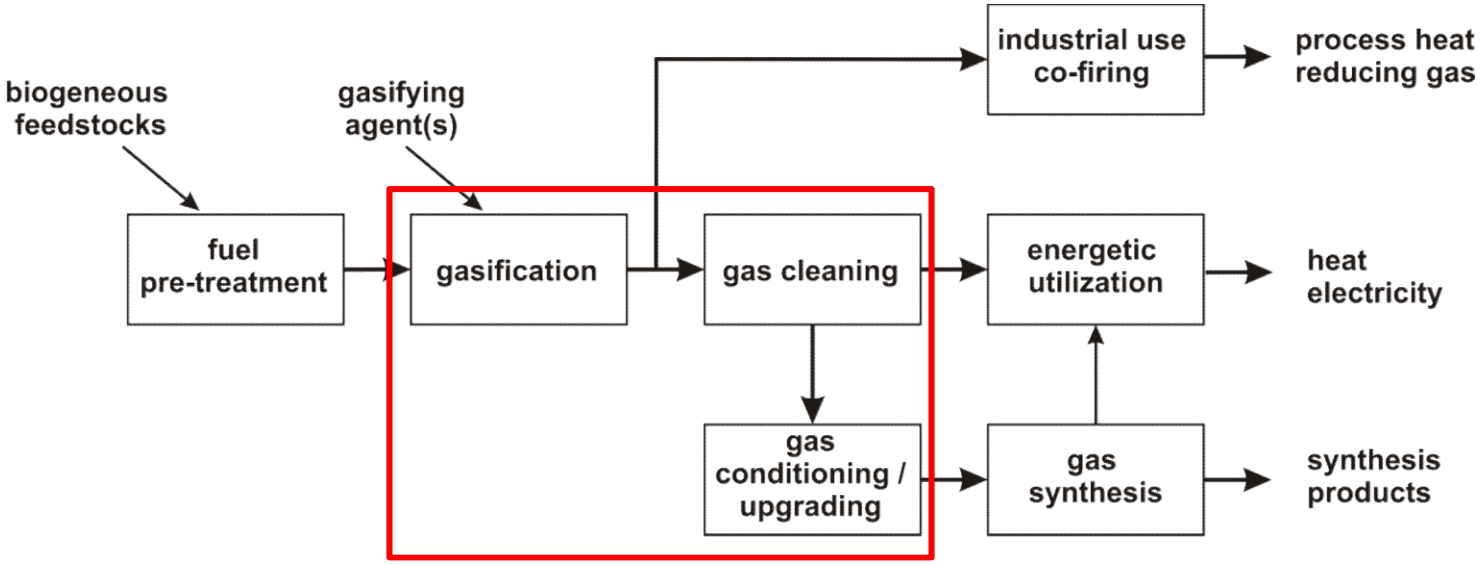
➢ Such a device needs to be applicable in the industrial environment (temperature, vibrations, dust, ex proof zones). To assure a long operating and life time, the direct contact of the measuring unit with the tar species especially in ‘raw’ gases needs to be avoided.

➢ 2 S W L F D O W H F K Q L T X H V such as UV-fluorescence spectroscopy offer a number of benefits for this purpose.

J D V I D P Ł Depending on process, fuel and location within the plant

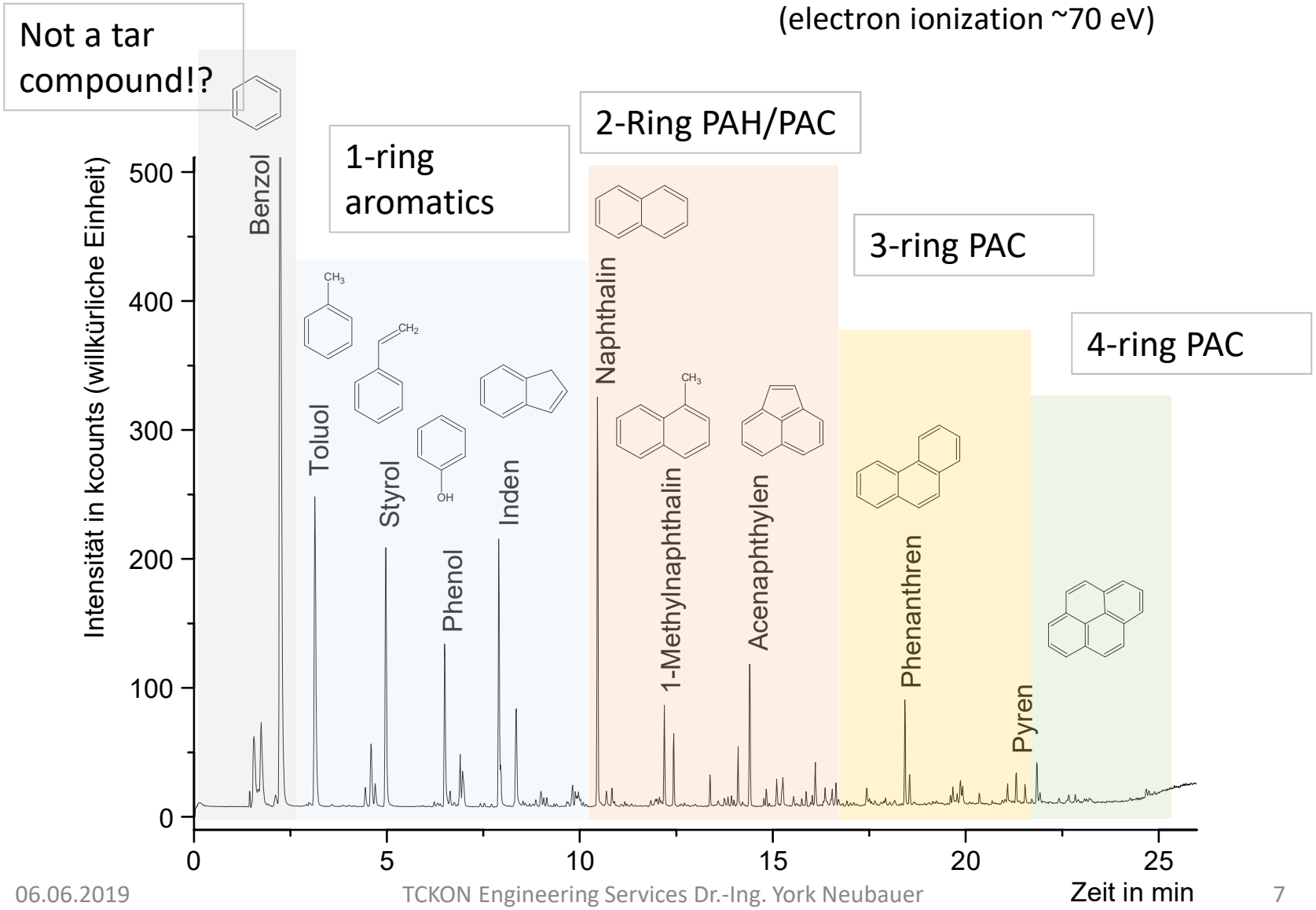


Locations →	①	②	③
	After Filter	After scrubber	After sorption bed

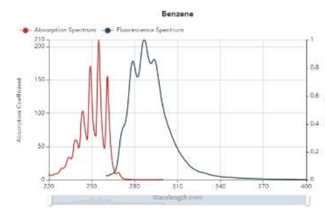
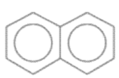
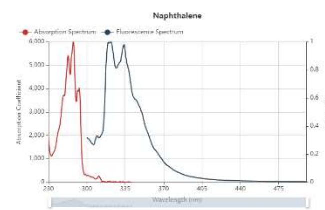
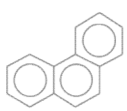
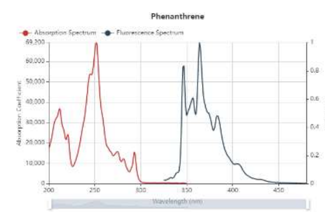
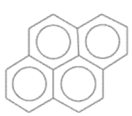
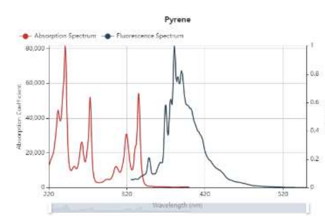


tar composition

gasification of woody biomass with air
(electron ionization ~70 eV)



Properties of selected tar ‚representatives'

1DPH	&$6	1R 0ROHFXODU ZHLJKW	0HOWLQJ SRLQW ƒ&	%RLOLQJ SRLQW ƒ&	2SWLFDO 3URSHUWLHV	$EVRUSWLRQ DQG (P
Benzene 	71-43-2	78,11	6	80	Absorption coefficient: 210 at 254.75 nm Fluorescence quantum yield: 0.053	
Naphthalene 	91-20-3	128,17	80	218	Absorption coefficient: 6000 at 275 nm Fluorescence quantum yield: 0.23	
Phenanthrene 	85-01-8	178,23	99	336	Absorption coefficient: 69200 at 252 nm Fluorescence quantum yield: 0.125	
Pyrene 	129-00-0	202,25	156	340	Absorption coefficient: 81700 at 241 nm Fluorescence quantum yield: 0.32	

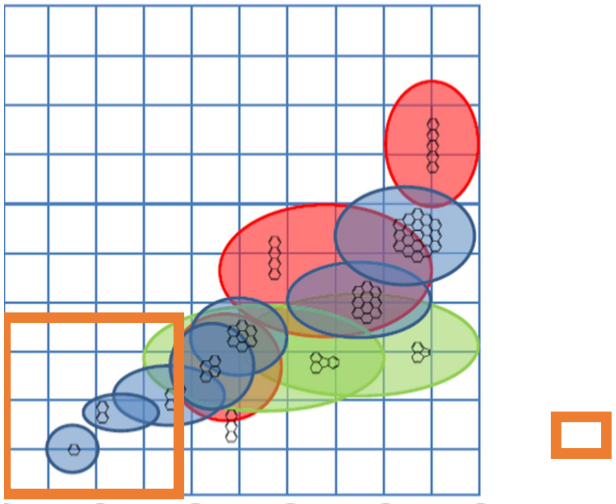
Taniguchi, M.; Du, H.; Lindsey, J. S. , PhotochemCAD 3: Diverse Modules for Photophysical Calculations with Access to Multiple Spectral Databases, Photochem. Photobiol. 2018, 94, 277–289.

Taniguchi, M.; Lindsey, J. S. , Database of Absorption and Fluorescence Spectra of >300 Common Compounds for Use in PhotochemCAD," Photochem. Photobiol. 2018, 94, 290–327.

Attempting to access aromatics contents in the process gases continuously on-line

Goal of fundamental research work:

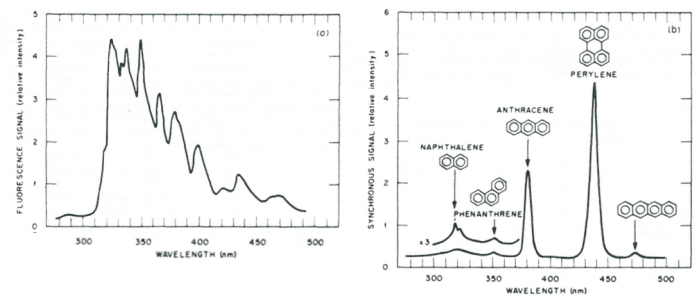
2 E W D L Q L Q J L Q I R U P D W L R Q
F R P S R X Q G V R U R Q F R P S R X
Z L W K 8 9 I O X R U H V F H Q F H V



examination of:

- Excitation-Emission matrices - EEM
- Synchronous fluorescence
- Fluorescence lifetime

➢ Comparisons between liquid solvent phase with tar species and high temperature gas phase

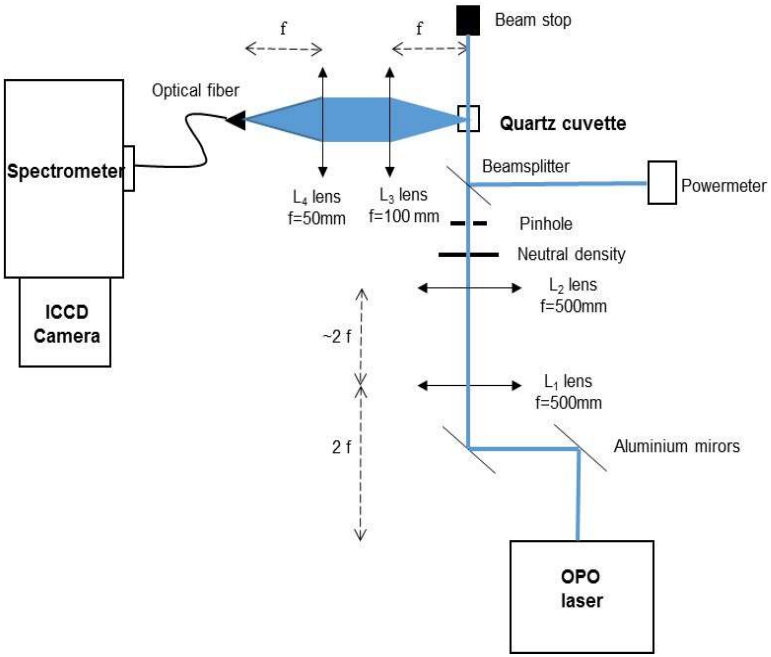


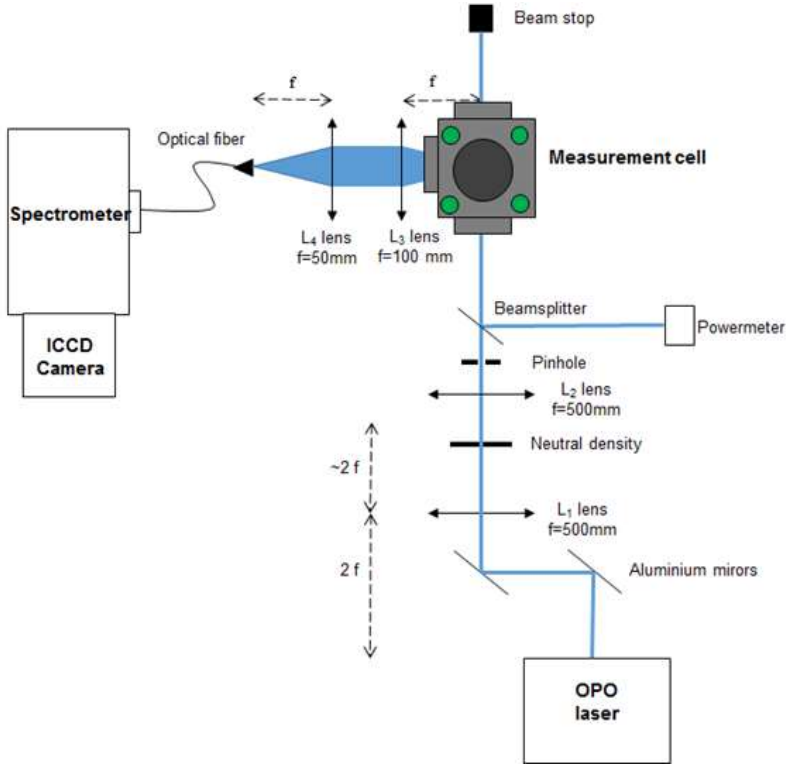
synchronuos luminescence spectroscopy [Vo Dinh 1978]

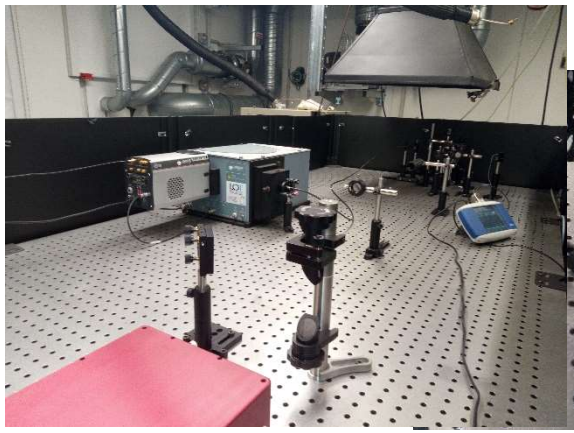
Picture on the upper right taken and adapted from:

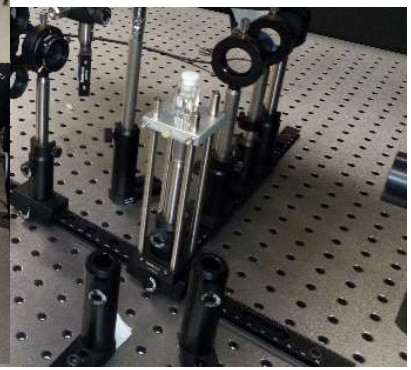
S. Bejaoui, X. Mercier, P. Desgroux, E. Therssen: Laser induced fluorescence spectroscopy of aromatic species produced in atmospheric sooting flames using UV and visible excitation wavelengths. Combustion and Flame 161 (2014) 2479–2491

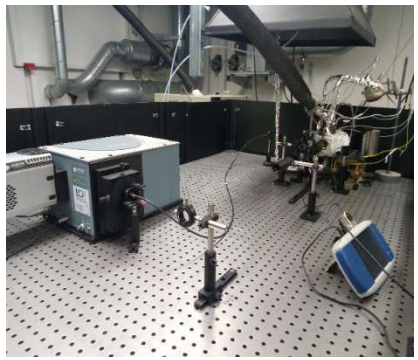
Principal setups for fundamental examinations

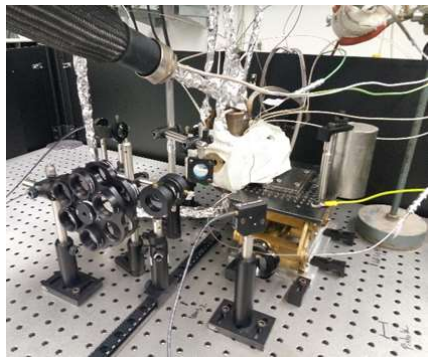




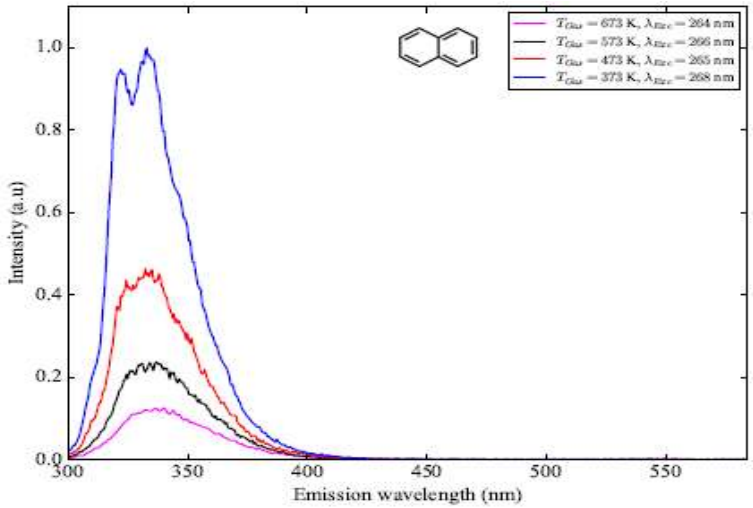






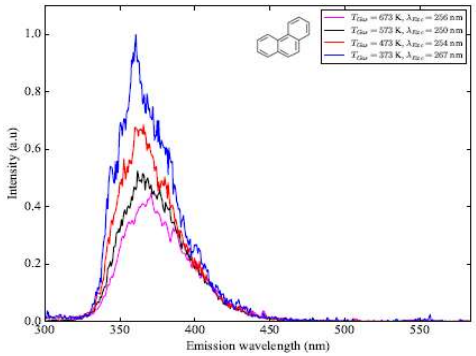


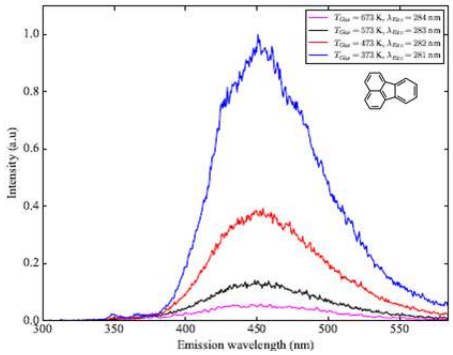
Temperature dependence of the fluorescence signal



Fluorescence intensities drop with increasing temperature

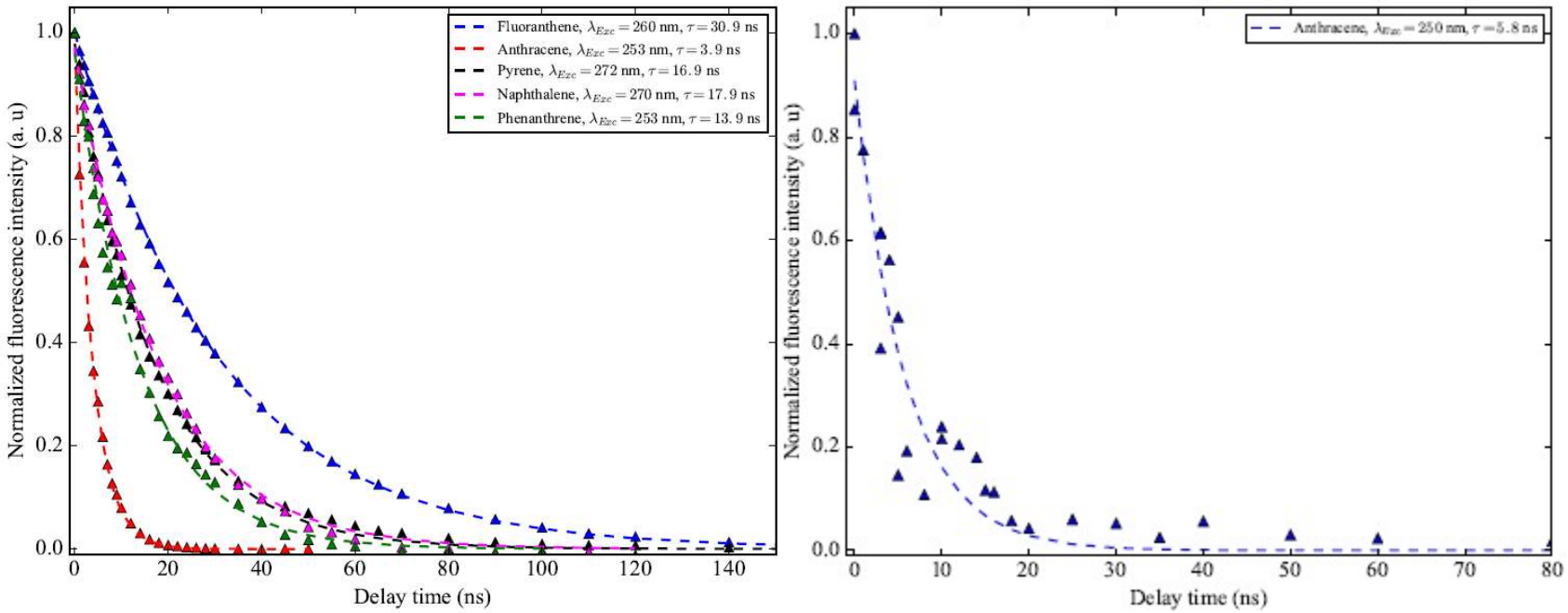
: high temperatures of 350 – 400°C for surely avoidung tar deposits are in contrast to spectral quality





Diluting could be a solution but represents a challenge on ist own – see work of gti or VTT!

Separation by fluorescence lifetime



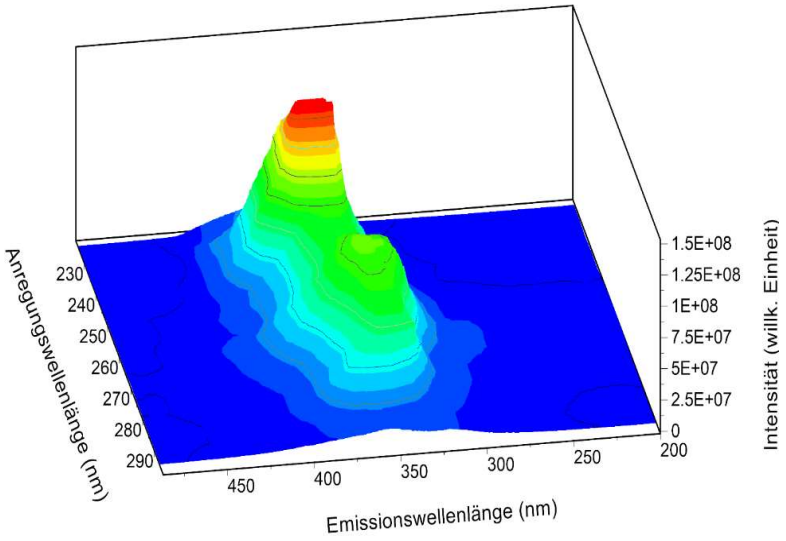
)OXRUHVFHQFH GHFD\ FXUYHV RI 3$+V XQGHU H[FLWDWLRQ DW QP DQG FXUYH RI DQWKUDFHQH REWDLQHG DW . DIWHU H[FLWDWLRQ

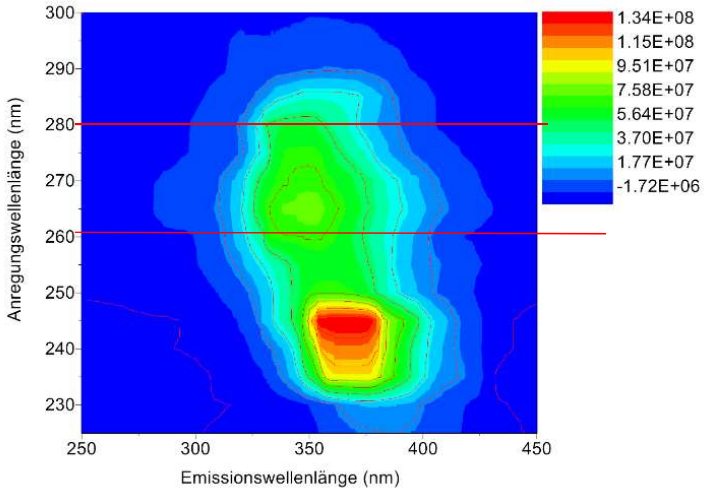
	270	17.9
	253	13.9
	253	3.9
	272	16.9
	260	30.9

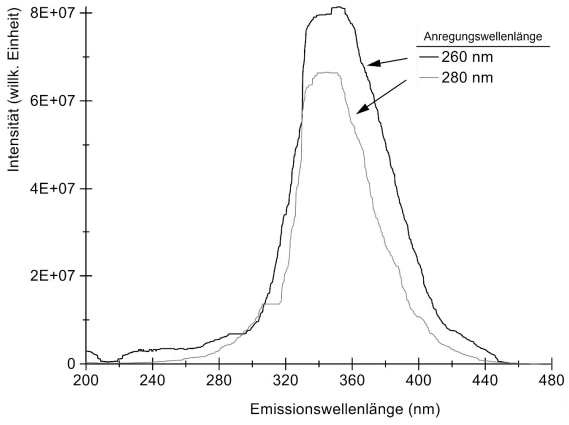
([SHULPHQWDO IOXRUHVFHQFH OLIHWLPHV RI 3$+V LQ F\FORKH[DQH

Excitation-Emission matrices – EEM‘s

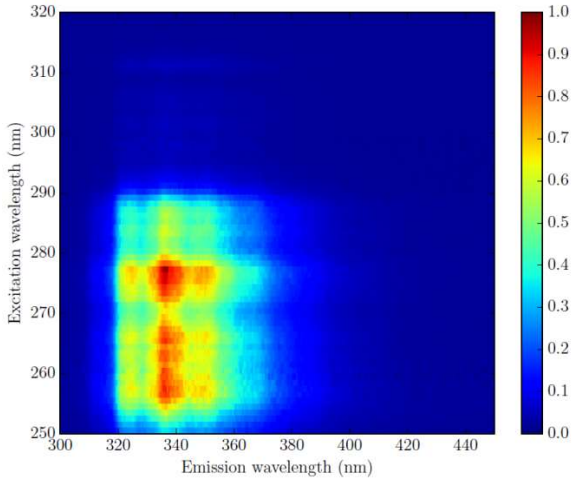
- EEM of phenanthrene
- Are EEM‘s a choice for mapping and fingerprinting?

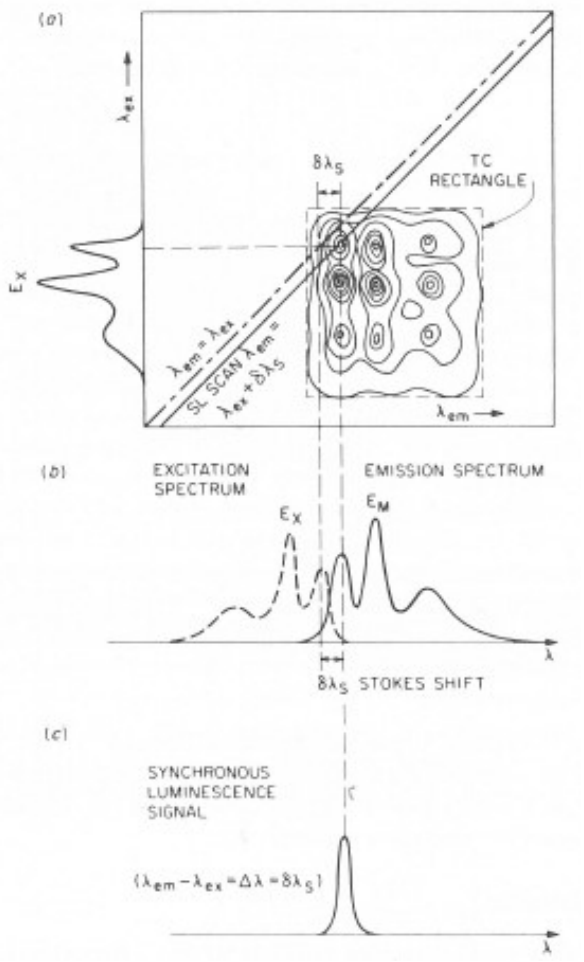






Excitation- Emission matrizes obtained with wavelength tunable OPO-laser

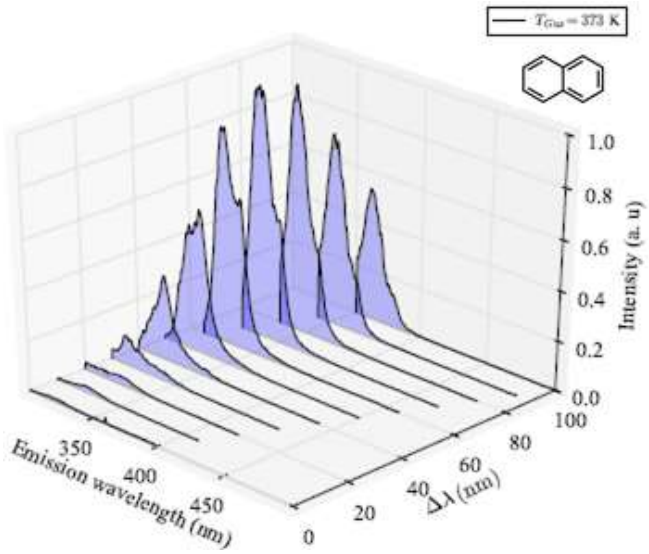


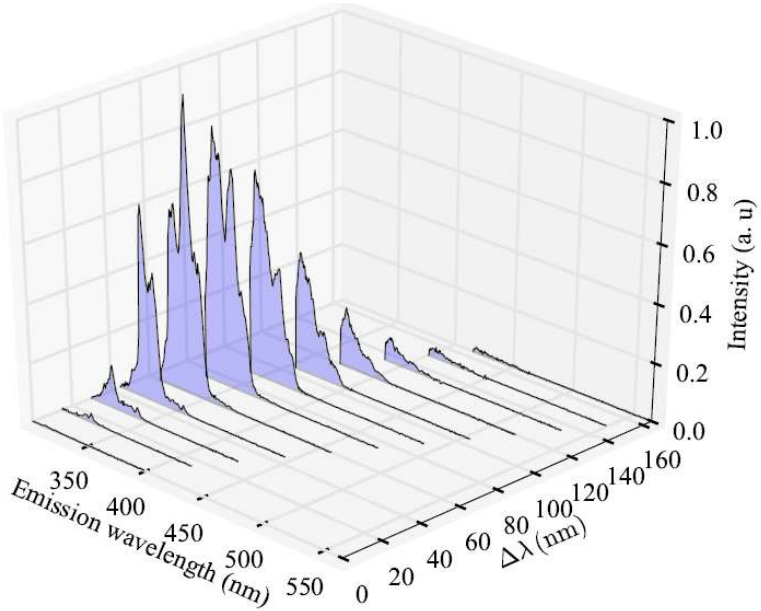


([FLWDWLRQ (PLVVLRQ PDWUL[XSSHU SDUW DQG H UHODWLRQVKLSV EHWZHHQ D ((H[FLWDWLRQ DQG HPLVVLRQ VSHFWUD ORZHU SDUW RI DQG HPLVVLRQ VSHFWUD DQG F V\QFKURQRXV IOXRSKHQDQWKUHQH LQ F\FORKH[DQH IRU D FRQFHQWUDWLRQ RI PRO /

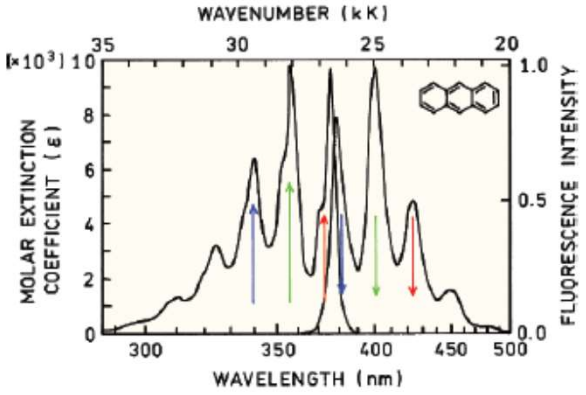
*E. Wehry, 'Modern fluorescence spectroscopy 4', Plenum Press, New York, 1981

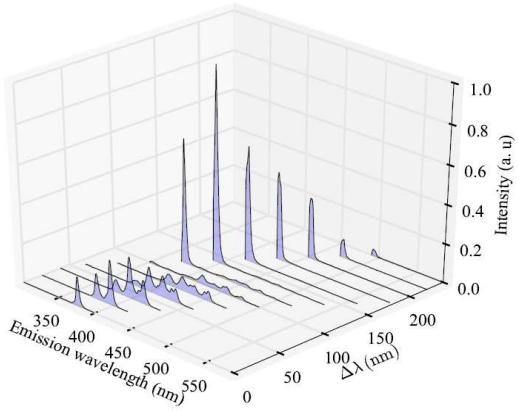
Synchronuous fluorescence



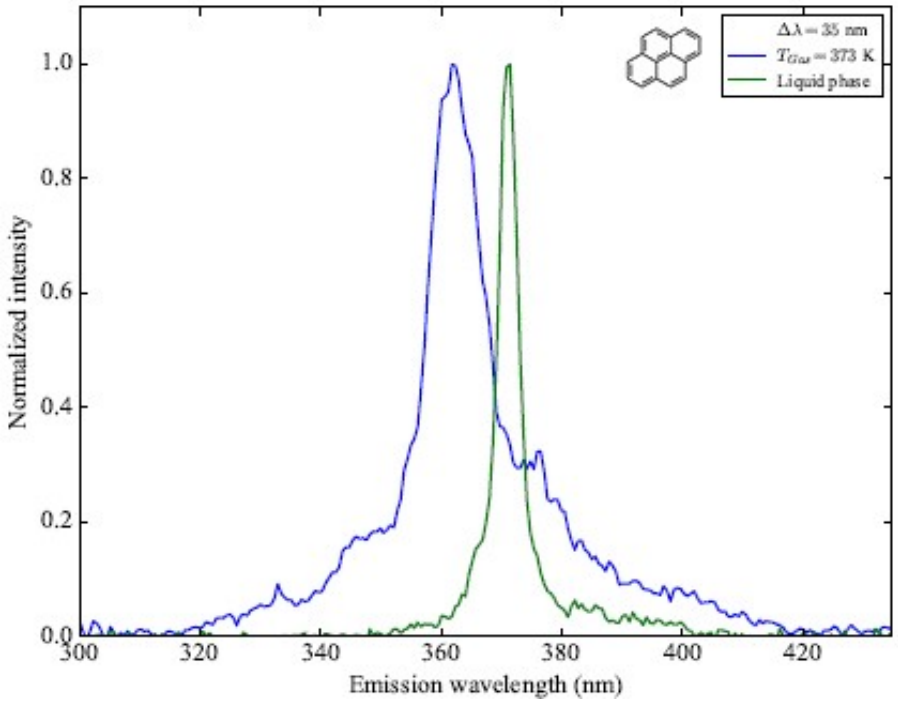


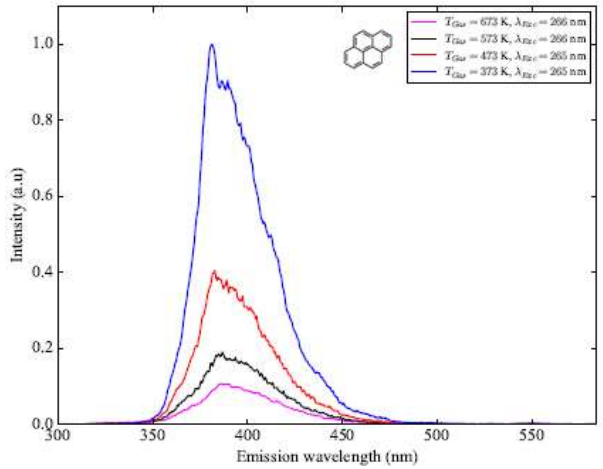
&RPSDULVRQ RI WKH V\QFKURQRXV IOXRUHVFHQFH VSHF OHIW DQG OLTXLG **Δλ**KDVH DW YDU\LQJ

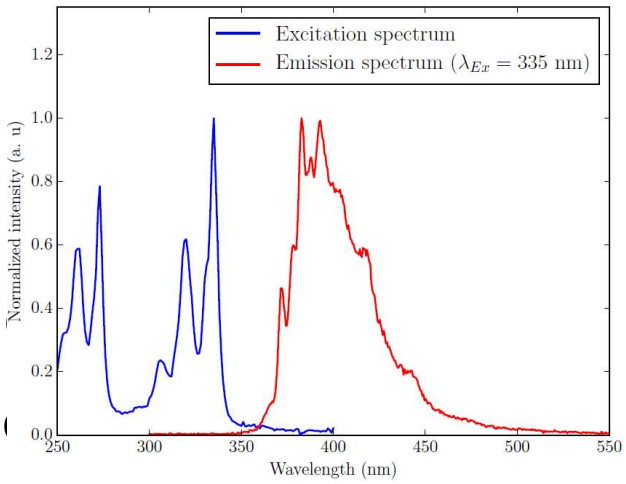




Synchronuous fluorescence







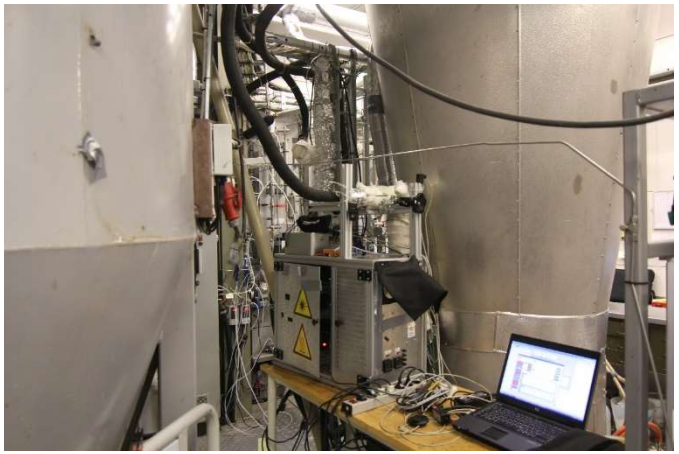
&RPSDULVRQ RI WKH V\QFKUR
IOXRUHVFHQFH VSHFWUD RI S Q G
JDV SKDVH DW D VS LF LILF YD

JDV SKDVH DQG OLTXLG SKDVH HPLVVLR

Towards industrial application for tar monitoring

5REXVW DQG UHOLDEOH	Avoiding contact of windows with sample gas flow by windows flushing with inert gas in specially constructed measurement cell
$V PXFK DQG DV ORQJ DV SRVVLEOH XQPDQQHG RSHUDWLRQ	Heated cell and main gas paths within an oven-like construction
/LWWOH PDLQWHQDQFH UHTXLUHPHQWV E\ WHFKQLFLDQV QRW DQDO\WLF H[SHUWV	No moving parts; use of ejector pump; one version with combustion of the off gas (no H2, no CO, no tar left over – safety issue!)
/HVV H[SHQVLYH DQG ZLWK UREXVW FRPSRQHQWV	Applying UV diodes instead of laser for excitation
(OLPLQDWLQJ IXUWKHU LQIOXHQFH IDFWRUV	Tempered (cooled) optics compartment for LED and for spectrometer; possibly addition of dilution unit for measuring at lower gas temperature

Field deployable set-ups



@CHALMERS University of Technology, Gothenburg, SE

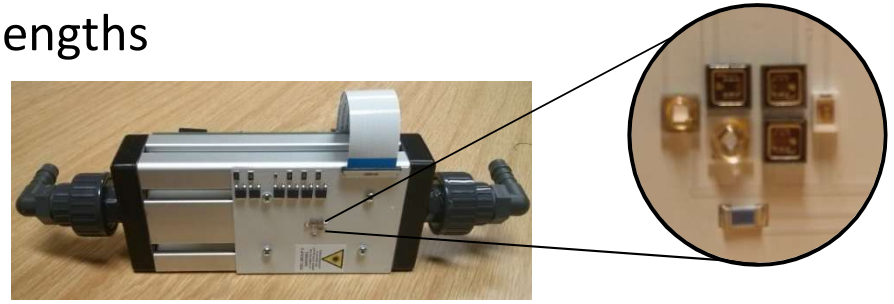
@ GoBiGas plant, Gothenburg, SE

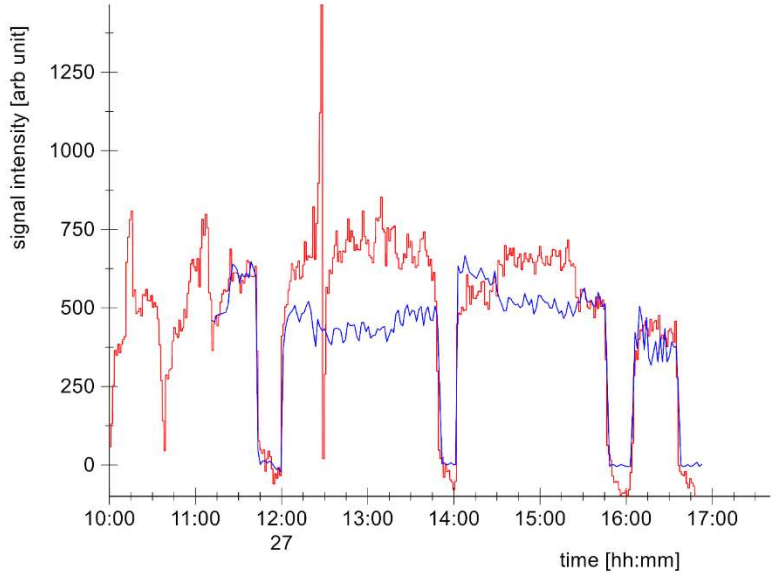
Comparison with FID device from Ratfisch Analysensysteme and University Stuttgart

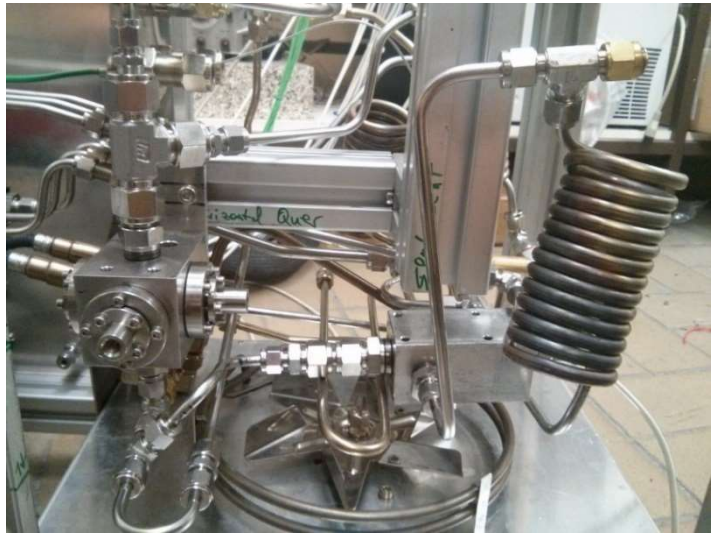
@PSI, Villigen, CH

Field deployable set-ups

UV LED diode array with different wavelengths
265, 280, 300, 340, 380, 455 nm







Comparison with FID device (blue curve) from
Ratfisch Analysensysteme and University Stuttgart

Acknowledgement

Special thanks to my former team members at TU Berlin Dr. Thomas Mouton, Halgurd Taher, Sandra Walther, Dr. Shaimaa Mahdi and Dr. Eva M. Brüning for their work and their patience for working out several spectroscopic options of individual tar species detection in the hot process gas.

The fundamental work was part of my PhD research project (2012-2018).

Federal Ministry of Education and Research via PtJ: FKZ: 03SF0442

In the BIGDEMO project (2014-2017) demonstration units applying the main design principles were tested and further adapted in field measurements at CHALMERS University and the GoBiGas plant.

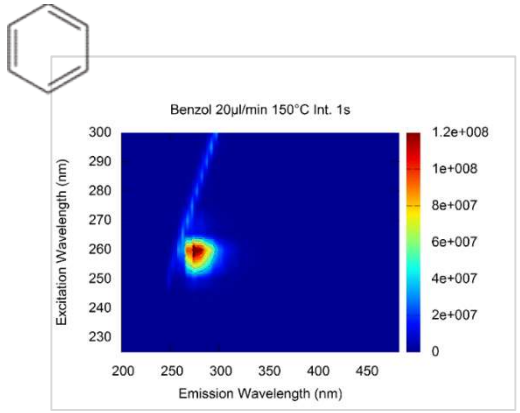
Federal Ministry of Food and Agriculture via FNR: FKZ: 22401814.

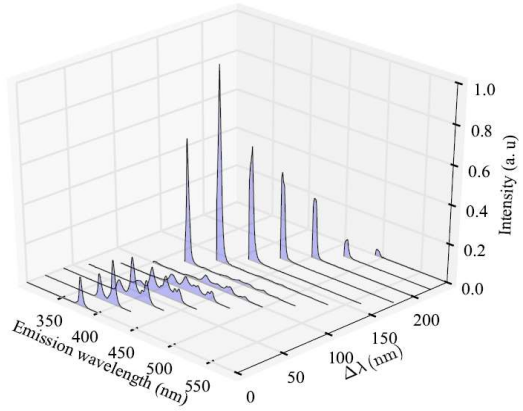
The journey continues…

Our solution:

- An optical instrument based on UV-fluorescence that measures by avoiding the direct contact with the gas.
- Special heated and tempered sections for process gas, utility gases and for sensitive optical and electronic parts of the device.
- Generating under-pressure for gas transport from the sampling point and combustion of the effluents by non moving solid parts, strongly reducing maintenance requirements!
- Industry-standard instrument control for easy adaptability in process environments including sensing device and auxiliary sampling system.
- Contact and latest developments: condensables.com

Thank you for your interest and for your attention!





Berliner Allee 38
13088 Berlin
Germany

Tel. +49 172 756 3452
york.neubauer@tckon.de