

05.12.2017

13. Dresdner Sensor-Symposium

# INNEN HUI UND AUßEN PFUI – SMARTE PROZESS-SENSOREN IN DER GEGENWÄRTIGEN AUTOMATISIERUNGS- LANDSCHAFT DER PROZESSINDUSTRIE

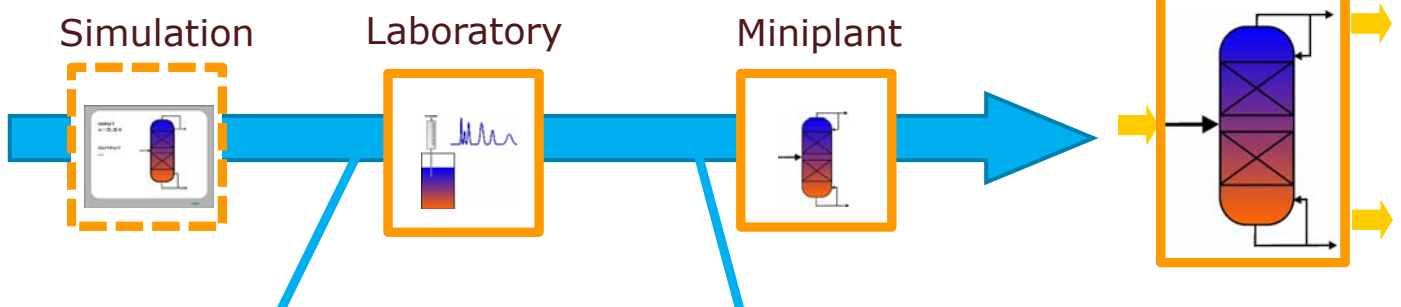
Michael Maiwald, Patrick Gräßer, Lukas Wander,  
 Svetlana Guhl, Klas Meyer, Simon Kern

Bundesanstalt für Materialforschung und -prüfung (BAM)  
 Division 1.4 Process Analytical Technology

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 D-12489 Berlin, Germany

## Integrated Process Design and Intensified Processes

### Current Trend: Hybrid Modular Plants



**Micro Reaction Technology**  
 (Example: Fraunhofer ICT, Pfinztal/D)

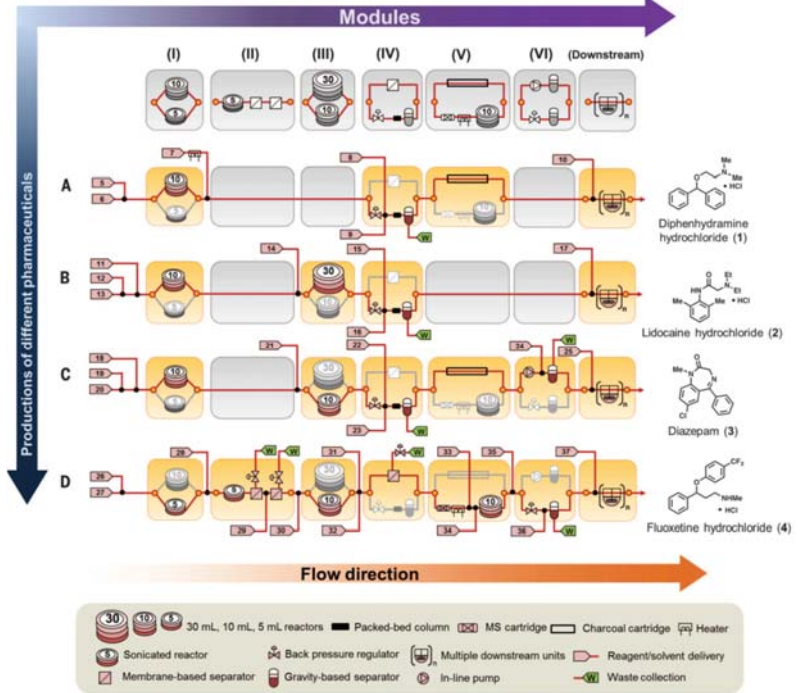
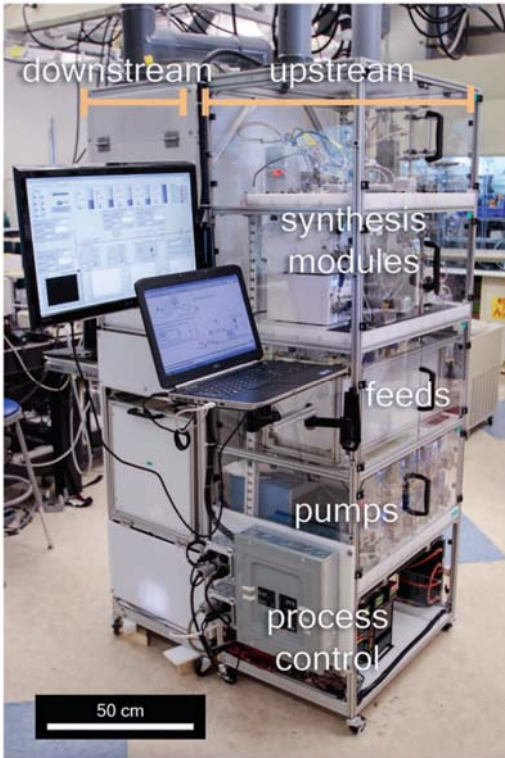


**Modular Production**  
 (Example: Foster Wheeler AG, Zug/CH)

*Trends. Anal. Chem.*  
 83 (2015) 39–52

# Integrated Process Design and Intensified Processes

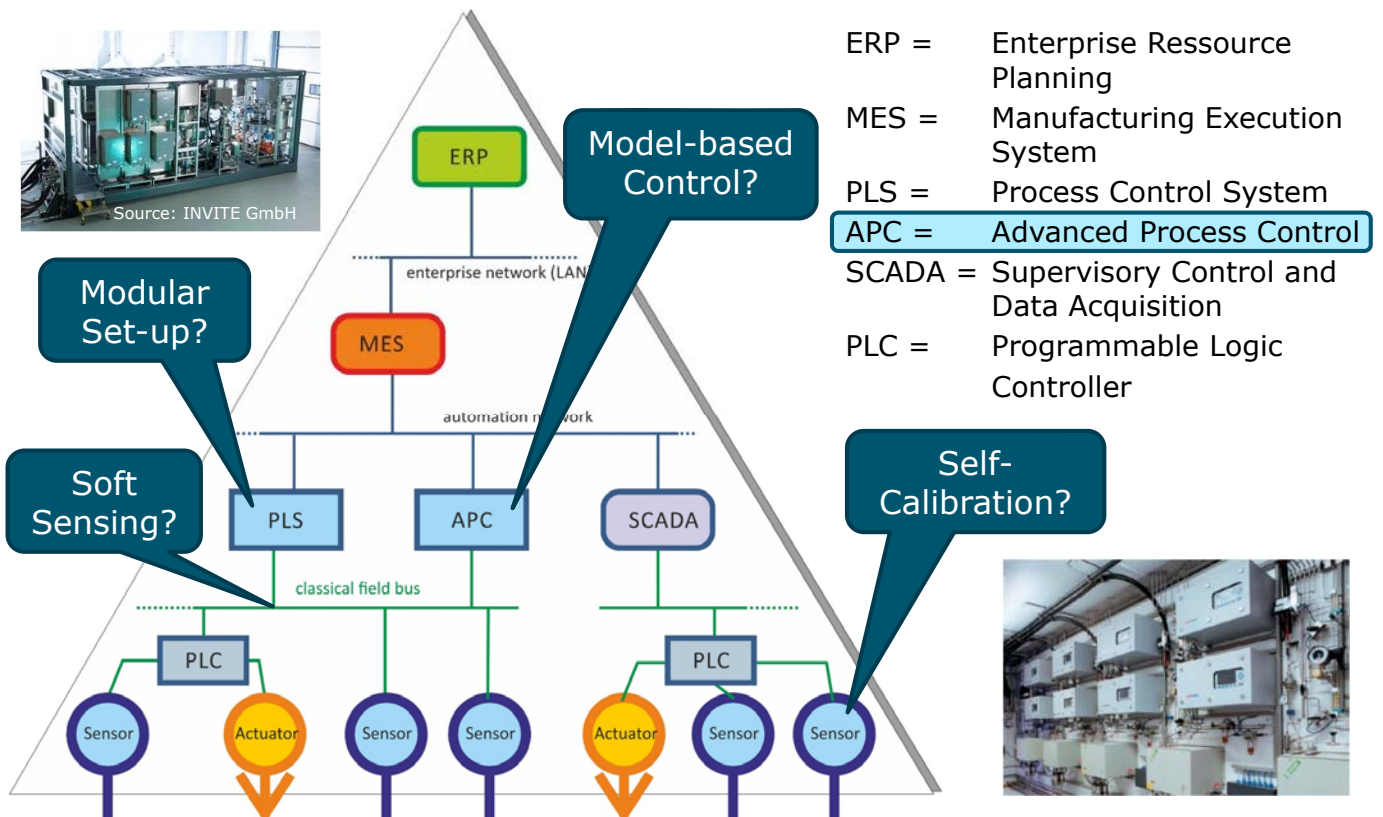
## Example: Continuous Flow Production of Pharmaceuticals at MIT



A. Adamo, R. L. Beingessner, M. Behnam et al., On-demand continuous-flow production of pharmaceuticals in a compact, reconfigurable system, *Science* 352(6281), 2016, 61-67

# Process Automation

## The Classical Automation Pyramid → is Outdated!



# Current and future requirements to process sensors

## Sensors go smart

- Smart process sensors are important parts of cyber-physical production systems and generate new business cases for users, instrument manufacturers, and service providers.
- „Smart“ sensors provide services within networks and use information out of the network.



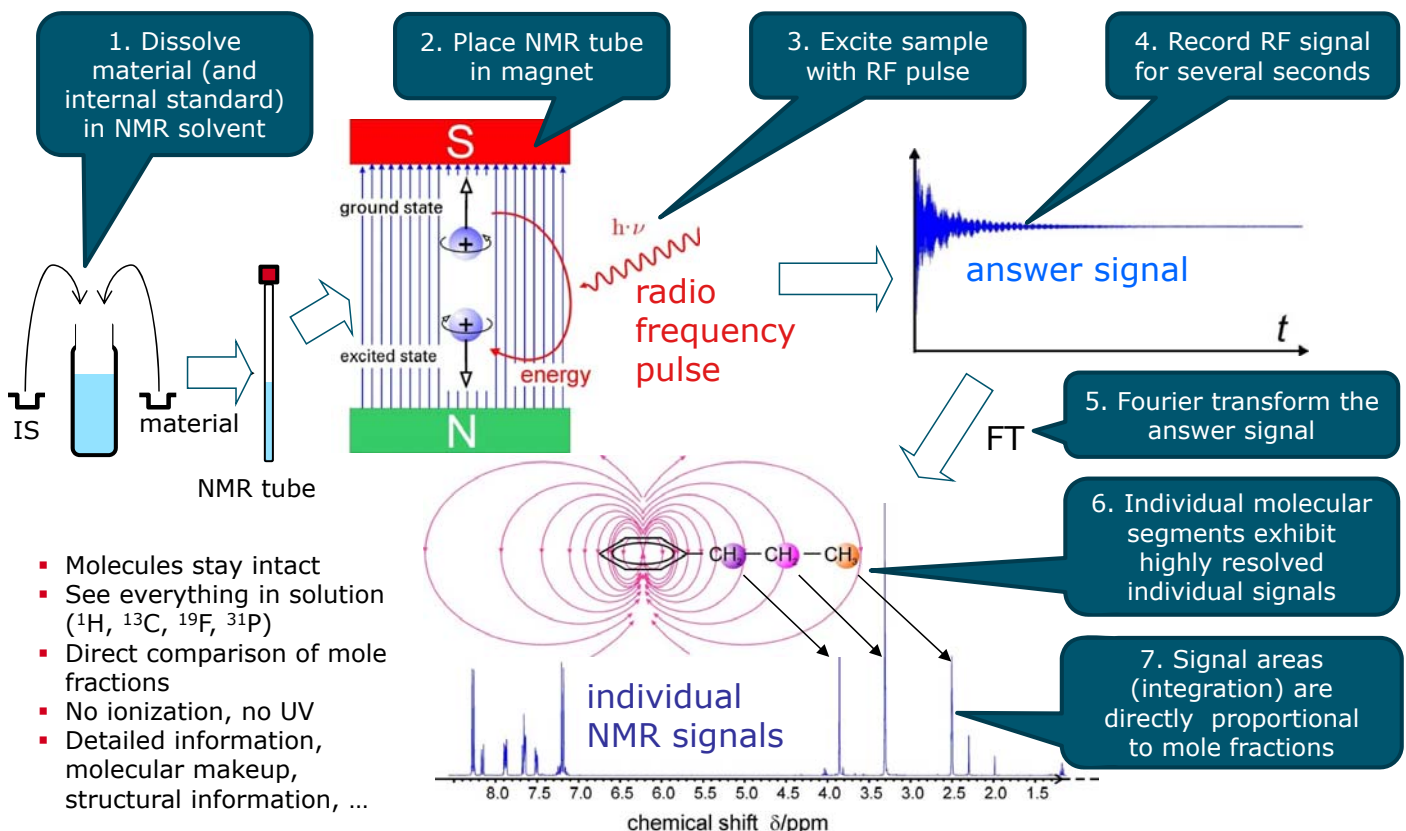
- Use of „complicated“ sensors has to be simplified towards „plug and play“

„NAMUR Roadmap Prozess-Sensoren 4.0“



# What is NMR?

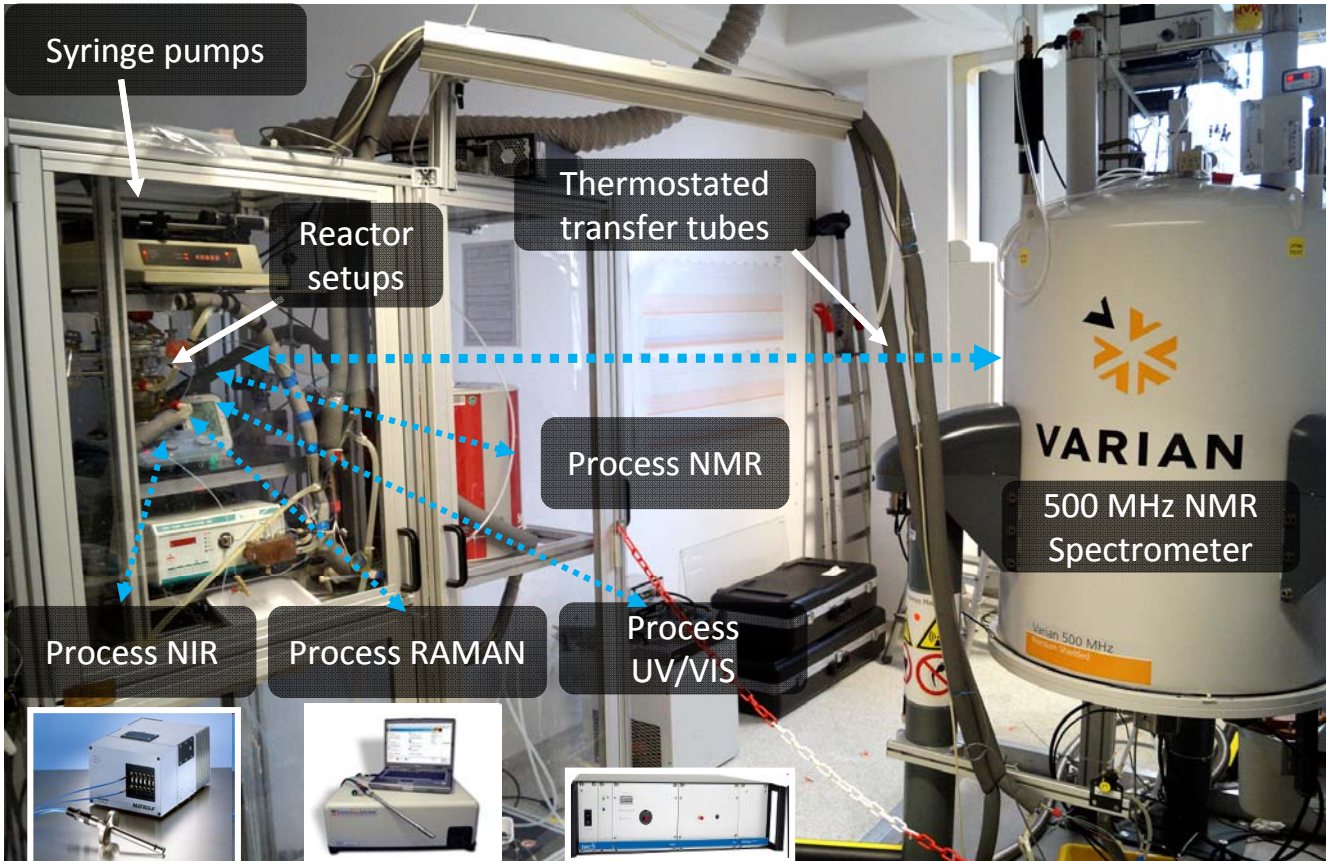
## Nuclear Magnetic Resonance



- Molecules stay intact
- See everything in solution ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ )
- Direct comparison of mole fractions
- No ionization, no UV
- Detailed information, molecular makeup, structural information, ...



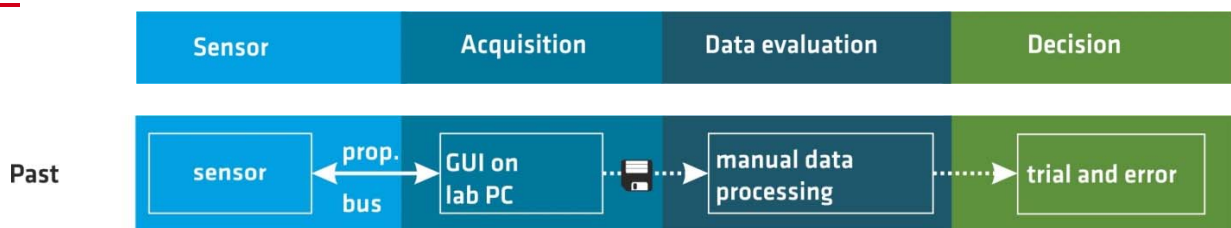
# Reaction Monitoring in Lab-scale at BAM



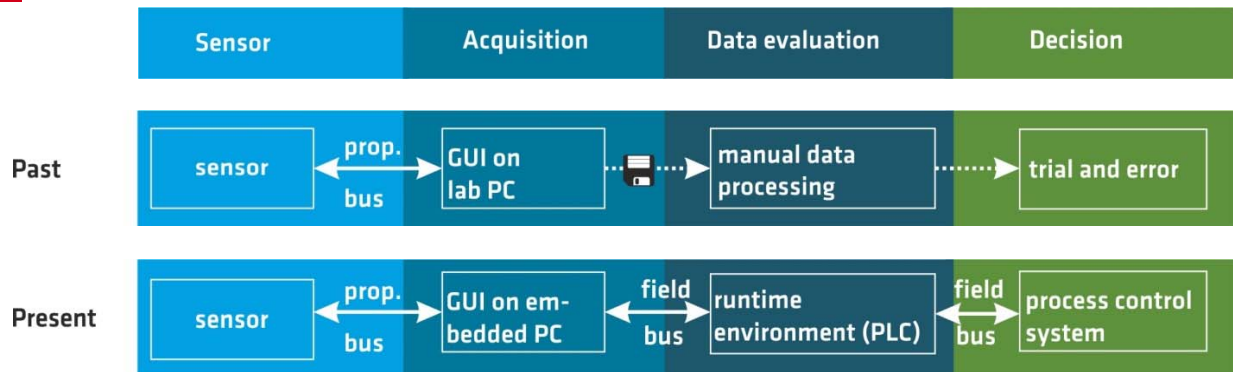
05.12.2017 M. Maiwald | BAM | „Innen hui und außen pfui“ | 13. Dresdner Sensor-Symposium 2017

# From Lousy Interfaces to “Industrie 4.0” Use of Runtime Environments

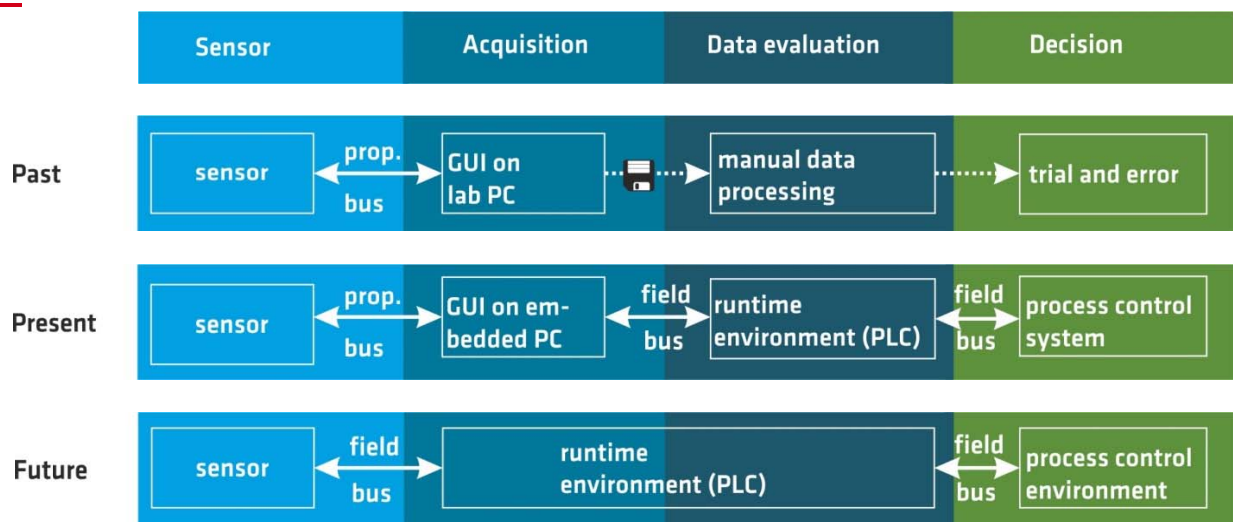
*Trends. Anal. Chem.*  
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# From Lousy Interfaces to "Industrie 4.0" Use of Runtime Environments



# From Lousy Interfaces to "Industrie 4.0" Use of Runtime Environments

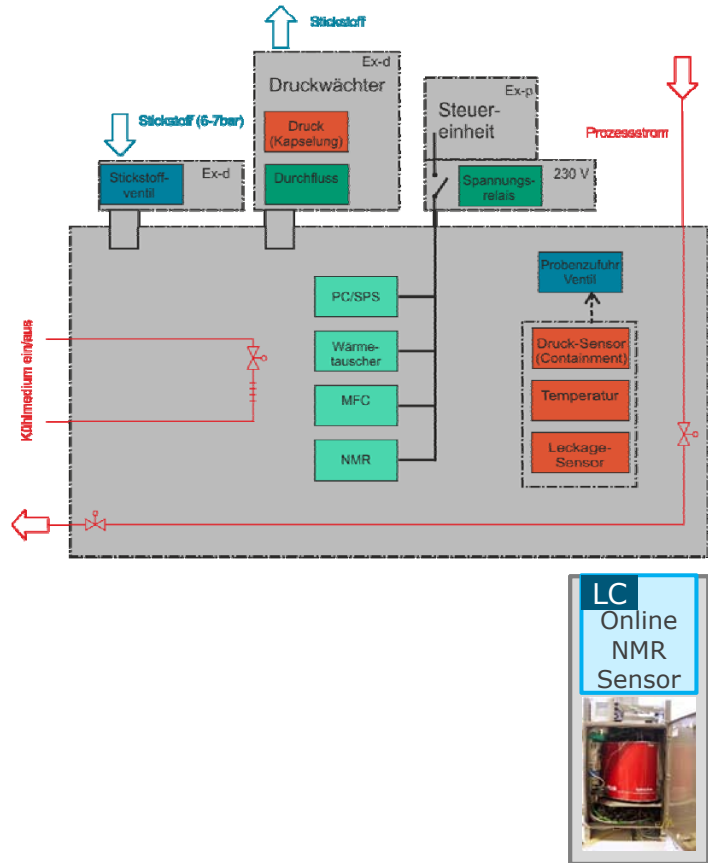






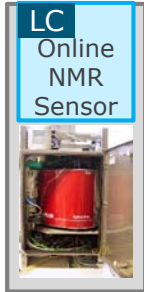
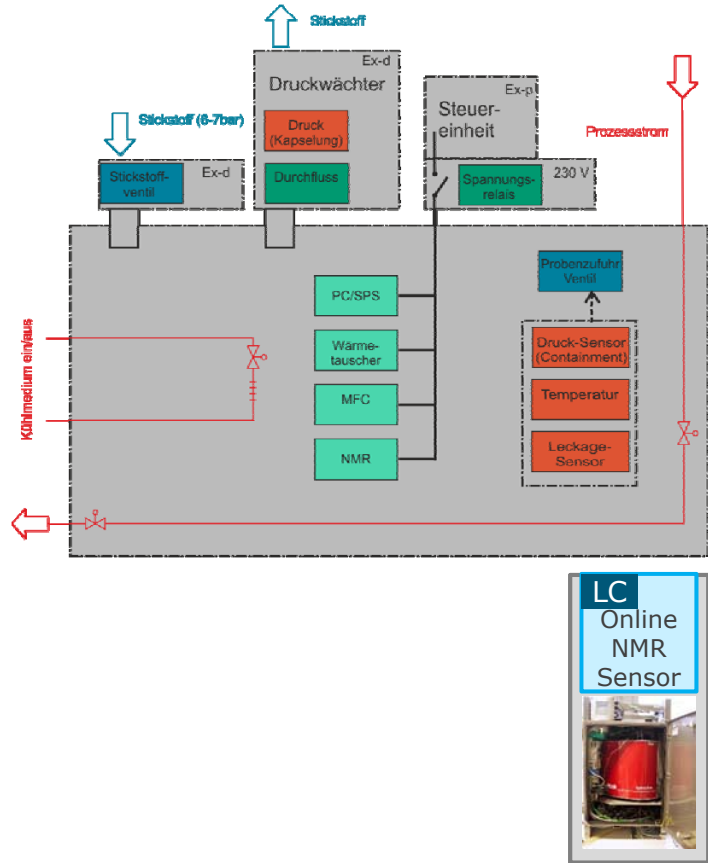
# Automated NMR-Analyzer Module

## Control and Safety Functions



# Automated NMR-Analyzer Module

## Control and Safety Functions

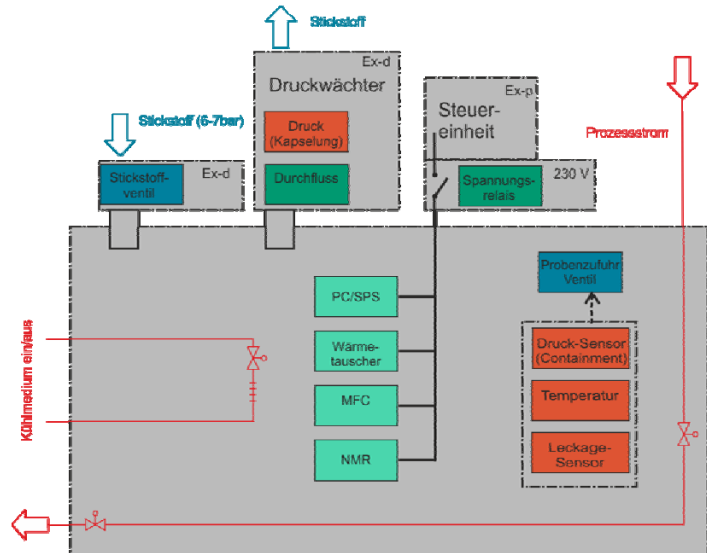


# Automated NMR-Analyzer Module

## Control and Safety Functions



Source: INVITE GmbH



# Automated NMR-Analyzer Module

## Certification and Documentation



**Power supply:**  
100 – 240 VAC, 10 A circuit breaker

**Cooling medium:**  
1 – 5 °C

**Sample feed:**  
28 °C, 10 bar  
(flow cell tested to 50 bar, 100 bar expected)

**Nitrogen purge:**  
6 - 7 bar, min. 140 L/min for purging (~ 2 min)  
Leakage rate at 1.9 mbar: 35 L/min

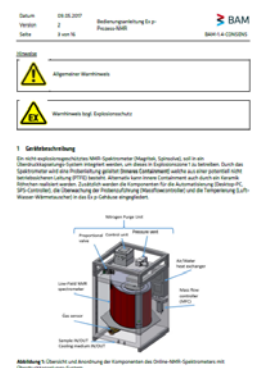
**EC Declaration of Conformity**  
**EC Low voltage Directive**



**ATEX certificate**



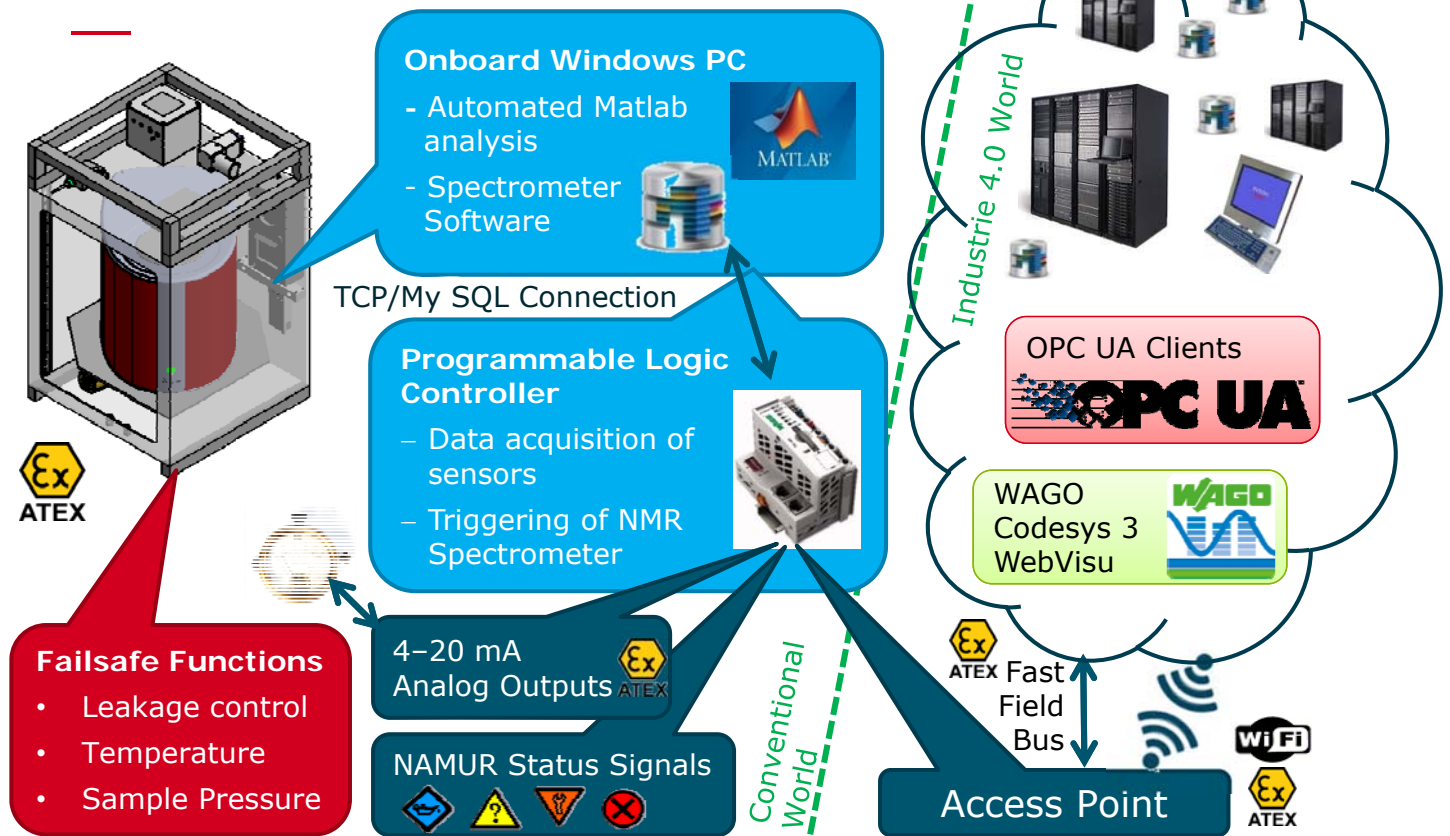
**Operating instructions**



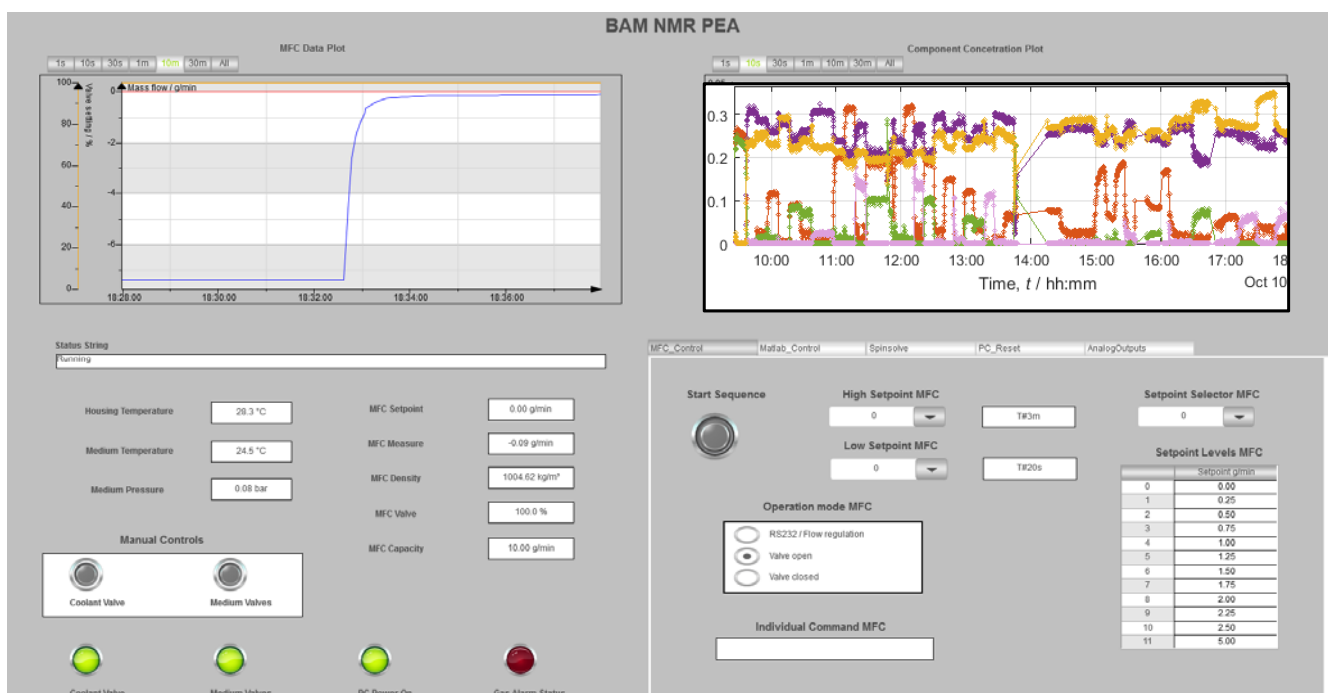
**Ex II 2 G Ex pxb db ib IIB T3 Gb**



# Automated NMR-Analyzer Module Communication and Data Analysis Concept

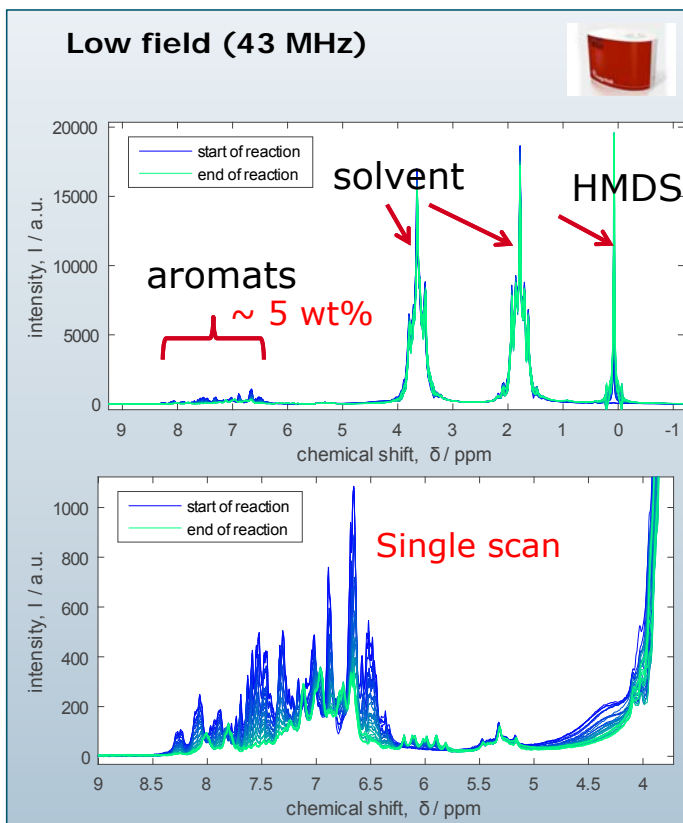
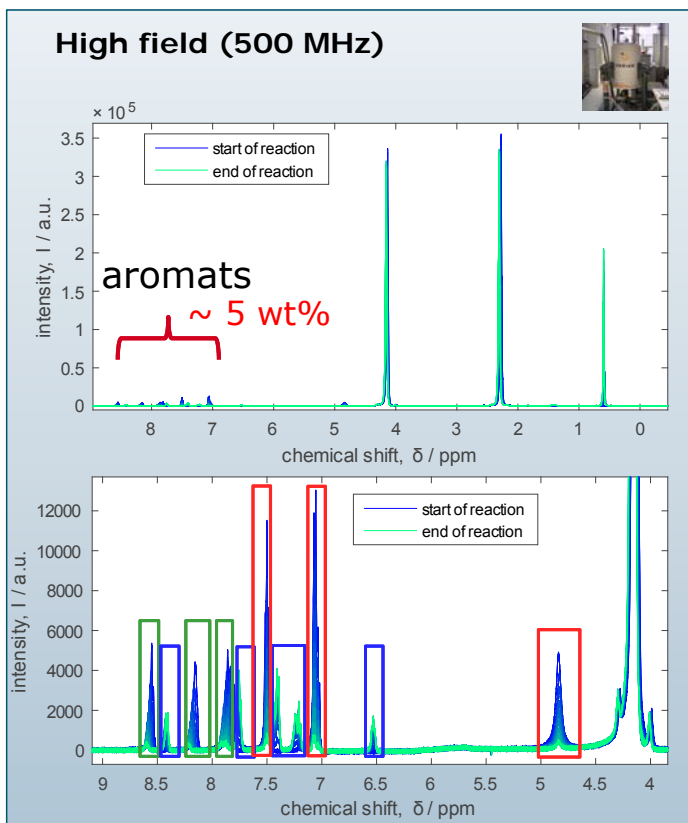


# Automated NMR-Analyzer Module Visualization and Control Web Interface (Expert)

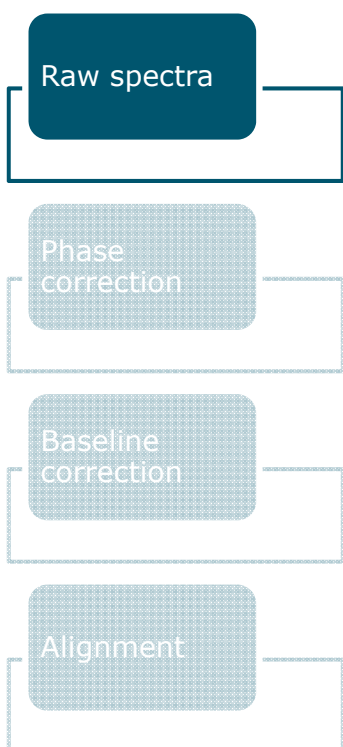


# Proton NMR Spectra 500 MHz vs 43 MHz

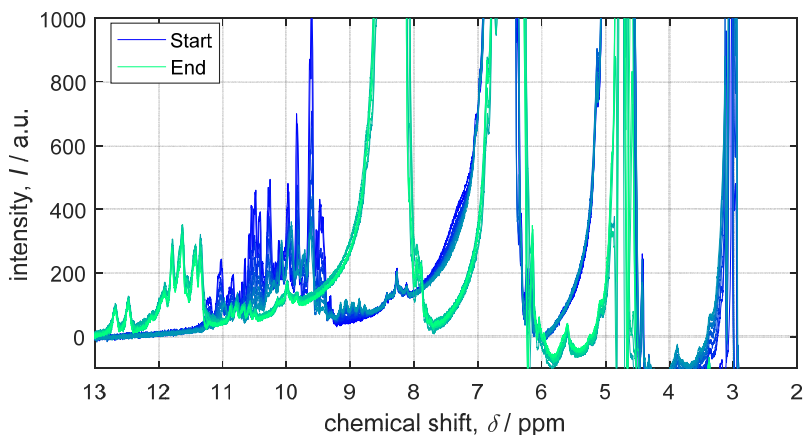
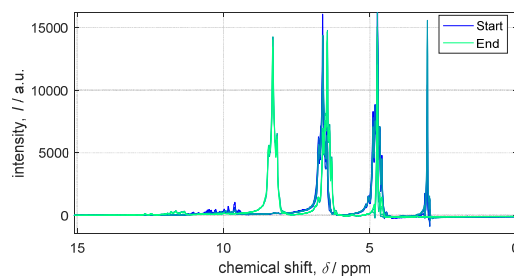
## Lab Experiments in Batch Along Reaction Co-ordinate



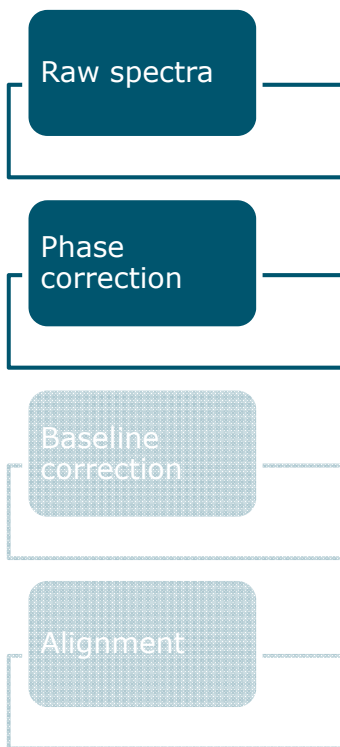
## Data Processing for Low-field NMR in Matlab



single scan  
each 15s  
in flow

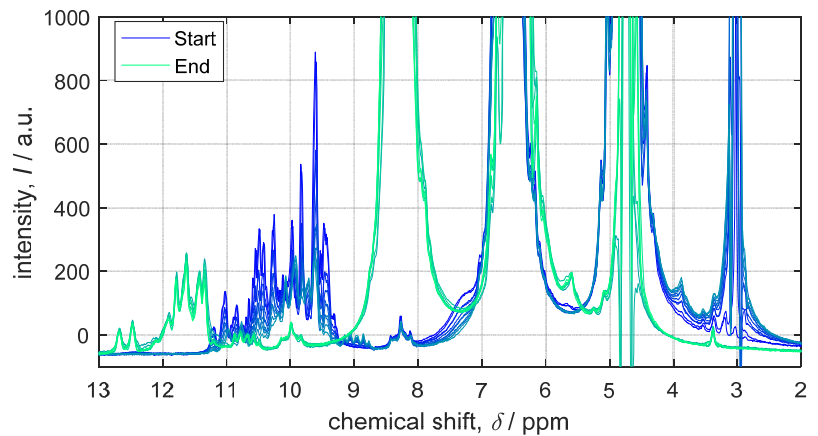
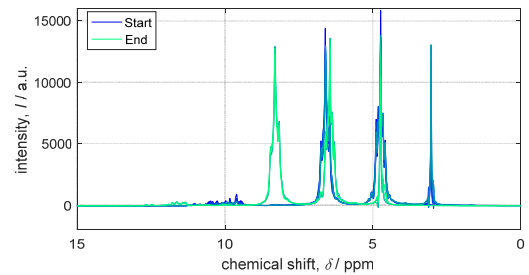


# Data Processing for Low-field NMR in Matlab

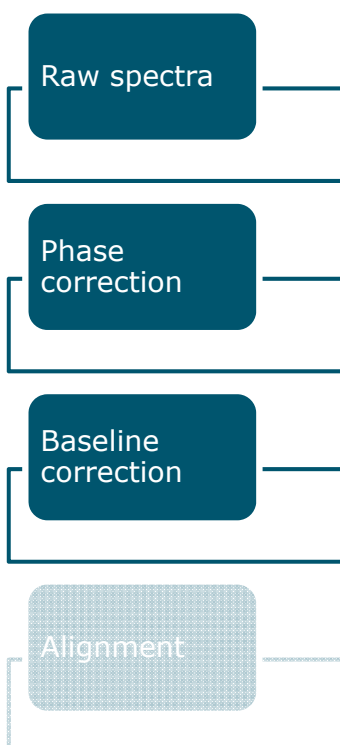


## Entropy minimization method:

Chen et al., *J. Magn Reson.* **2002**, *158*, 164-168

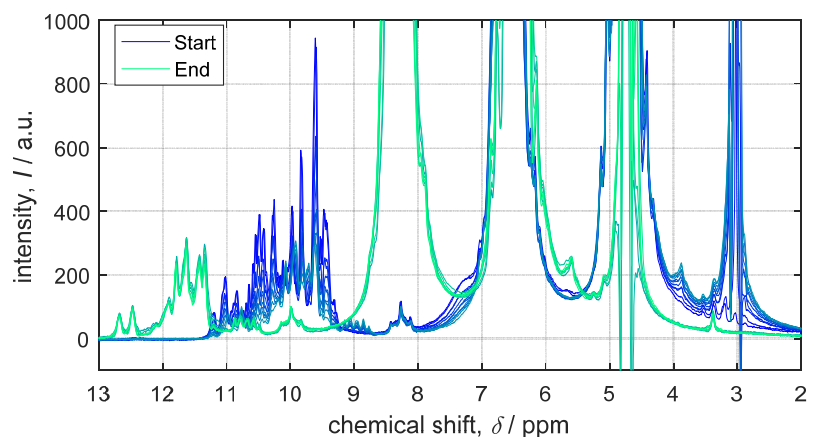
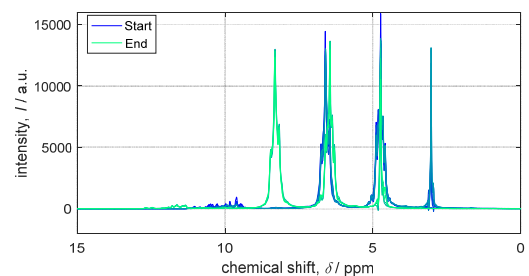


# Data Processing for Low-field NMR in Matlab

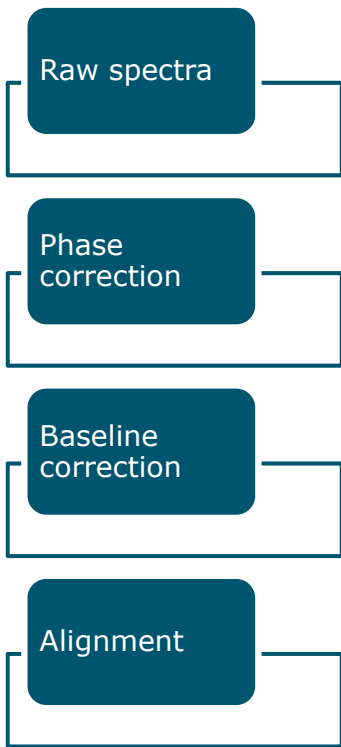


## Low-order Polynomial fit:

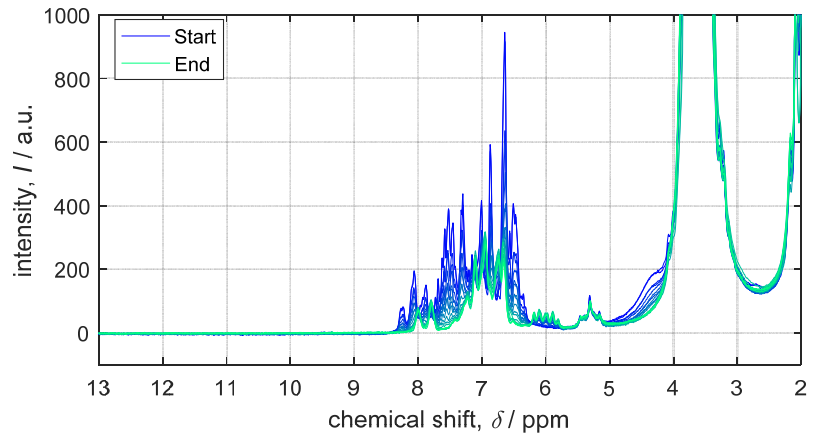
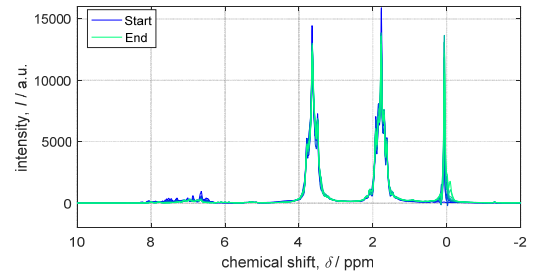
Mazet et al., *Chemometrics Intell. Lab. Sys.* **2005**, *76*, 121-133.







**Alignment to reference signal (THF) using *icoshift*:**  
 Savorani et al., *J. Magn Reson.* **2010**, *2*, 190-202



## Indirect Hard Modeling (IHM)

- Modeling** peak fitting of pure component spectra → mixture model
- Analysis** “component fitting” → calculation of component area

- Group of peaks represent pure component spectra

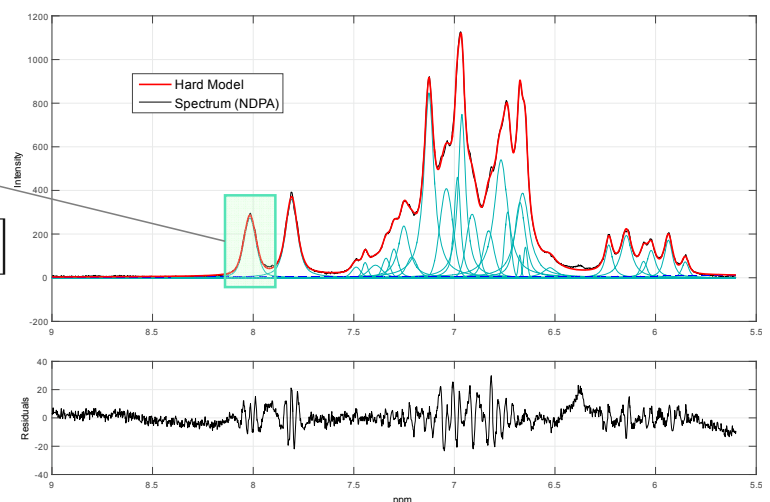


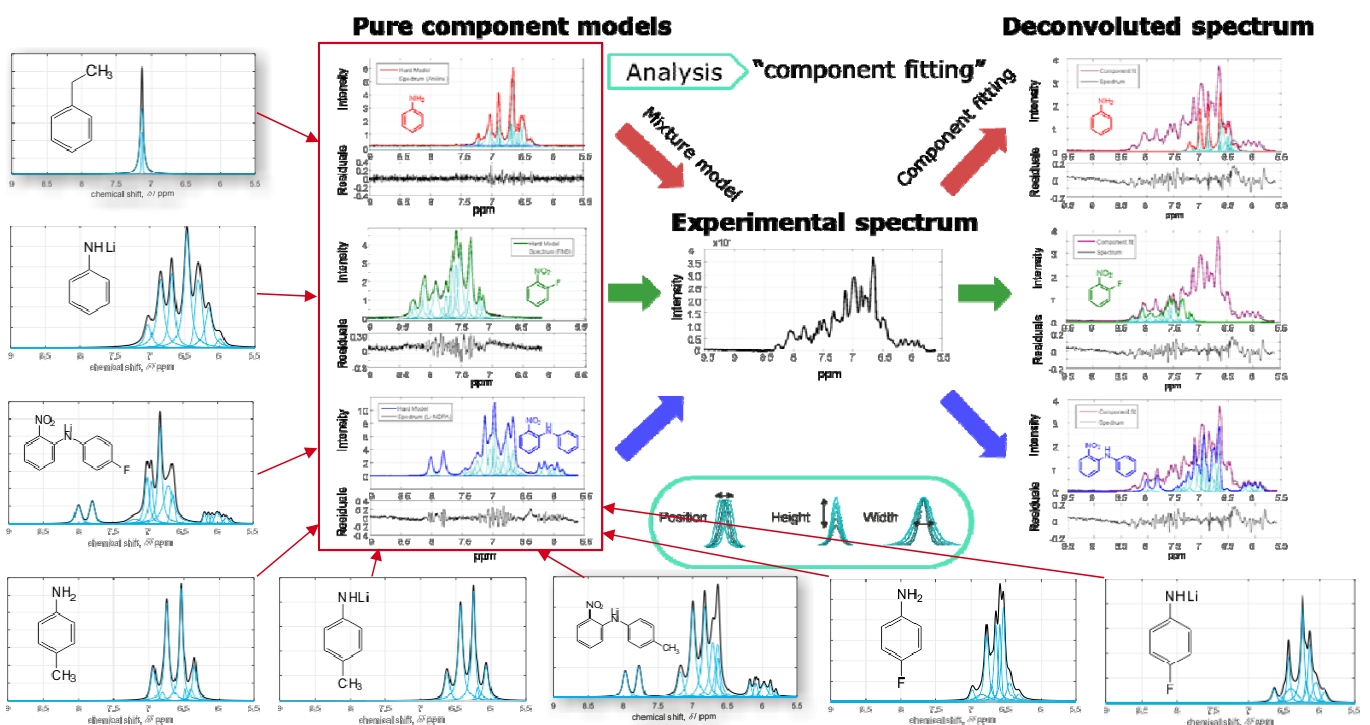
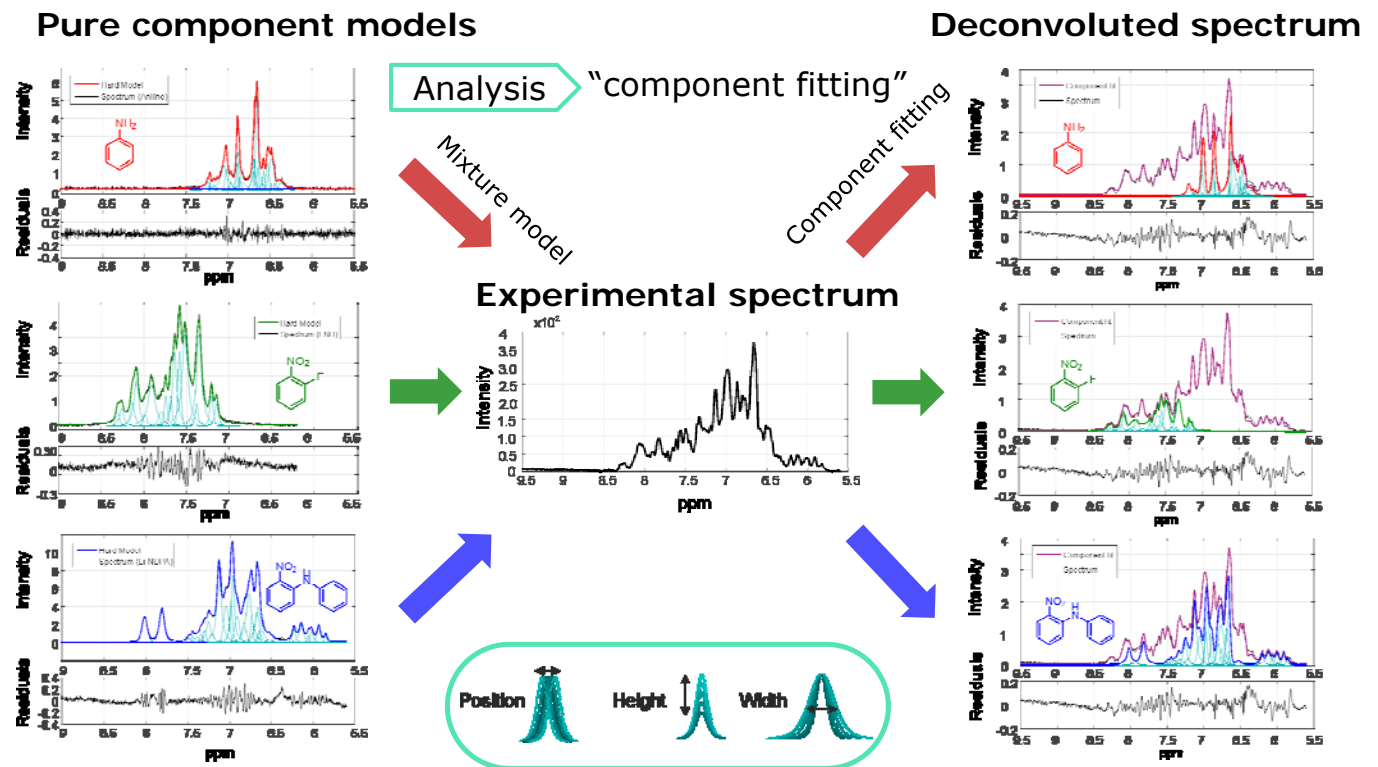
- Pseudo-Voigt function

$$V = \alpha \left[ \beta \cdot \exp\left(-\ln(2) \frac{(x - \delta)^2}{\gamma^2}\right) + (1 - \beta) \frac{\gamma^2}{(x - \delta)^2 + \gamma^2} \right]$$

- $\alpha$  = peak maximum
- $\beta$  = Gaussian-Lorentzian-ratio
- $\gamma$  = half width
- $\delta$  = center position

### Hard model for pure components



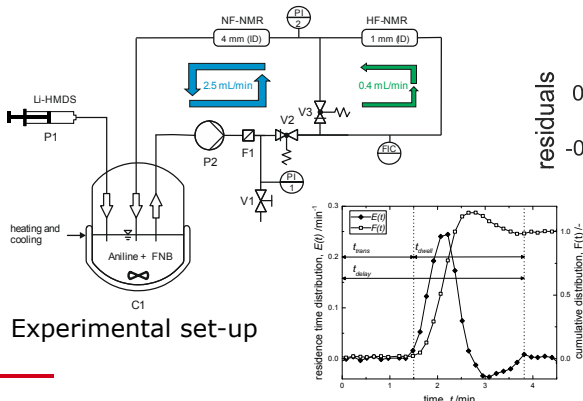
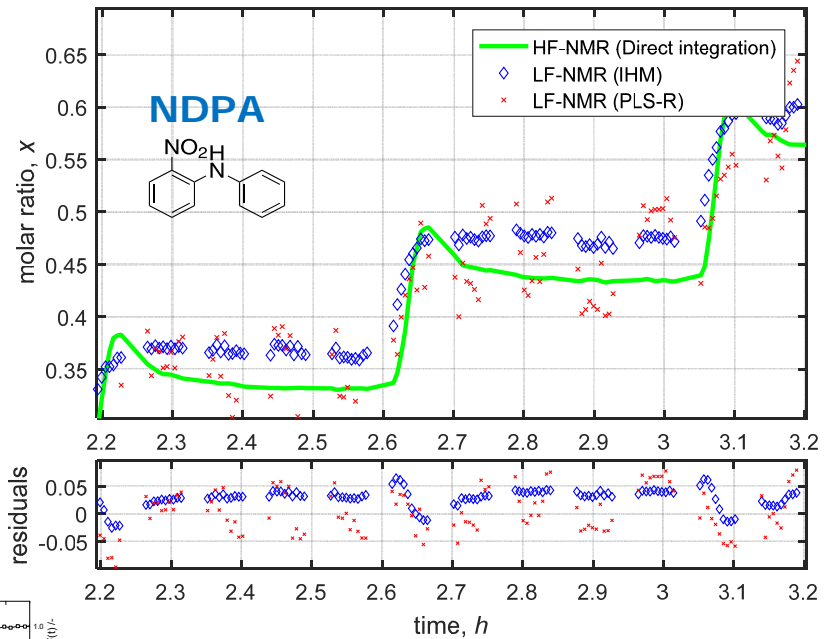
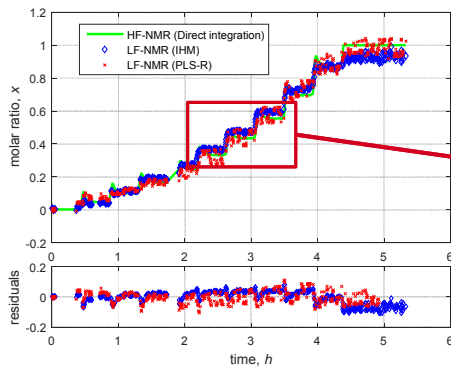


# (1) Model Building: IHM and PLS-R

## Lab Experiments in Batch Along Reaction Co-ordinate

### Validation with HF-NMR

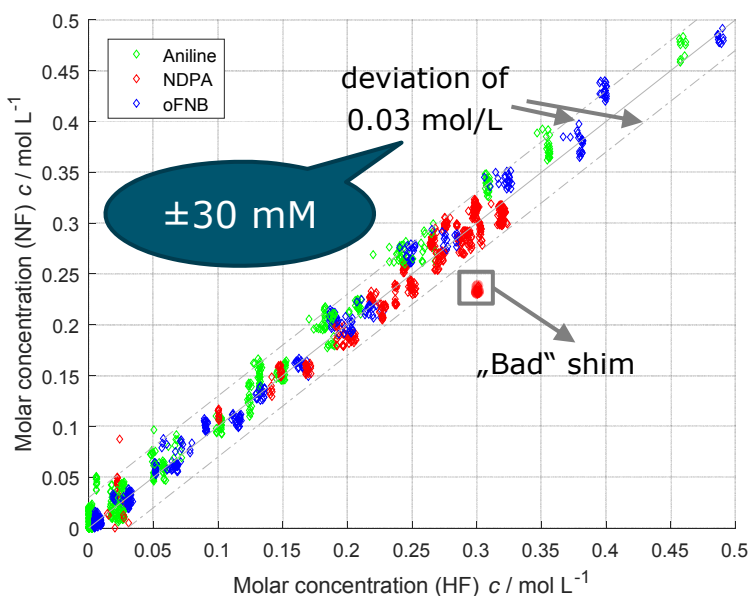
IHM = Indirect Hard Modeling; PLS-R = Partial Least Squares Regression



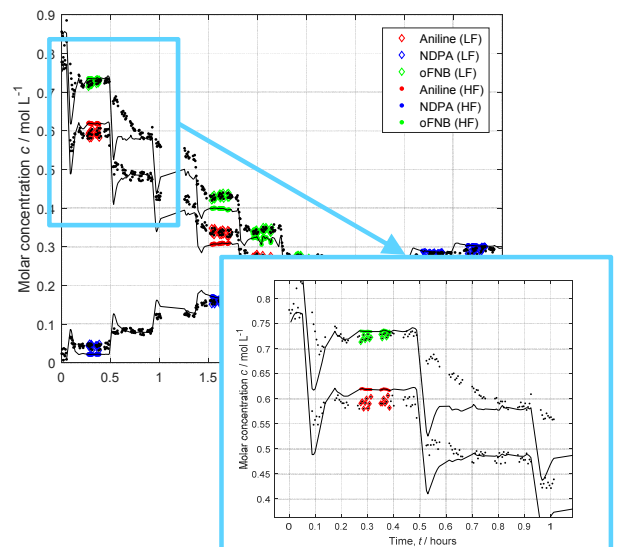
# (1) Results: Reaction Characterization

## Lab Experiments in Batch along Reaction Co-ordinate

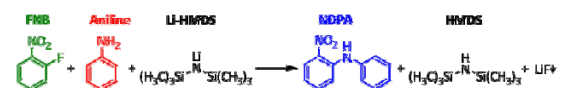
3 semi-batch reaction with varying starting concentrations  
1500 Spectra for each HF- and NF-NMR



### Classification of steady states



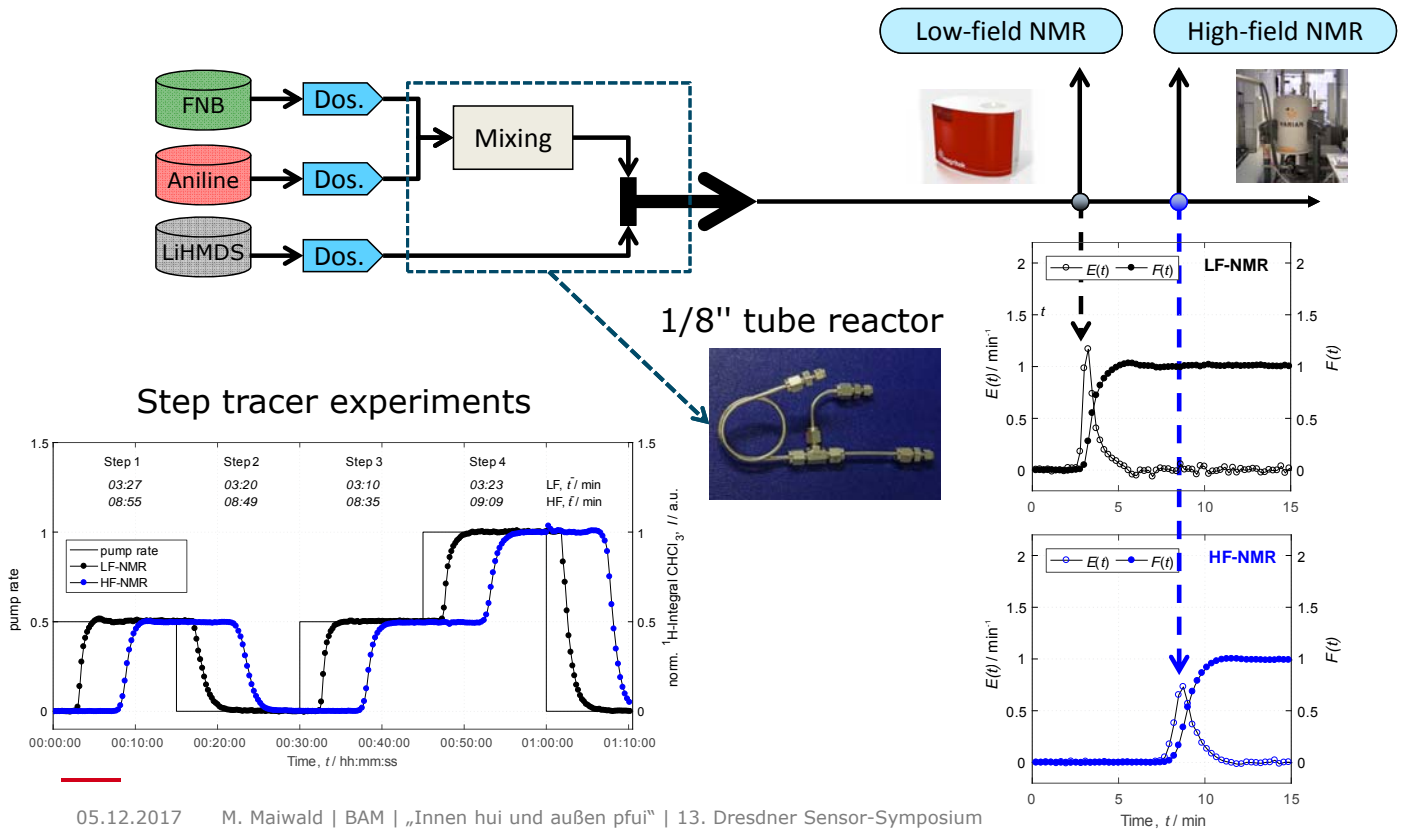
### Reaction Scheme:





## (2) Validation of Lab Experiments in Tube Reactor

### Continuous Lithiation Reaction Set-up at BAM

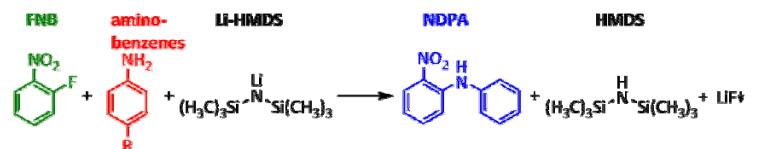


## (2) Experimental Design

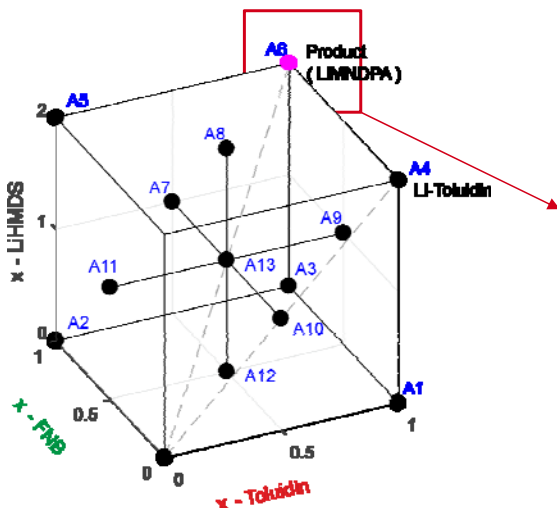
### Continuous Lithiation Reaction Set-up at BAM

- Independent variation of flowrates / stoichiometric conditions

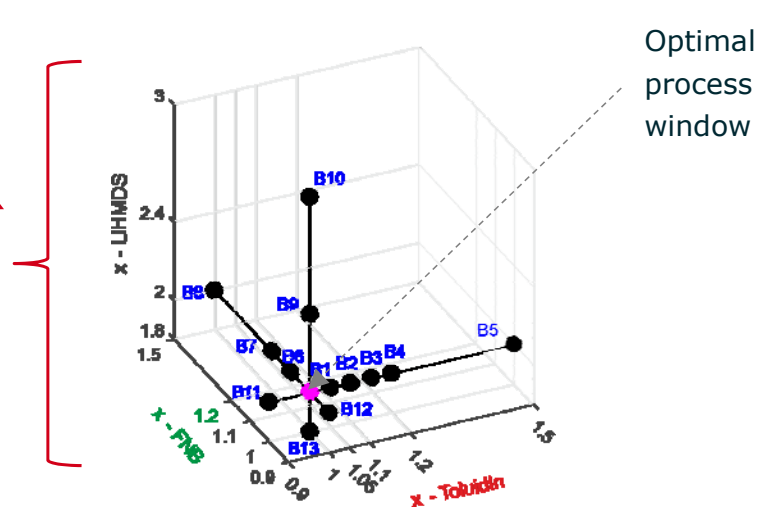
#### Reaction Scheme:



#### Coarse variation:



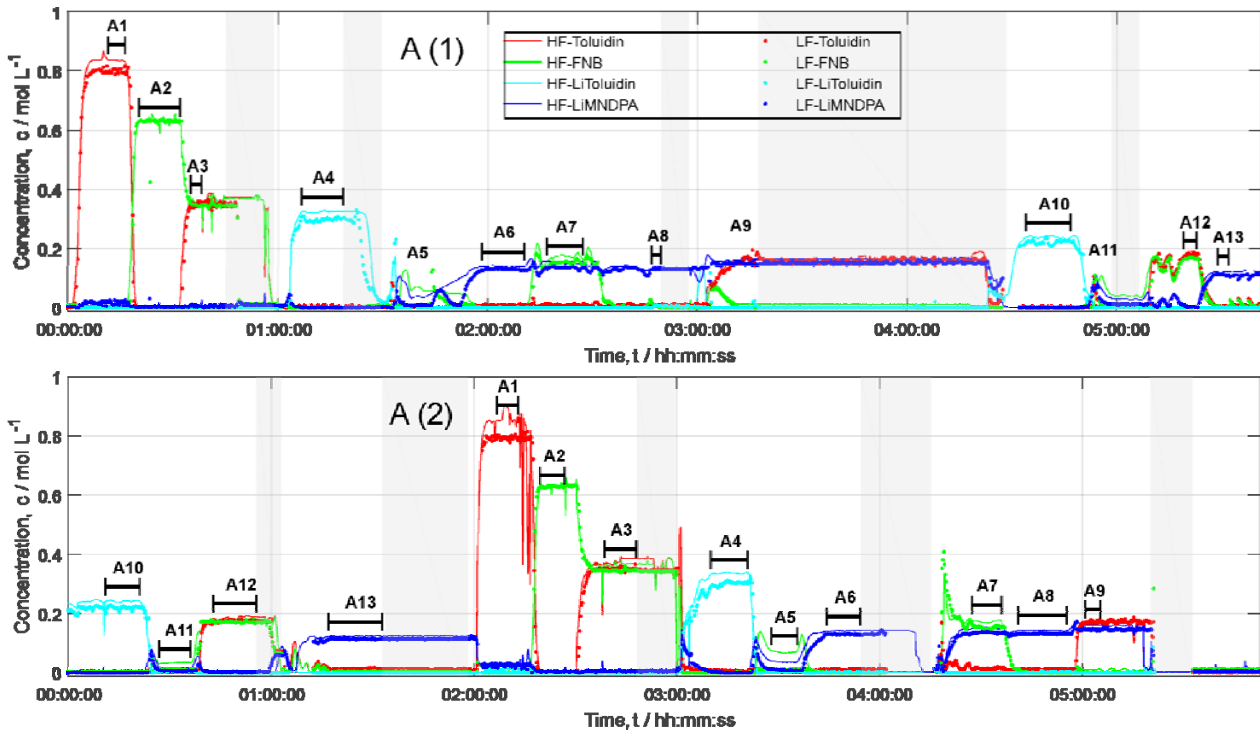
#### Fine variation:



## (2) Validation Instead of Calibration

Variation of Set-Points according to Experimental Design

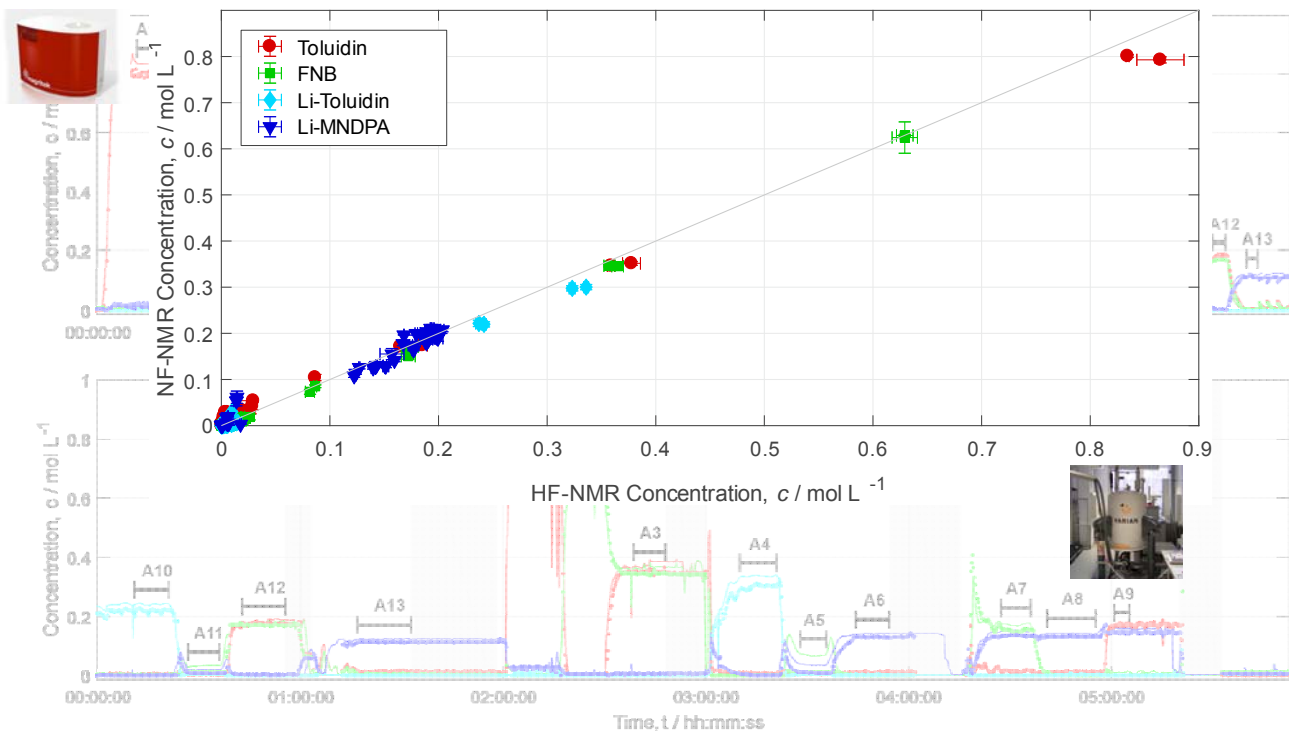
### Low-Field versus High-Field NMR Spectroscopy



## (2) Validation Instead of Calibration

Variation of Set-Points according to Experimental Design

### Low-Field versus High-Field NMR Spectroscopy







### (3) Validation in Modular Plant

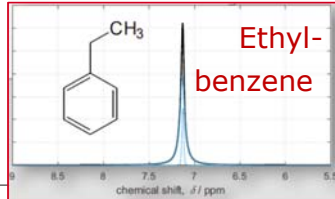
#### Additional Component Found (Stabilizer at 10 wt-%)

- Stabilizer Ethylbenzene at 10 wt-% in Li-HMDS reagent
- Modular extension of IHM model from laboratory data successful

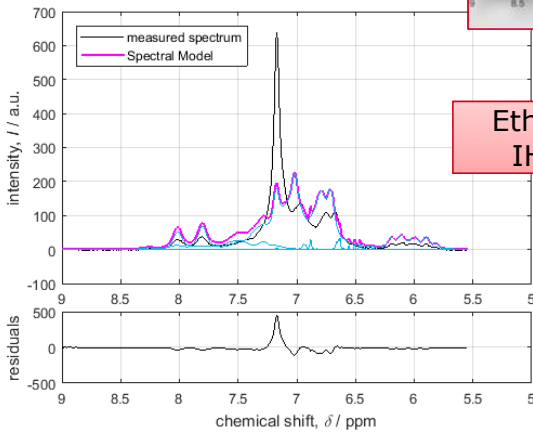


Containerized modular plant  
Source: INVITE GmbH

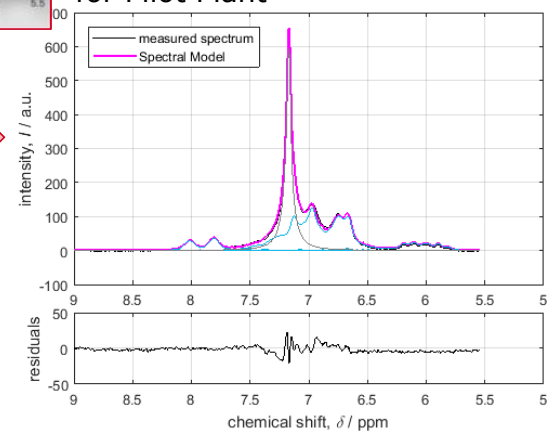
Preliminary IHM Model from Lab



Extended IHM Model for Pilot Plant



Ethylbenzene  
IHM Model

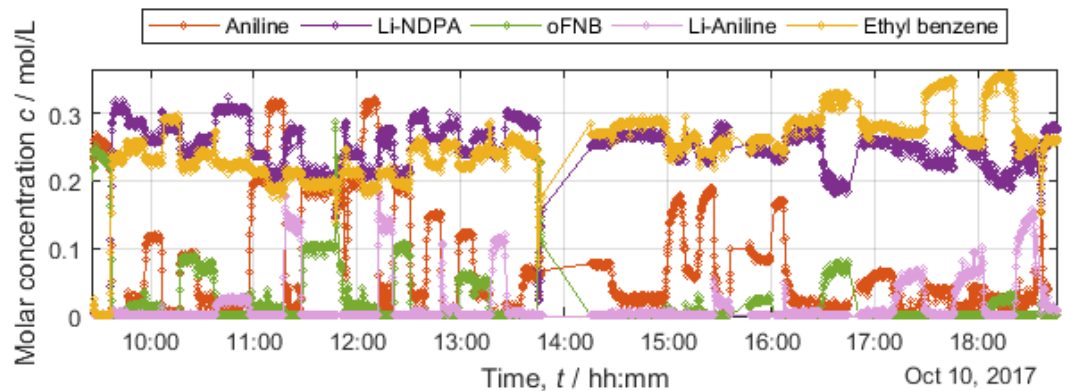


### (3) Validation in Modular Plant

#### Final Validation Runs in Pilot Plant

NMR Module

Five Components

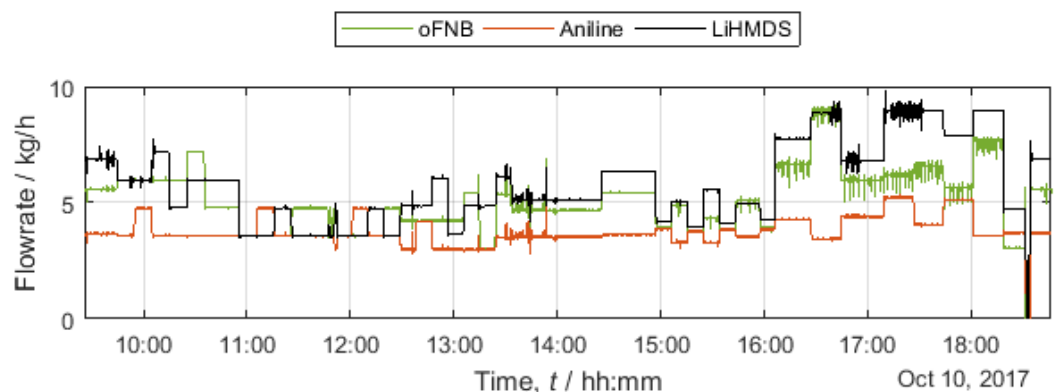


Flow Setpoints

iRTO Results

Iterative real-time optimization (iRTO) by Sebastian Engell and Anwesh Reddy Gottu Mukkula

TU Dortmund

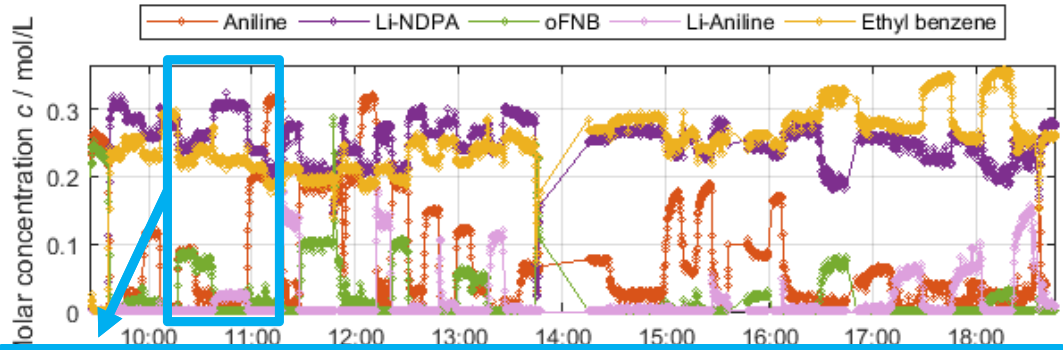


# (3) Validation in Modular Plant

## Final Validation Runs in Pilot Plant

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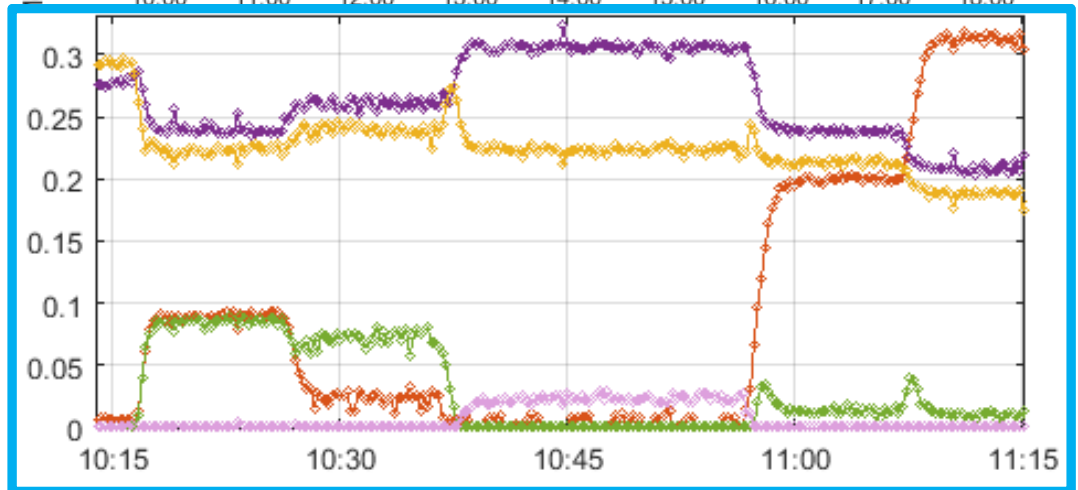


Flow Setpoints

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TU Dortmund



# Conclusion and Outlook

Smart Sensors

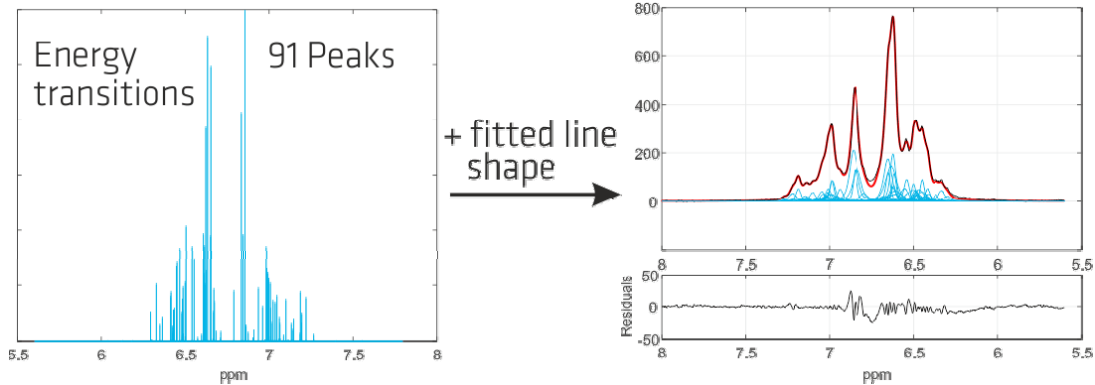
- Integrated Process Design and Intensified Processes  
→ Current Trend: Hybrid Modular Plants
- Smart process sensors and actuators are important parts of cyber-physical production systems
- Smart field devices generate new business cases for users, instrument manufacturers, and service providers.
- Use of „complicated“ sensors has to be simplified towards „plug and play“
- The classical automation pyramid is not suited for smart field devices

Smart NMR Analyzer Module

- Classical field integration and automation of NMR shown
- Physical Modeling (IHM) enables modular and calibration-free use of NMR  
→ Validation instead of calibration

## Modular Calibration

- Improvement of Physical Modeling (IHM)
- Derivation from „First Principles“ Methods (i.e., Quantum Mechanics)



- „Semantic“ Models

# Thank You!

Jürgen Kolz

Magritek

Clemens Minnich S-Pact

Ullrich Koch

Magritek

Dirk Engel S-Pact

Juan Perlo

Magritek

Sebastian Engell TU Dortmund

Mike Bernstein

Mestrelab

Anwesh Reddy

Harald Pape

PTB

Gottu Mukkula TU Dortmund

CONSENS – Integrated Control and Sensing for Sustainable Operation of Flexible Intensified Processes, funded by the European Union’s Horizon 2020 research and innovation programme under grant agreement N° 636942; [www.consens-spire.eu](http://www.consens-spire.eu)