BAM
Bundesanstalt für Materialforschung und -prüfung

Sicherheit in Technik und Chemie

13.10.2016

High-pressure qNMR spectroscopy in condensed- and gas-phase towards determination of impurities and compositions of gas mixtures

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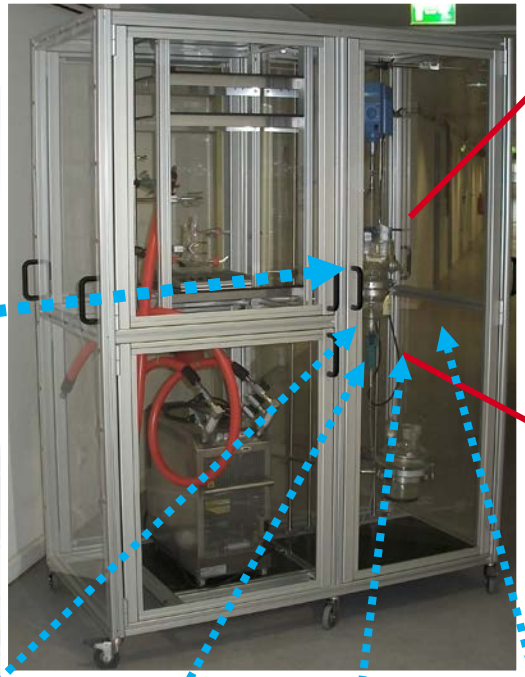
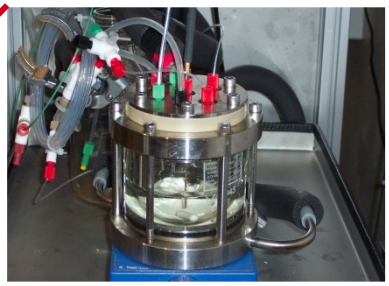
Online NMR Spectroscopy as Reference

Hyphenation to reactors and devices

500 MHz
Online NMR



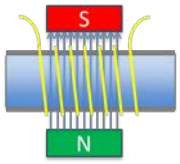


reactors

Process NIR

Process
UV/VIS

Process
Raman



Process
NMR

Complex reacting multicomponent mixtures

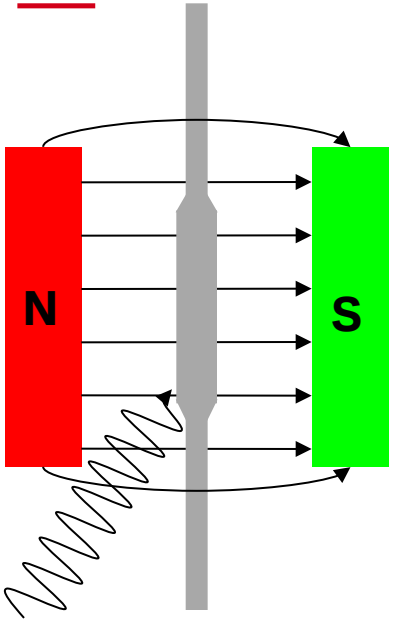
- quantitative information
- qualitative („chemical“) information
- highest possible dispersion

Direct coupling to reactors

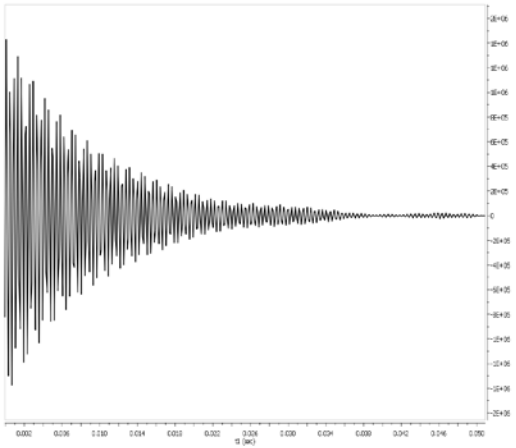
- fast and direct sample transfer
- automation
- extended pressure range

How does NMR work ?

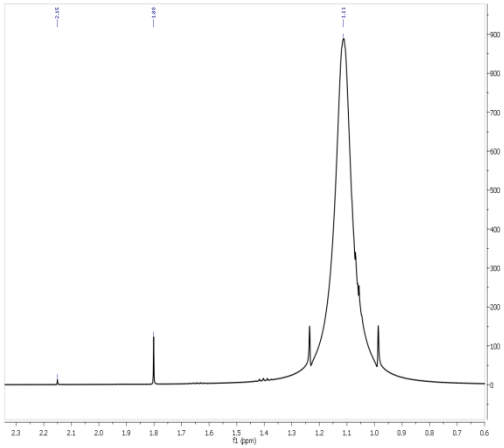
NMR stands for **N**uclear **M**agnetic **R**esonance



FT: Fourier Transformation



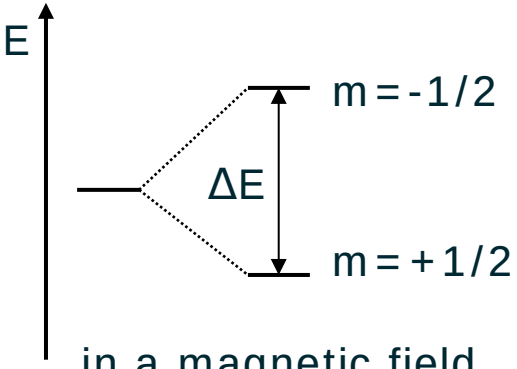
FT



Free Induction Decay (FID)

1D NMR spectrum

Radio Frequency pulse



For I = 1/2

in a magnetic field

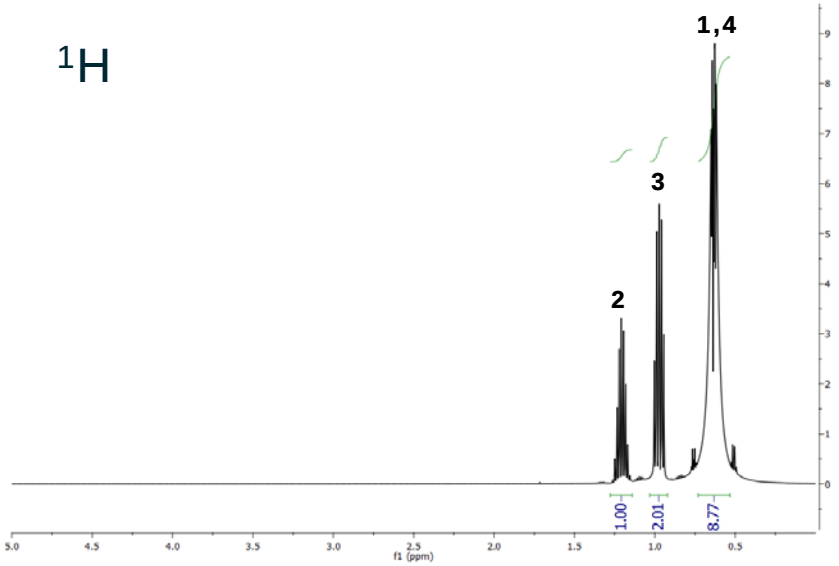
- e.g. ^{1}H, ^{13}C
- High dispersion of signals
- Absolute comparable method
- Quantitative information by integration

Quantitative NMR spectroscopy

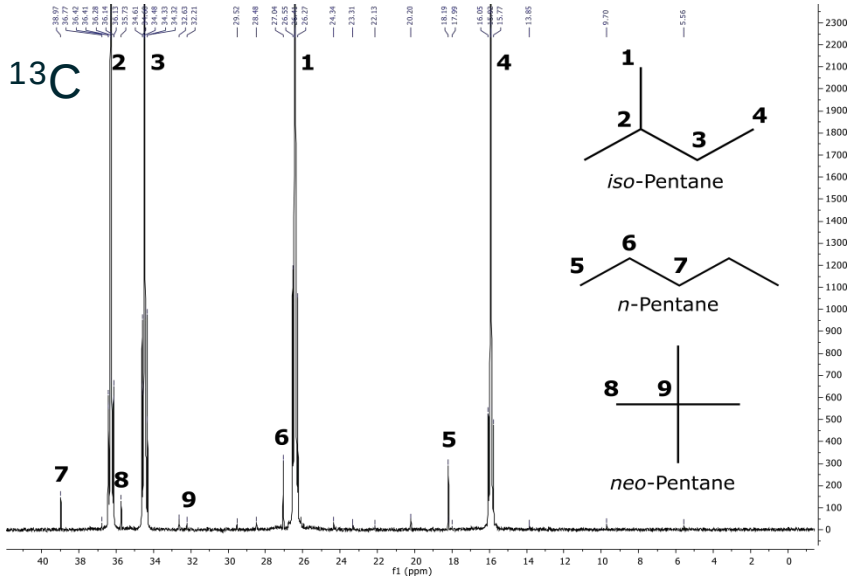
Purity assessment of raw materials

- *iso*-Pentane for production of Primary Reference Gas Mixtures

^{1}H



^{13}C



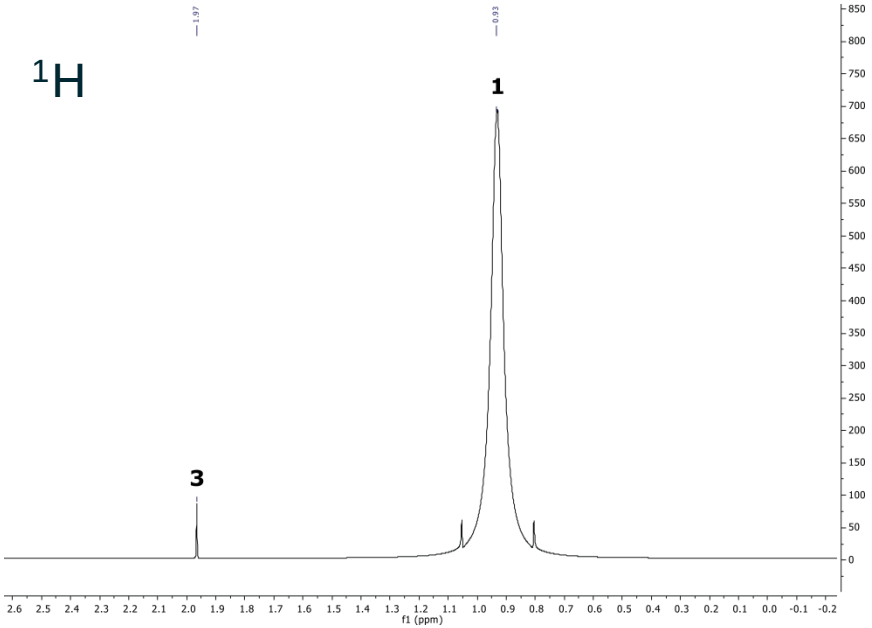
- Orientational results from ^{13}C-NMR
- Comparison with estimated GC-MS

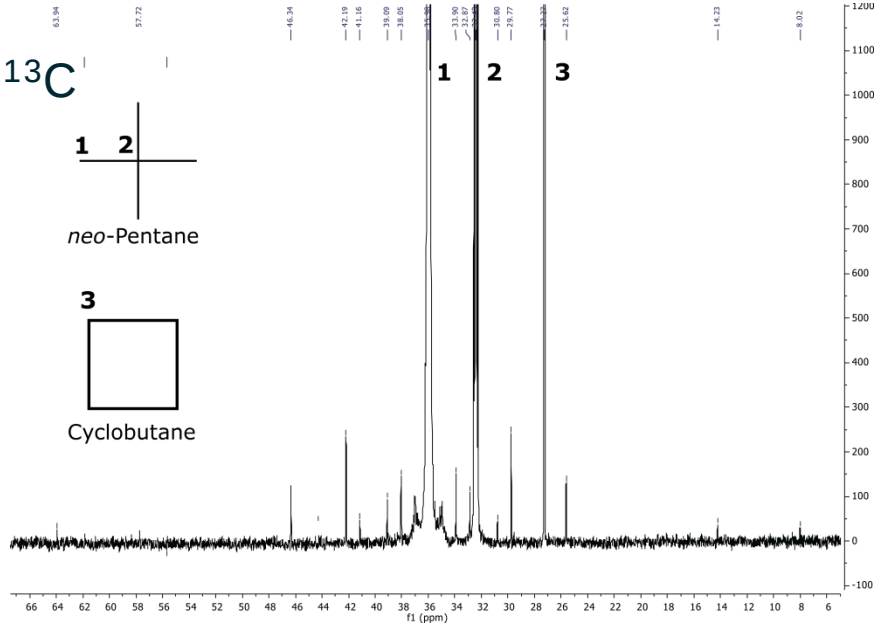
Component	x_{NMR} / %	x_{GC-MS} / %
iso-Pentan	99.794	99.771
n-Pentane	0.170	0.187
neo-Pentane	0.036	0.038

Quantitative NMR spectroscopy

Purity assessment of raw materials

- *neo*-Pentane: problem of available purity limited to 2.0



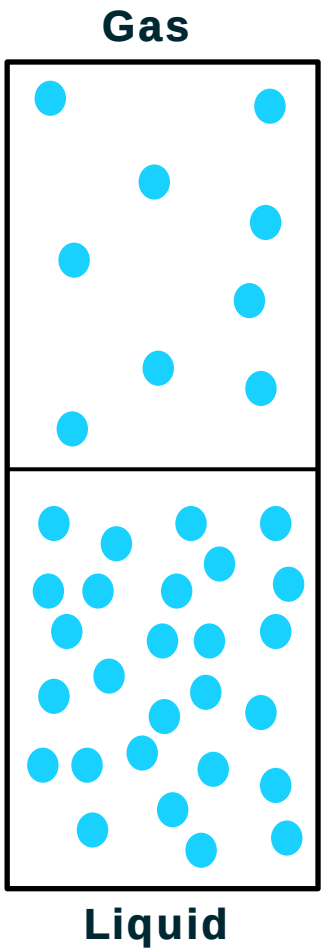


- Results from 7 spectra
- Uncertainty ~120 ppm (n/n)

Component	x_{NMR} / %	$u(x_{NMR}, k=2)$ / %
neo-Pentane	98.945	0.012
Cyclobutane	1.055	0.012

High-Pressure NMR spectroscopy

Application in gas and condensed phase



- Higher density of nuclei
- Direct connection to gas cylinder
- Pressure ≤20 MPa (up to 100 MPa possible)

→ Increasing sensitivity,

→ ^{13}C-NMR in the gas phase

- Sampling from piston cylinders
- Circulation for homogenization

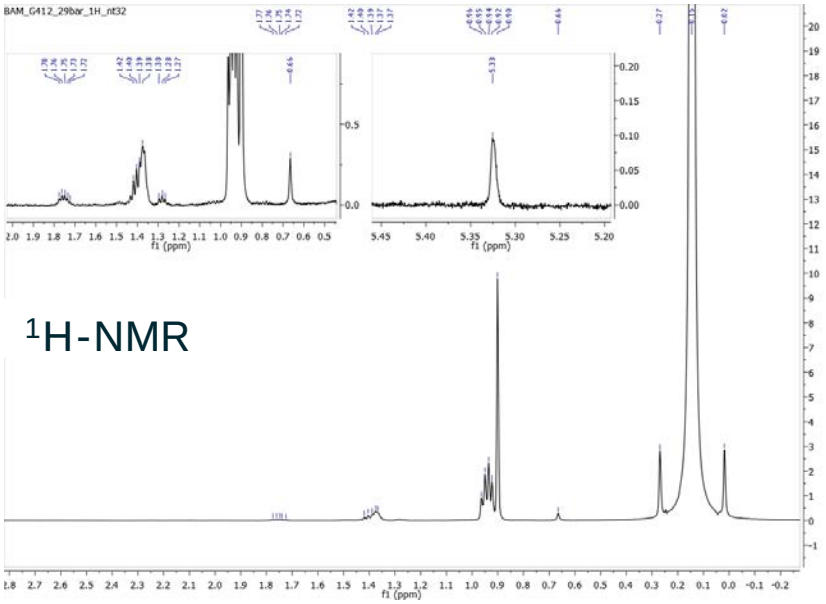
→ Direct quantitation in liquids

→ No sample preparation

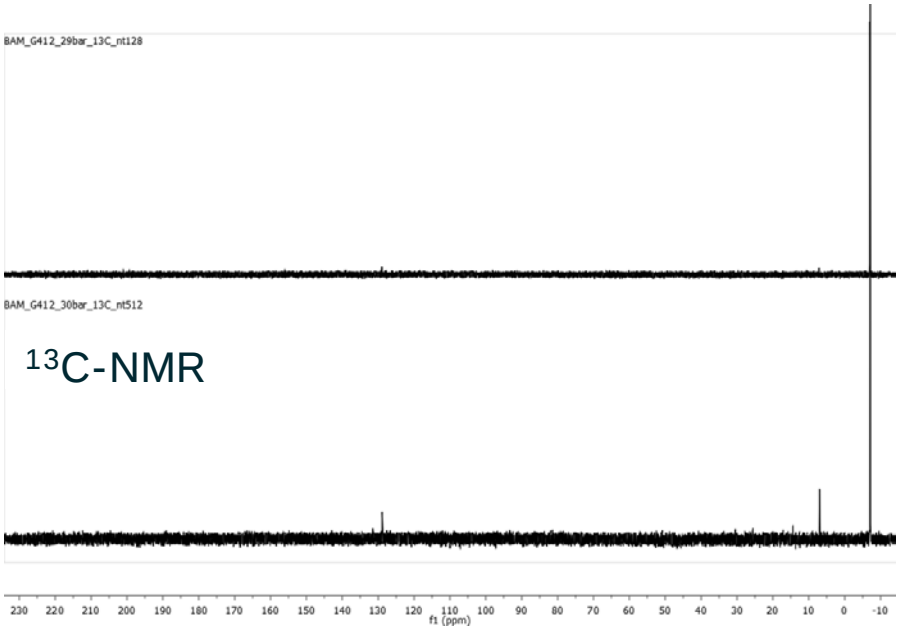
Gas-phase NMR spectroscopy

Primary Reference Gas Mixtures

- Methane-based mixture with components up to C_5 (BAM-G412, H1-8K)
- Available filling pressure: ~3 MPa



^{1}H-NMR



^{13}C-NMR

32 Scans, time ~10 min

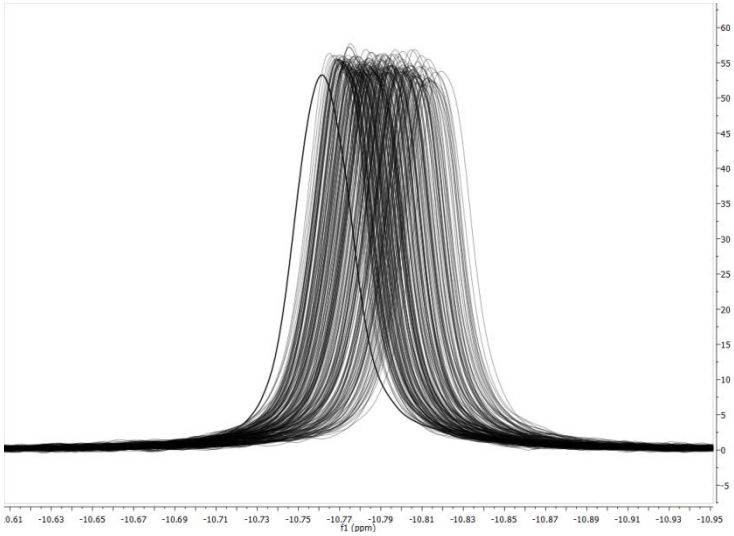
128 Scans, time ~ 68 min
512 Scans, time ~ 273 min

→ Several hours of measurement time is needed, especially for ^{13}C-NMR

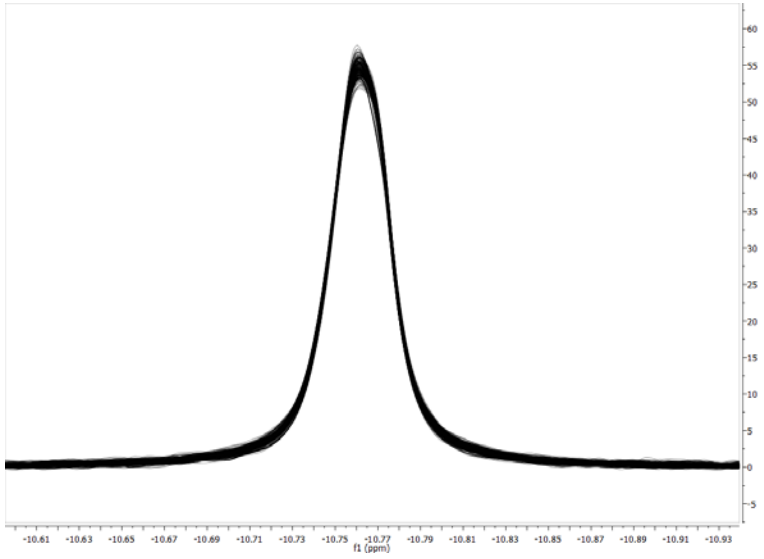
Gas-phase NMR spectroscopy

Long-term measurements

- No deuterated substances for field-frequency-lock
- Signal drifts during experiment
- Standard procedure of accumulation not suitable
- Alignment required before accumulation of spectra



without alignment

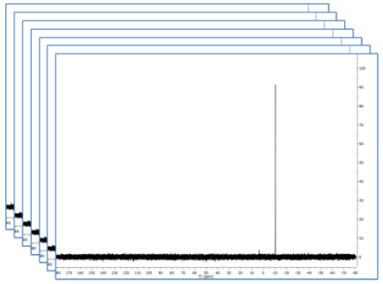


after alignment

Gas-phase NMR spectroscopy

Accumulation procedure

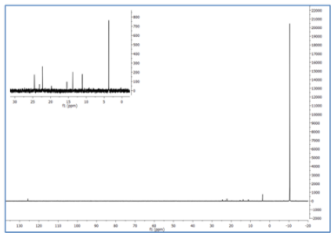
- Accumulation of single spectra in frequency domain
- Preprocessing required → Phasing, Baseline correction
- Accumulated spectrum can be treated like standard NMR data



Single spectra, e.g. 64 scans each

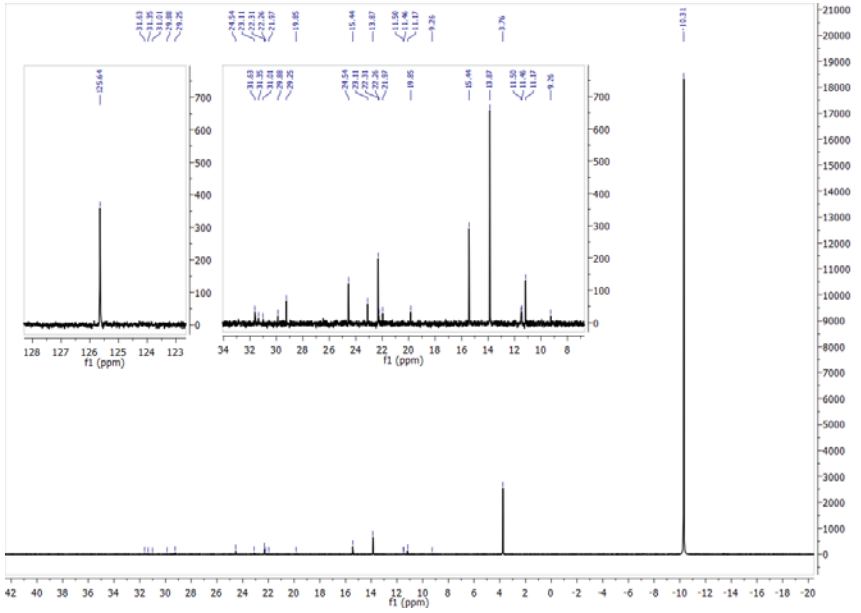
ASCII-Export

Matrix .csv File



Alignment

Accumulation



BAM-G430, p = 4.4 MPa
160 spectra with 64 Scans ≙ 90.6 h

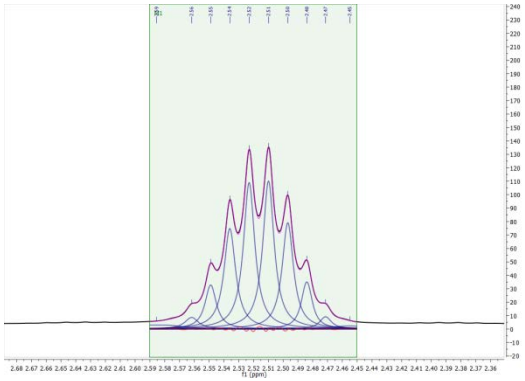
Gas-phase NMR spectroscopy

Primary Reference Mixture BAM-G412

Degree of Equivalence

$$\frac{x_{NMR}}{x_{cert}} - 1$$

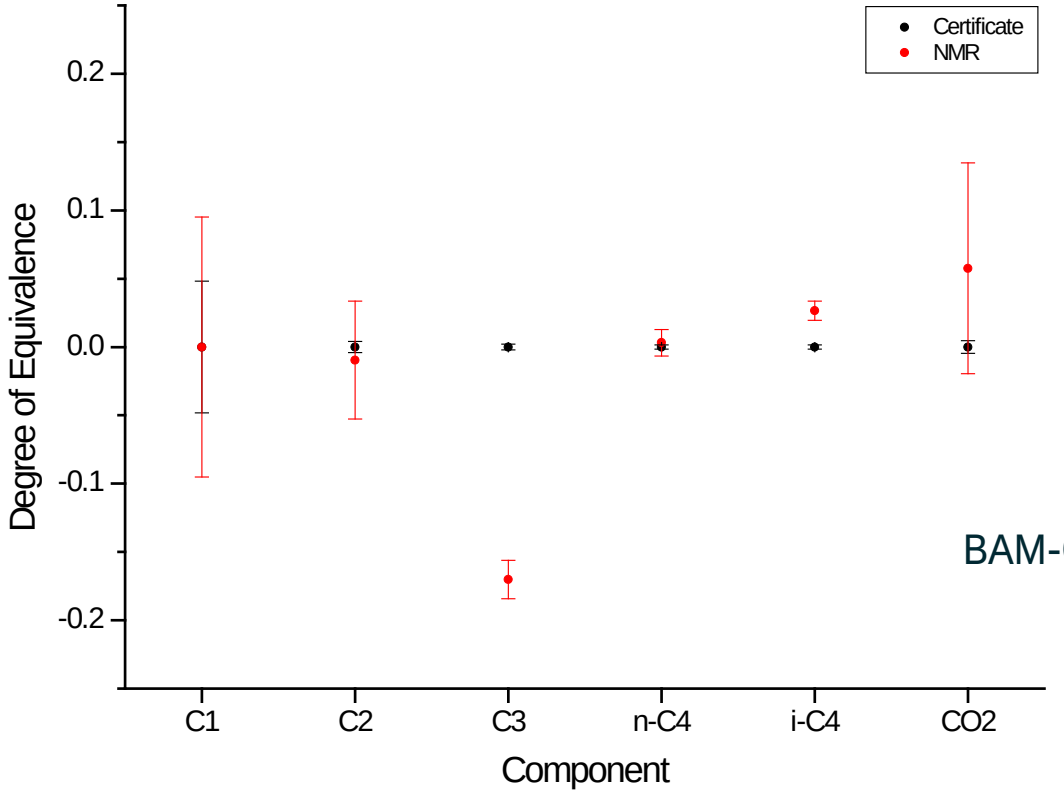
- Linefit with gaussian/lorentzian functions for signal area
- Relative quantification with 100%-approach
- Expanded uncertainty (k = 2):
  - Contribution of repeated measurement
  - Contribution of repeated data analysis
- Comparison with certified gravimetric value



	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}	iso-C_4H_{10}	CO_2
x(certified)	**97.283**	**1.028**	**0.253**	**0.208**	**0.204**	**0.965**
u_x(CRM cat., k = 2)	**±0.0482**	**±0.0040**	**±0.0020**	**±0.0016**	**±0.0016**	**±0.0045**
t = 47.2 h	97.354	1.051	0.198	0.200	0.203	0.994
t = 133.1 h	97.401	0.978	0.222	0.217	0.210	0.972
t = 161.6 h	97.241	1.028	0.210	0.208	0.216	1.097
x(NMR)	**97.332**	**1.019**	**0.210**	**0.208**	**0.210**	**1.021**
u_x(combined, k = 2)	**±0.0951**	**±0.0432**	**±0.0141**	**±0.0098**	**±0.0071**	**±0.0772**
Degree of Equivalence	**-8.877E-05**	**-0.0096**	**-0,1702**	**0.0031**	**0.0265**	**0.0576**

Gas-phase NMR spectroscopy

Degree of Equivalence BAM-G412



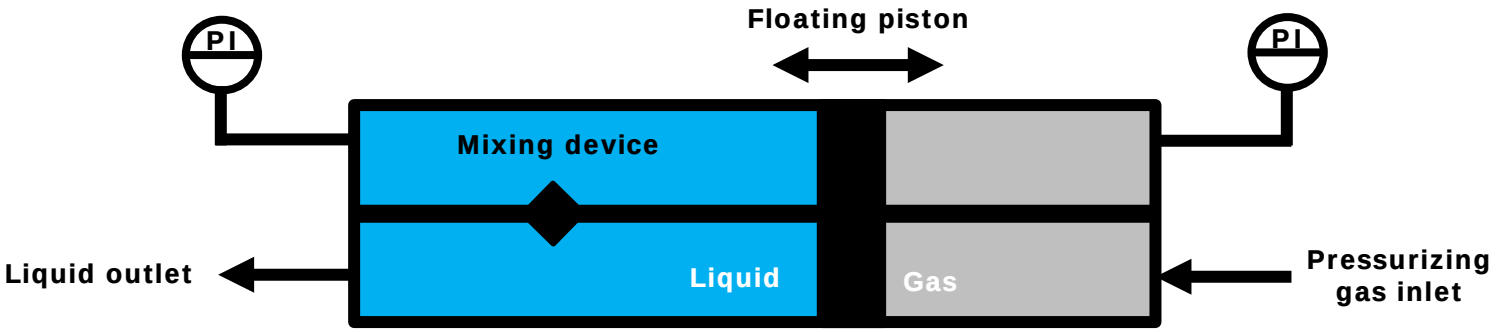
BAM-G412 (~3 MPa)

- Certified value mostly within uncertainty range of NMR measurements
- Unresolved deviation in case of propane

NMR spectroscopy in condensed phase

Idea and Motivation

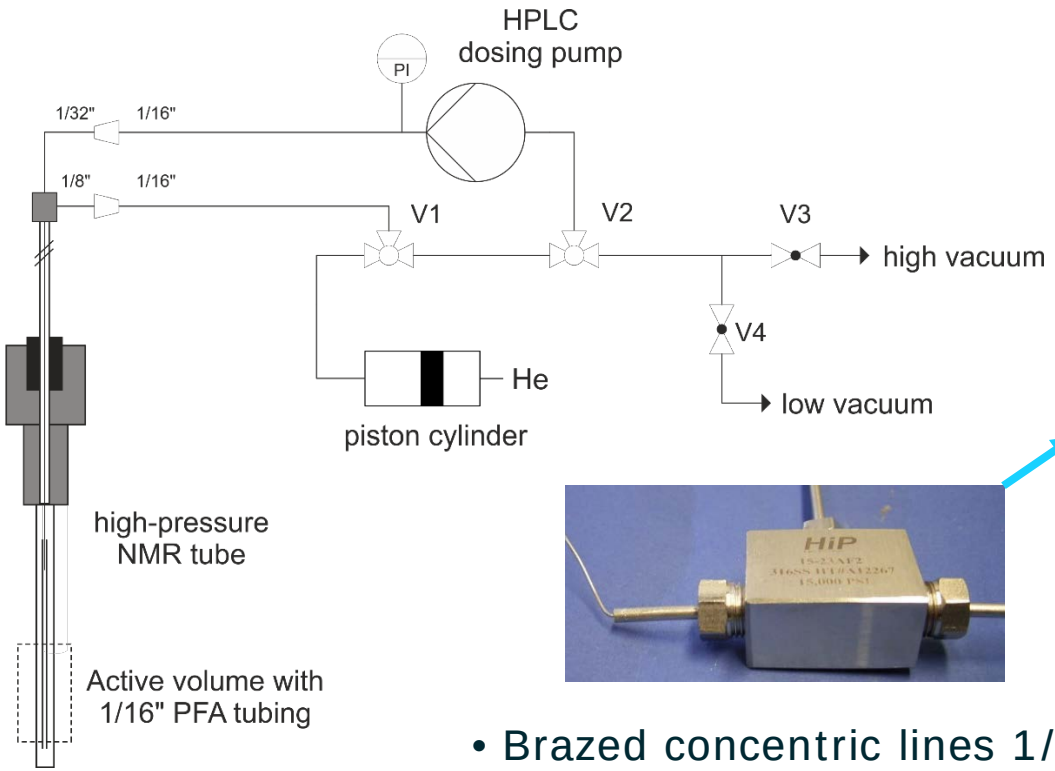
- High-purity hydrocarbon mixtures commonly provided in piston cylinders
- In use for key comparisons, e.g., EURAMET.QM-S6/1195 (NPL)

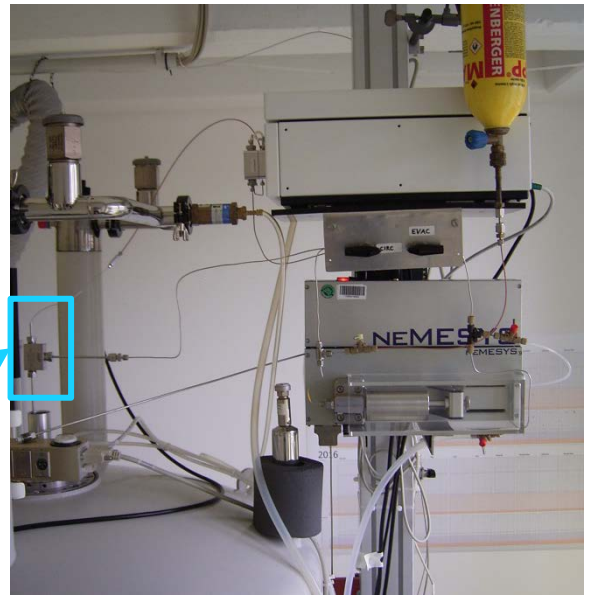


- Avoiding of evaporation for homogeneous withdrawal of content
- Enrichment of light volatile components in NMR cell expected

NMR spectroscopy in condensed phase

Experimental setup for circulation



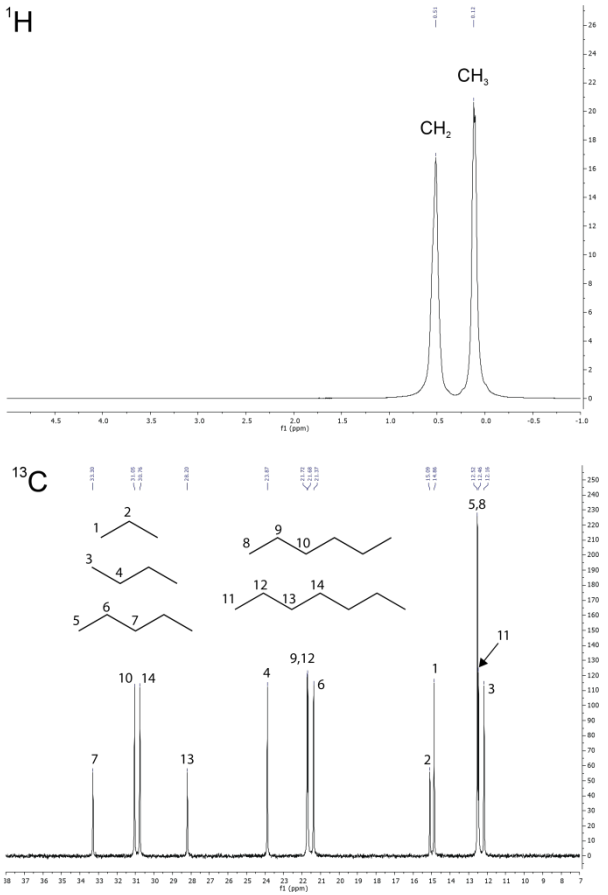


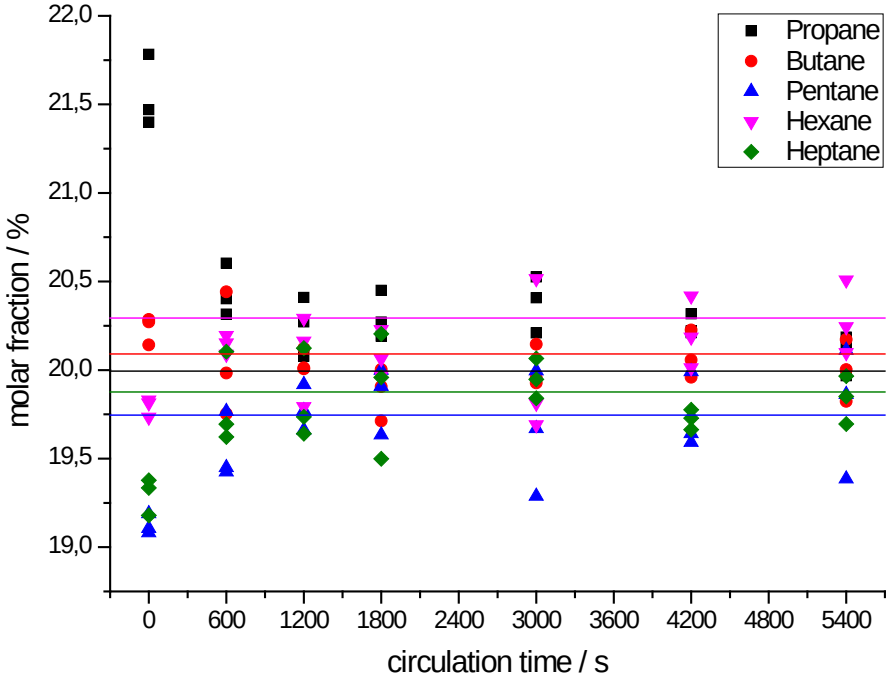
- Brazed concentric lines 1/32” in 1/8”
- Circulation of low viscosity fluids like liquefied gases
- PFA tubing in active region of spectrometer
- Currently tested up to 6 MPa (higher expected)

NMR spectroscopy in condensed phase

Results on liquefied hydrocarbons

- Commercial mixture, linear alkanes C_3 to C_7 (~20 mol-% each)



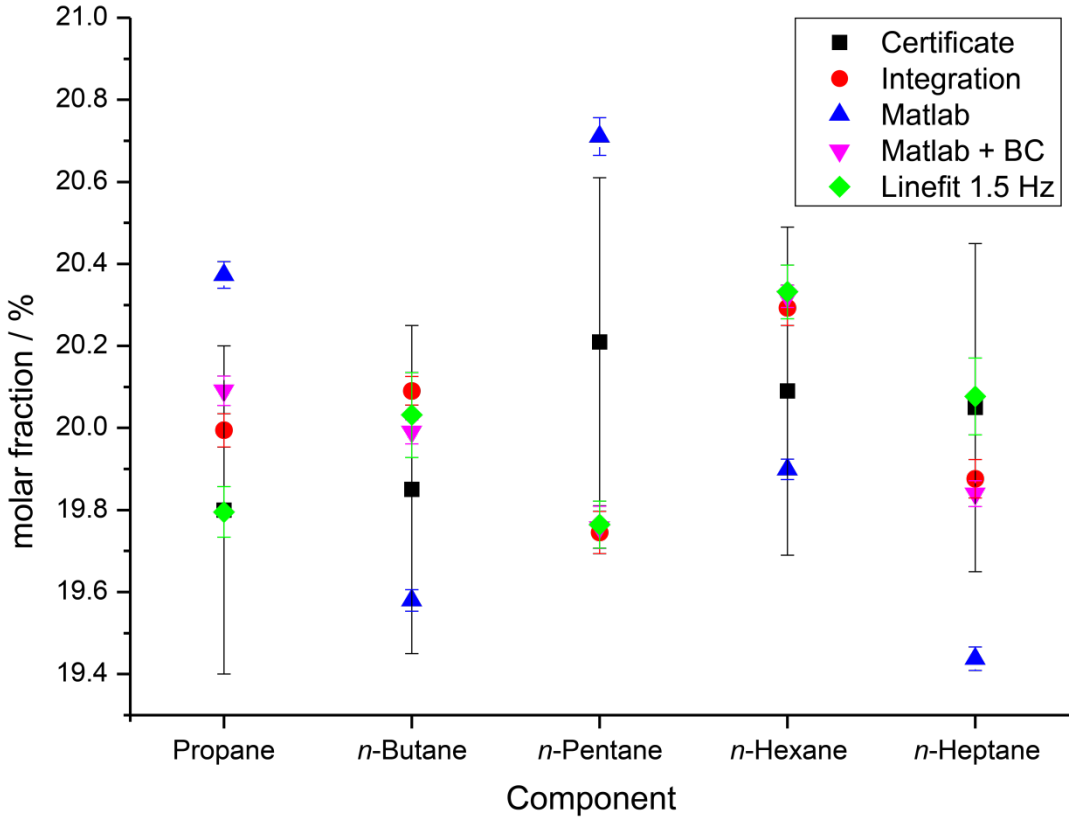


- Enrichment and Homogenization observed
- Unexpected high scatter in repeatability

NMR spectroscopy in condensed phase

Results on liquefied hydrocarbons

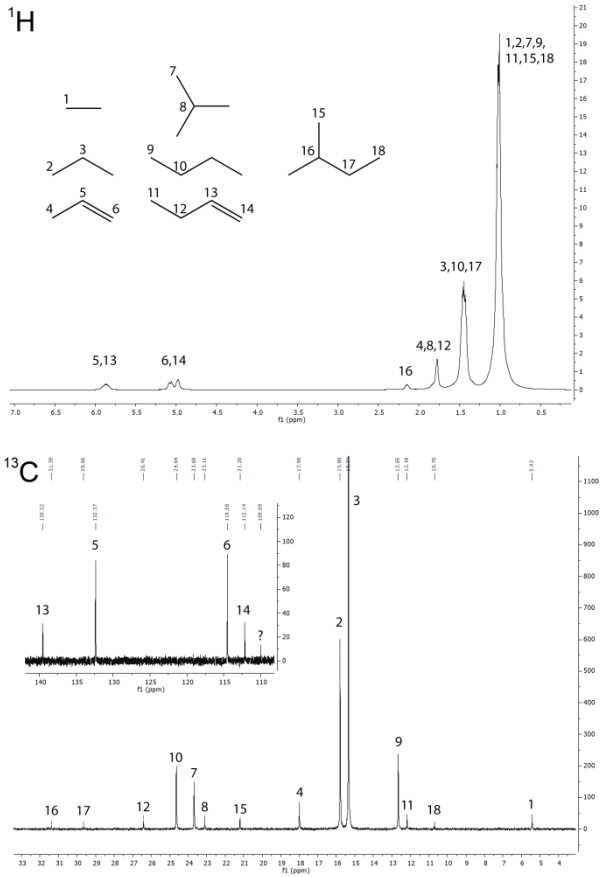
- Comparison of spectra pretreatment and evaluation methods
- Uncertainties (k=2) ~600–2000 ppm estimated based on repeatability

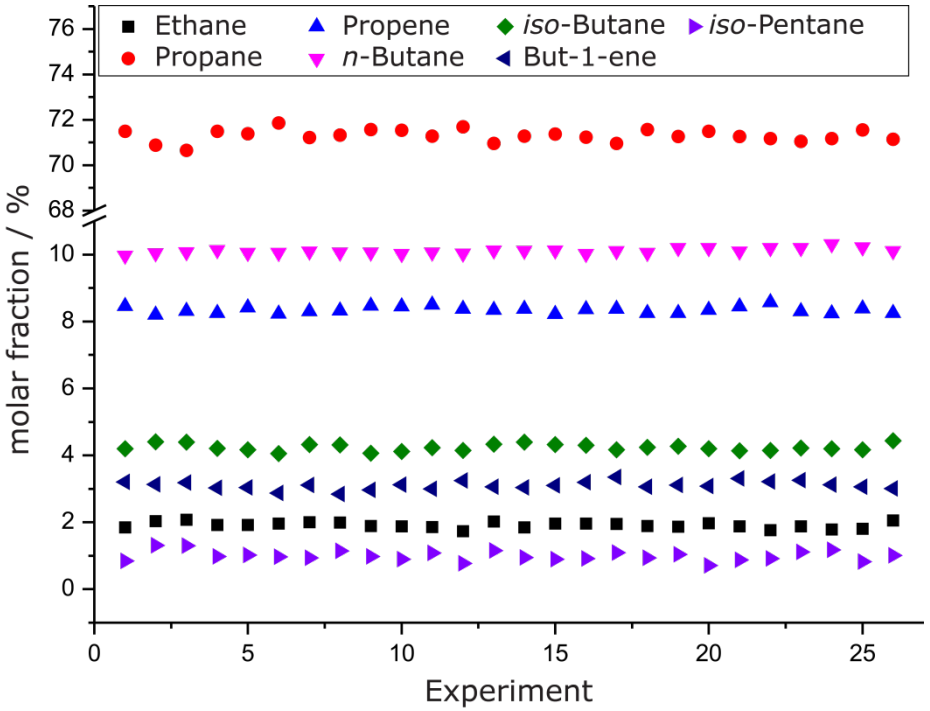


NMR spectroscopy in condensed phase

Results on liquefied hydrocarbons

- Two sample cylinders from CCQM-K119 key comparison



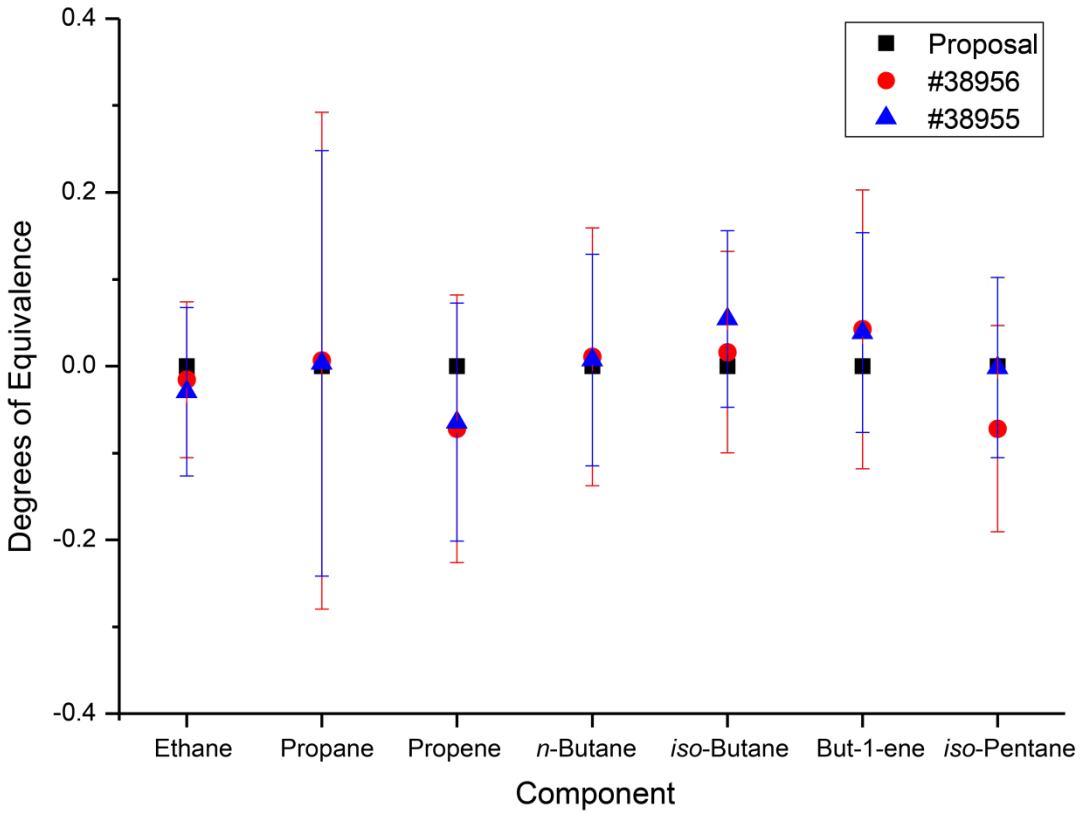


- All signals can be used for integration
- Better repeatability in static mixture

NMR spectroscopy in condensed phase

Results on liquefied hydrocarbons

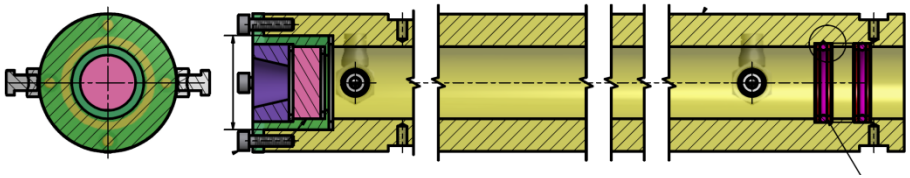
- Four samplings from cylinder with 7-10 spectra on each sample
- Uncertainties between 900 and 2800 ppm (n/n) → problem 100%-method

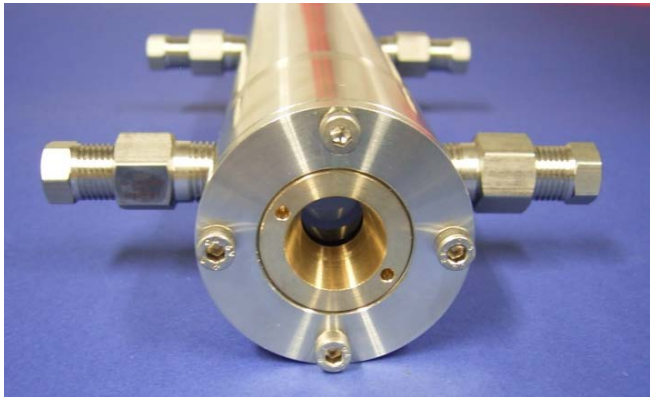


NMR spectroscopy in condensed phase

Construction of a piston cell

- Displacement element for increasing pressure of gas samples
- Measurements in expanded liquid phase and supercritical fluids
- Sapphire window for visual observation and optical methods



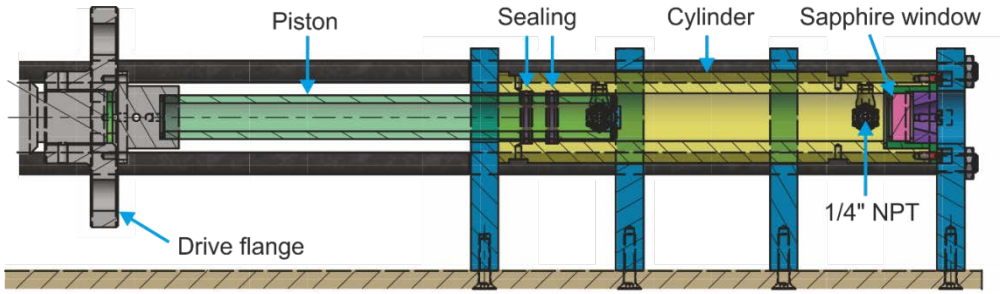


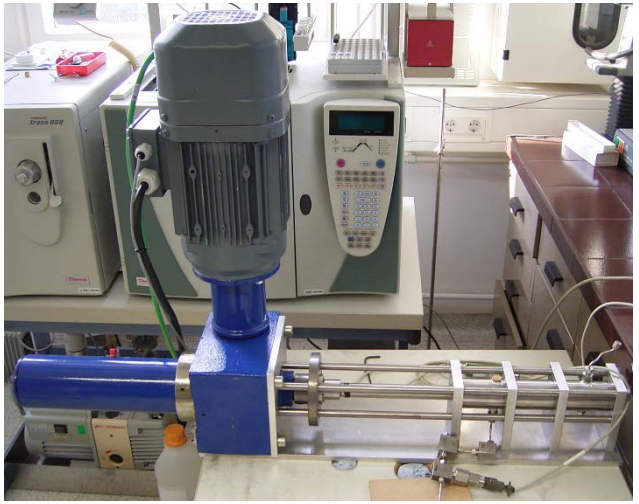
- Pressure up to 60 MPa, temperature planned up to 130 °C
- Prototype available

NMR spectroscopy in condensed phase

Construction of a piston cell

- Mounting in a reinforced frame with guide rails
- Spindle drive unit for piston movement, x = 0.25 mm / turn





- Long-term pressure tests at 60 MPa (water)
- Tests with Helium showed good pressure stability

NMR spectroscopy of technical mixtures

Summary

Purity assessment with qNMR

- Determination of impurities in raw materials for PRG production
- Identification of compounds, no prior calibration necessary

NMR in the gas phase

- High-pressure setup for gas sampling up to 20 MPa
- Long-term ^{13}C-NMR measurements on primary reference gas mixtures
- Development of accumulation procedure with drift correction

NMR in condensed phase

- Setup for studies of liquefied hydrocarbons from piston cylinders
- Investigations on test mixture and samples of CCQM-K119 comparison

Acknowledgement

Paul Brewer

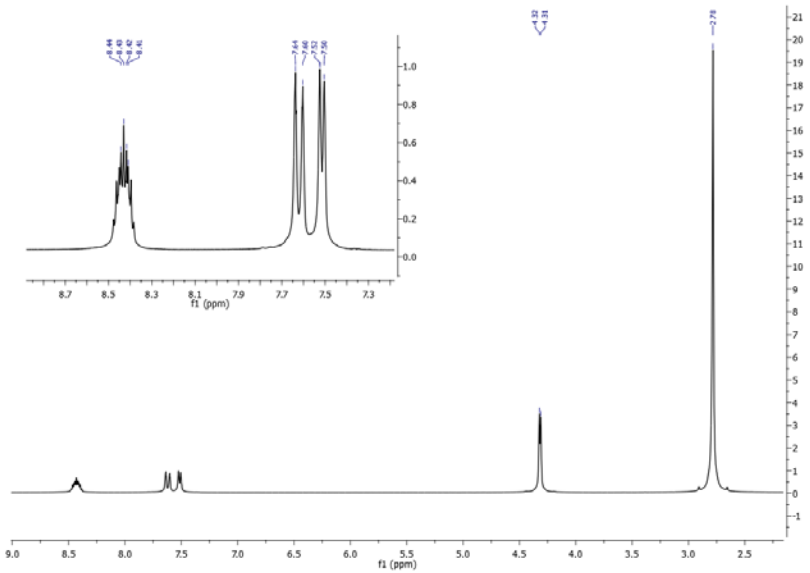
Lucy Culleton

Thank you for your attention !

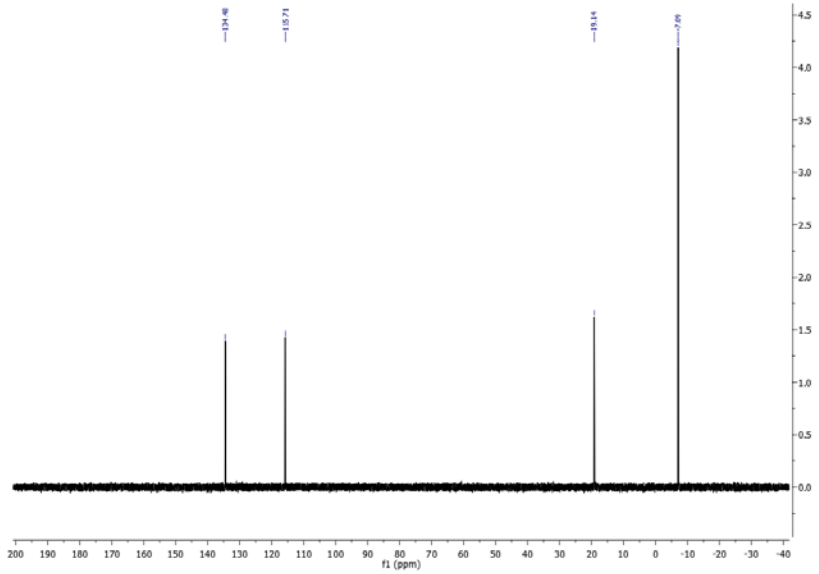
Gas-phase NMR spectroscopy

Advantages of high pressure

- mixture of Propene 3.5 and Methane 5.5
- T = 27 °C, p = 10.6 MPa



^{1}H-NMR
1 Scan ≙ 5 s



^{13}C-NMR
8 Scans ≙ 750 s

→ Significant savings in measurement time with increase of pressure