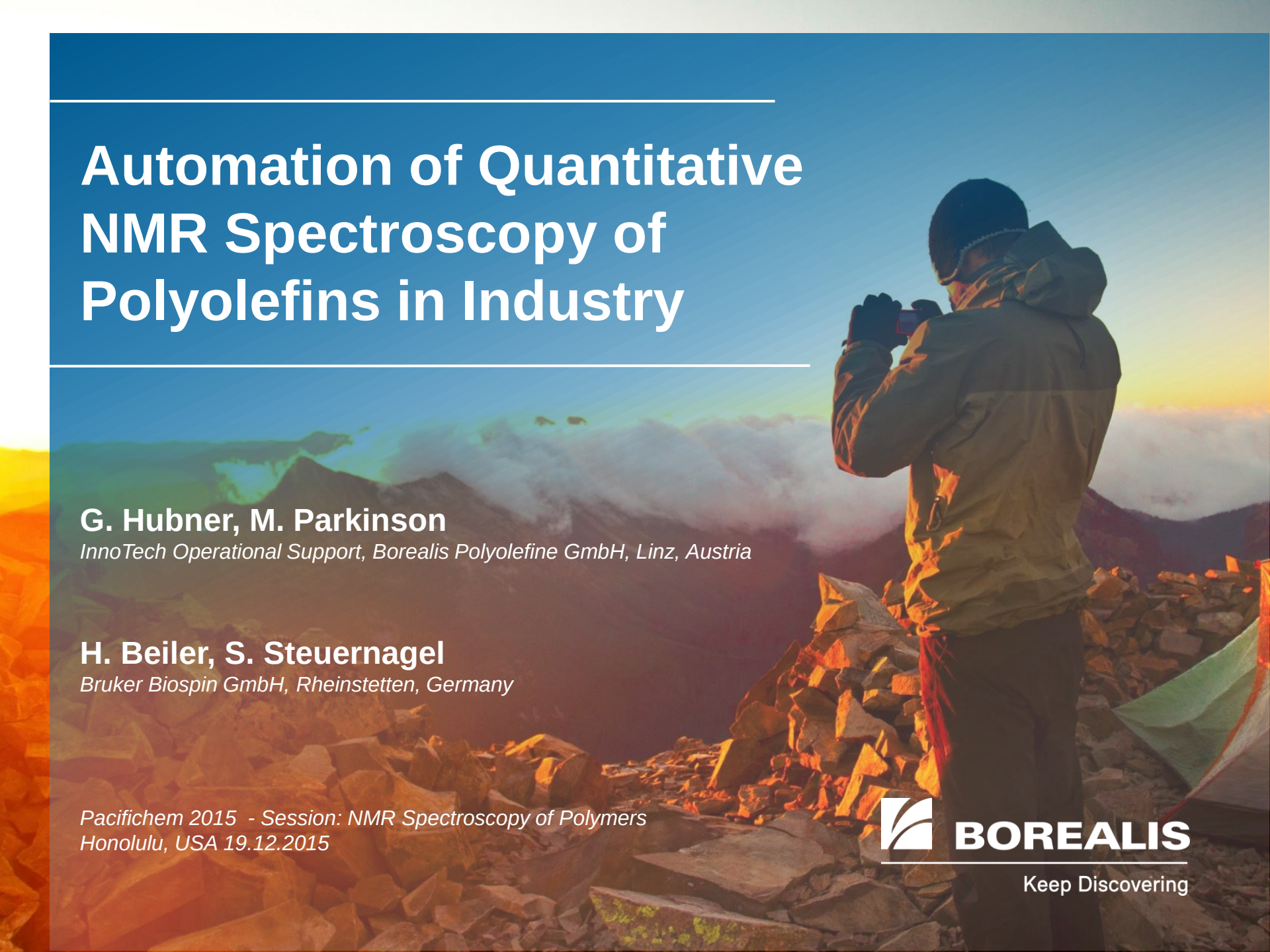
Automation of Quantitative NMR Spectroscopy of Polyolefins in Industry



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Pacifichem 2015 - Session: NMR Spectroscopy of Polymers
Honolulu, USA 19.12.2015

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Keep Discovering

Outline

- Polyolefin chain microstructure and quantitative NMR spectroscopy
- Automation of polyolefin solution-state NMR spectroscopy
  - spectral analysis
- Automation of polyolefin melt-state NMR spectroscopy
  - sample exchange
- Summary and Conclusion

Polyolefin Chain Microstructure & Quantitative NMR Spectroscopy

Polyolefin Chain Microstructure & NMR

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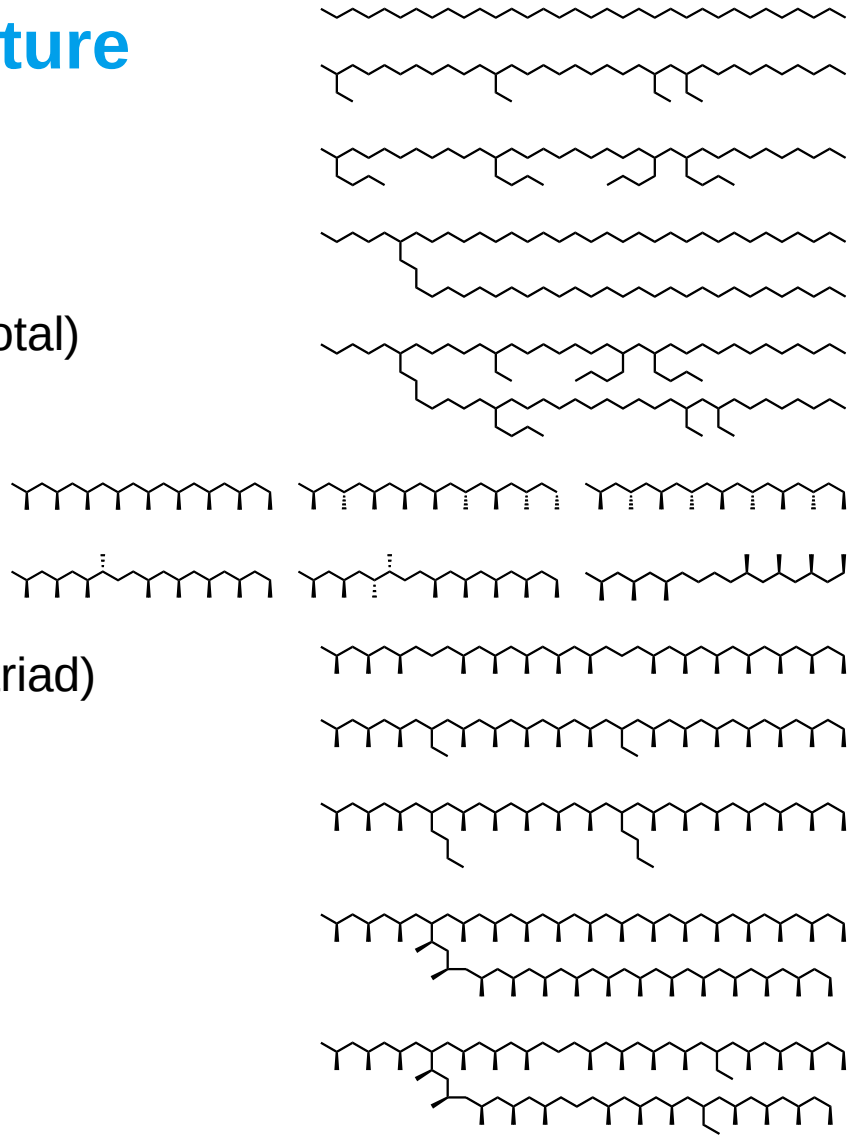
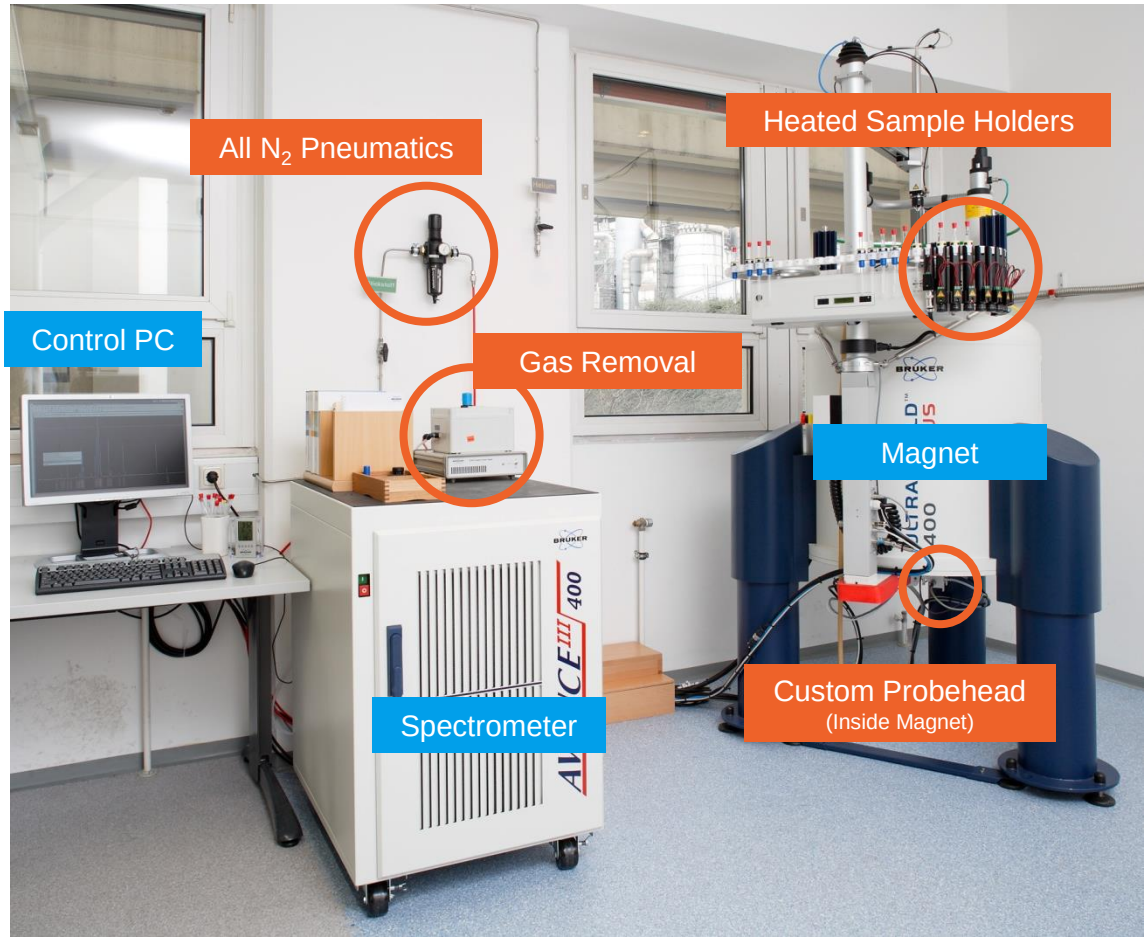
Polyolefin Chain Microstructure

- Isotacticity
- Comonomer content
- Short-chain branch distribution (kCbb, kCtotal)
- Regio-defect content (2,1e, 2,1t, 3,1 ...)
- Tacticity distribution (dyad, triad, pentad)
- Unsaturation content
- Unsaturation distribution
- Comonomer sequence distribution (dyad, triad)
- End-group distribution
- Long-chain branch content
- End-group content (Mn)
- Grafting content
- Oxidation



- All possible from a single ^{13}C NMR spectrum with no calibration (primary method)

Solution-State NMR Spectroscopy of Polyolefins



- Polyolefins: 10 mm probehead and tube, TCE-d_2, 120°C, ^{13}C detection

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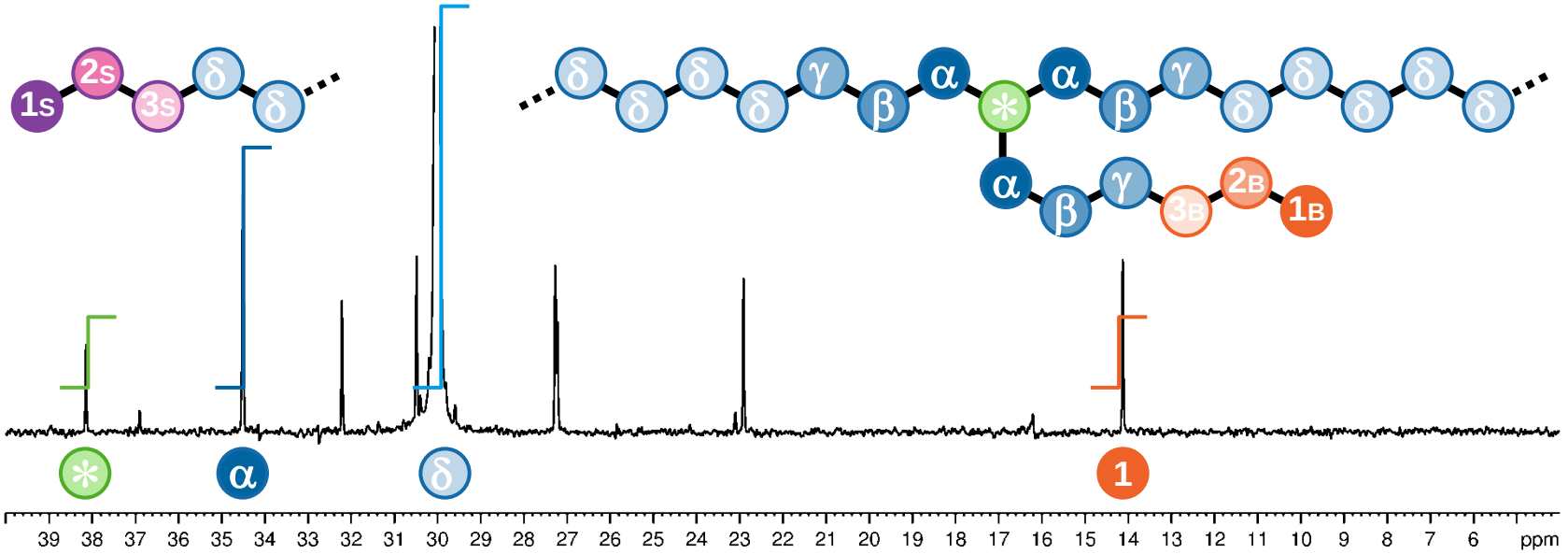
Modern Automated NMR spectroscopy

- Modern NMR spectrometers are very complicated but easy to use
  - Seriously amazing amount of automation (very high degree of abstraction)
  - Key aim of vendors: Better ease of use leads to more installations

1. Sample Track / LIMS interface
2. IconNMR / Automation interface
3. TopSpin / GUI interface — automated by macros (linear CLI)
4. Backend / API — automated by AU API (full C-program)
5. Embedded spectrometer control computer
6. Advanced timing hardware
7. Signal generation > Amplifies > Pulses > Probehead > Receiver > FID

Quantitative ^{13}C NMR Spectroscopy of Polyolefins



- Direct relative microstructure quantification from singles 1D spectrum
  - Quantitative NMR spectroscopy is easy in theory
    - Quantitative ^{13}C{^{1}H} NMR not easy in practice
    - Quantitative ^{13}C{^{1}H} NMR of polyolefins is difficult (valid)

$$\frac{*}{\delta} \qquad \frac{\frac{1}{3}\alpha}{\delta} \qquad \frac{1}{\delta}$$

- Must consider whole process of quantitative NMR

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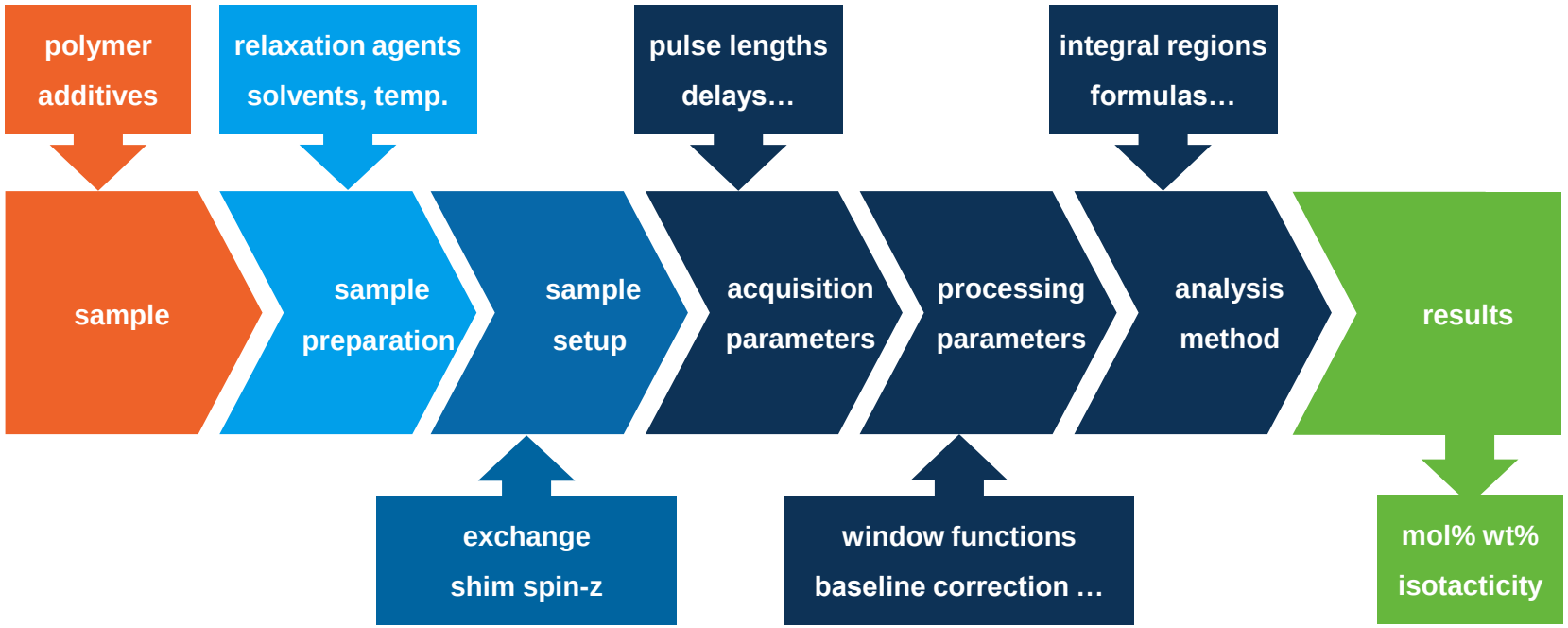
Quantitative NMR Spectroscopy Process



- Method development process works in reverse
  - fix what do we really want to know; define problem
  - how do we calculate it from a truly quantitative spectrum; implement quant method
  - asses if spectrum is quantitative by varying conditions and adjust

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Automated Solution-State NMR Spectroscopy of Polyolefins

Automated Polyolefin Solution-State NMR

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Custom Spectral Analysis: quant AU Programs

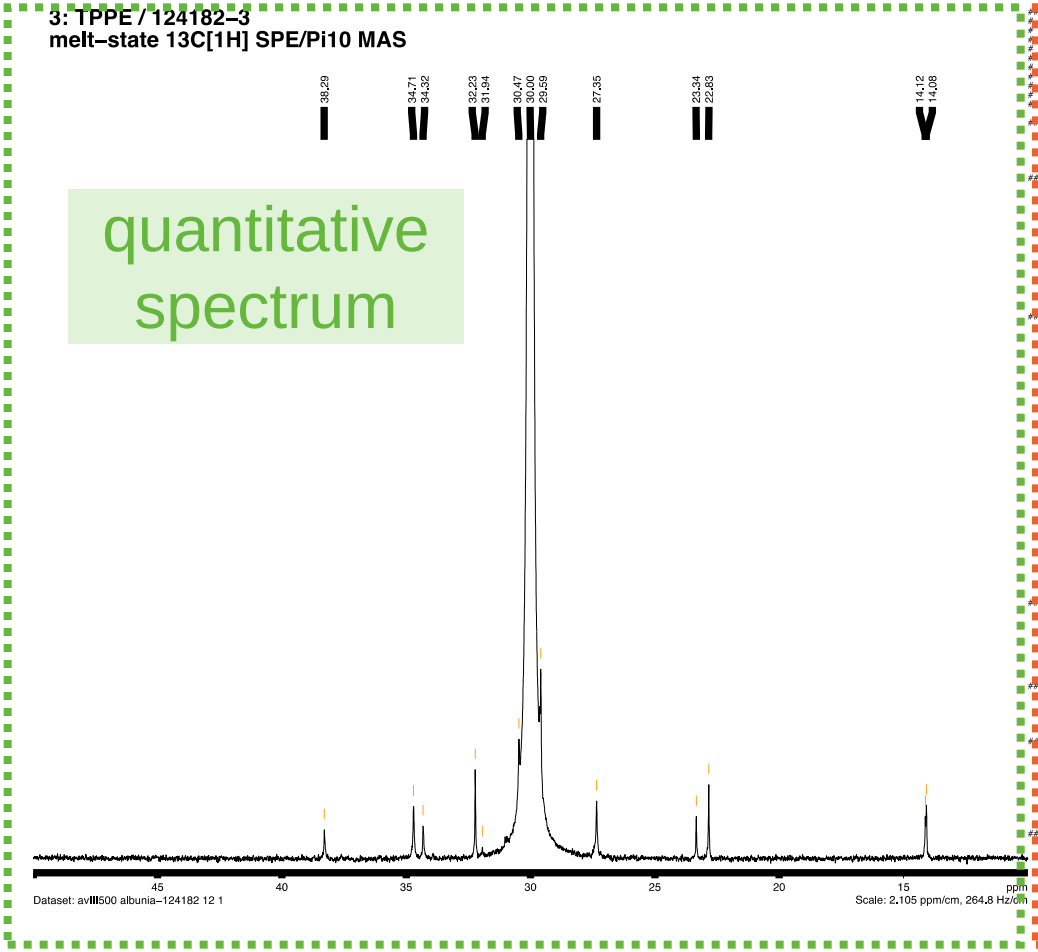
- Bruker TopSpin command line AU: quant-pb

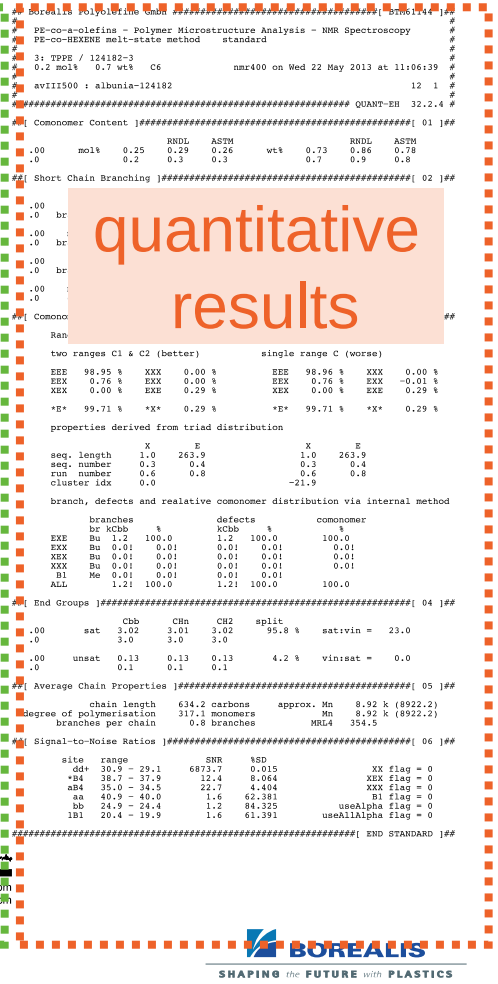
1. Pass command line flags for flow control (21e noxx noends)
2. Integrate
3. Assign representative integrals/do compensation
4. Calculates primary microstructure quantities (contents, distributions)
5. Calculated secondary microstructure quantities (statistics)
6. Stochastic fitting (linear, non-linear)
7. Report in various formats (screen, PDF, CSV, TXT, LIMS)

- Multiple methods (literature regions/equations, custom in-house)
  - quant-ep-83 currently determines ethylene content in 26 different ways per spectrum

- Approximately 2500 line of code in C
  - readability more important than optimisation

Reporting: quant-eh-32 PDF





- Topspin > processpe; quant-eb xx xex; pdf quant; catcsv

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Reporting: quant-eh-32

```
##[ Comonomer Content ]#################################################[ 01 ]##

                            RNDL     ASTM                          RNDL     ASTM
  .00       mol%     0.25    0.29     0.26       wt%     0.73     0.86     0.78
  .0                 0.2     0.3      0.3                0.7      0.9      0.8
```

comonomer content

```
##[ Short Chain Branching ]#############################################[ 02 ]##

                    Cbb      CHn      CH2                            RNDL     ASTM
  .00      butyl    1.23     1.22     1.23 mol%C6 -> brB4/Cbb        1.45     1.30
  .0    branches    1.2      1.2      1.2                            1.4      1.3

  .00     methyl    0.00!    0.00!    0.00!
  .0    branches    0.0!     0.0!     0.0!

  .00      total    1.23     1.22     1.23
  .0    branches    1.2      1.2      1.2   sum butyl and methyl branches

  .00     methyl    4.25     4.23     4.26
  .0      groups    4.3      4.2      4.3   all per defined 1000 carbon atoms
```

SCB content

Reporting: quant-eh-32

```
##[ Comonomer Distribution ]#############################################[ 03 ]##

   Randall89a triad method for systems with > 3 mol% copolymer

   two ranges C1 & C2 (better)            single range C (worse)

   EEE    98.95 %     XXX     0.00 %        EEE    98.96 %     XXX     0.00 %
   EEX     0.76 %     EXX     0.00 %        EEX     0.76 %     EXX    -0.01 %
   XEX     0.00 %     EXE     0.29 %        XEX     0.00 %     EXE     0.29 %

   *E*    99.71 %     *X*     0.29 %        *E*    99.71 %     *X*     0.29 %
```

triad comonomer distribution

```
   properties derived from triad distribution

                      X         E                    X         E
   seq. length      1.0     263.9                  1.0     263.9
   seq. number      0.3       0.4                  0.3       0.4
   run  number      0.6       0.8                  0.6       0.8
   cluster idx      0.0                          -21.9
```

triad derived properties

```
   branch, defects and realative comonomer distribution via internal method

          branches                 defects              comonomer
          br kCbb      %           kCbb      %             %
   EXE    Bu  1.2    100.0         1.2    100.0          100.0
   EXX    Bu  0.0!     0.0!        0.0!     0.0!           0.0!
   XEX    Bu  0.0!     0.0!        0.0!     0.0!           0.0!
   XXX    Bu  0.0!     0.0!        0.0!     0.0!           0.0!
    B1    Me  0.0!     0.0!        0.0!     0.0!
   ALL        1.2!   100.0         1.2!   100.0          100.0
```

defect distribution

Reporting: quant-eh-32

```
##[ End Groups ]#############################################################[ 04 ]##

                    Cbb       CHn      CH2     split
 .00        sat    3.02      3.01     3.02       95.8 %     sat:vin =    23.0
 .0                3.0       3.0      3.0

 .00      unsat    0.13      0.13     0.13        4.2 %     vin:sat =     0.0
 .0                0.1       0.1      0.1

##[ Average Chain Properties ]#######################################[ 05 ]##

            chain length     634.2 carbons      approx. Mn     8.92 k (8922.2)
degree of polymerisation     317.1 monomers             Mn     8.92 k (8922.2)
      branches per chain       0.8 branches          MRL4    354.5

##[ Signal-to-Noise Ratios ]#################################################[ 06 ]##

       site    range                SNR      %SD
         dd+   30.9 - 29.1      6873.7     0.015                  XX flag = 0
        *B4    38.7 - 37.9        12.4     8.064                 XEX flag = 0
        aB4    35.0 - 34.5        22.7     4.404                 XXX flag = 0
         aa    40.9 - 40.0         1.6    62.381                  B1 flag = 0
         bb    24.9 - 24.4         1.2    84.325            useAlpha flag = 0
        1B1    20.4 - 19.9         1.6    61.391         useAllAlpha flag = 0
```

end groups

average chain properties

SNR & runtime flags

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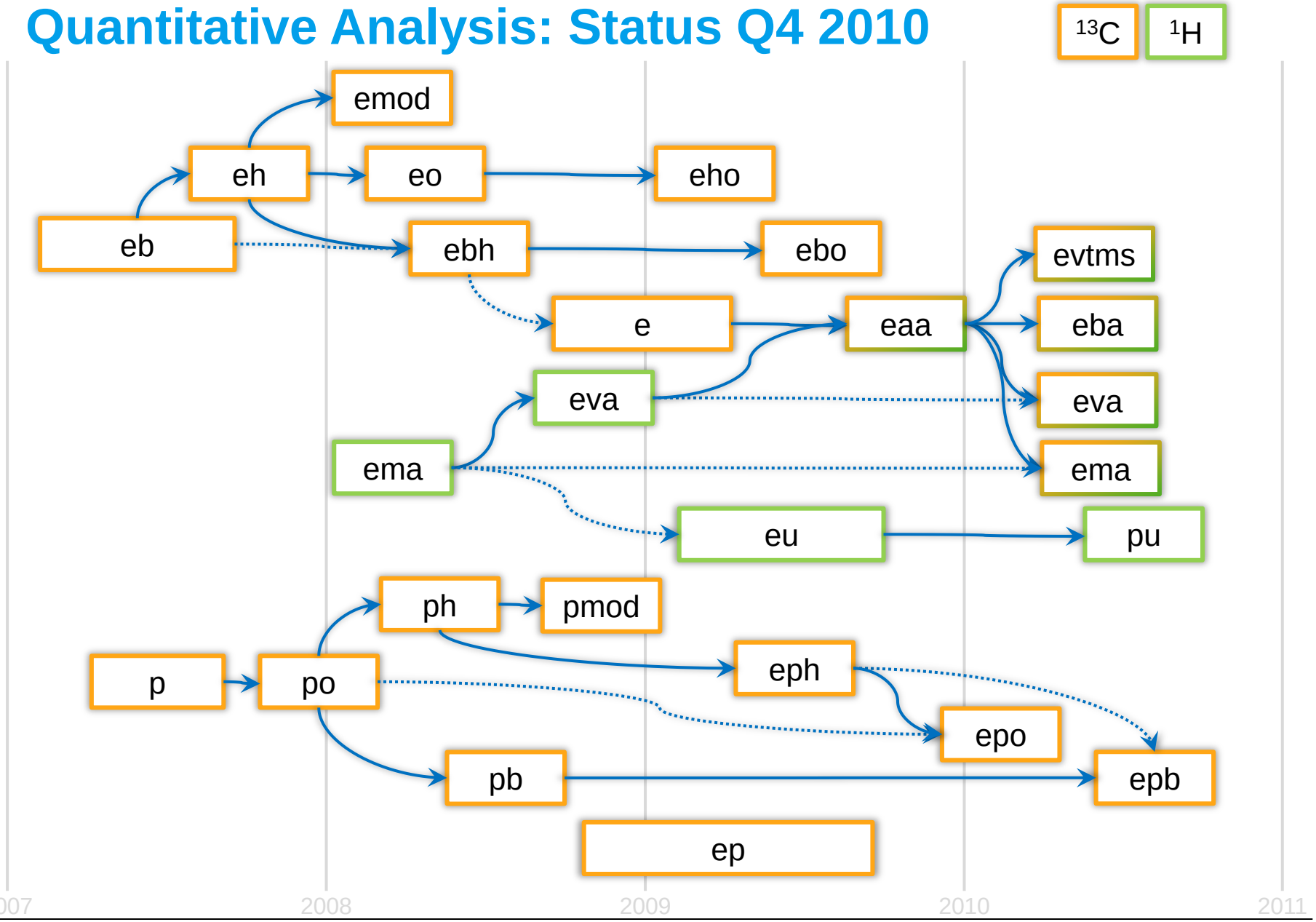
Quantitative Analysis: Status Q4 2010



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Automated Melt-State NMR Spectroscopy of Polyolefins

Automated Polyolefin Melt-State NMR

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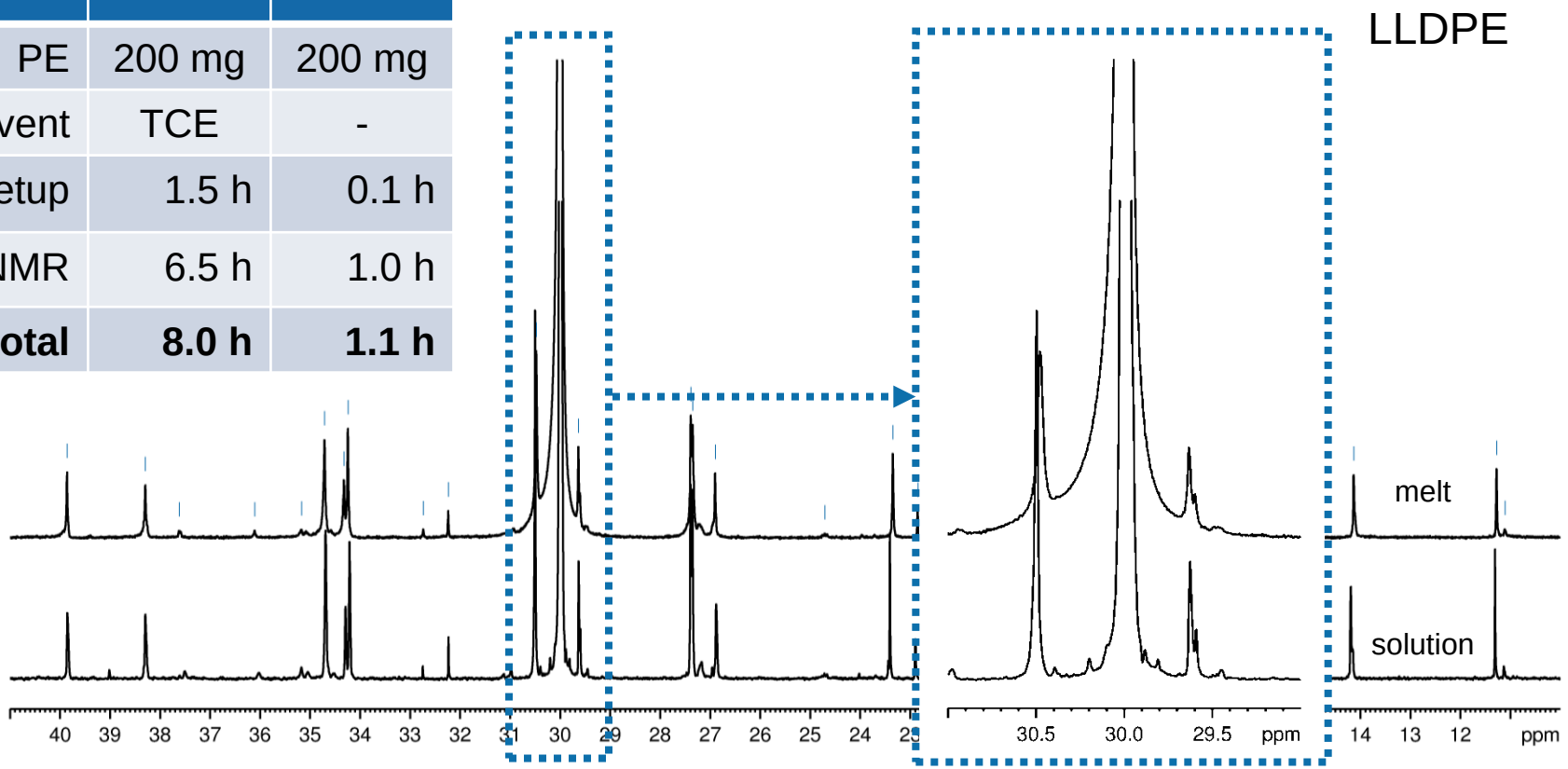
Melt-state MAS Vs Solution-State NMR Spectra

	solution	melt
PE	200 mg	200 mg
solvent	TCE	-
setup	1.5 h	0.1 h
NMR	6.5 h	1.0 h
total	**8.0 h**	**1.1 h**



- Non standard technique based on solid-state NMR spectroscopy method
  - Compromise between sensitivity (higher) and resolution (lower)
  - Key technique is Magic-Angle Spinning (MAS)

M. Parkinson, et al. ACS Symp. **2011**, 1077, 24, 401

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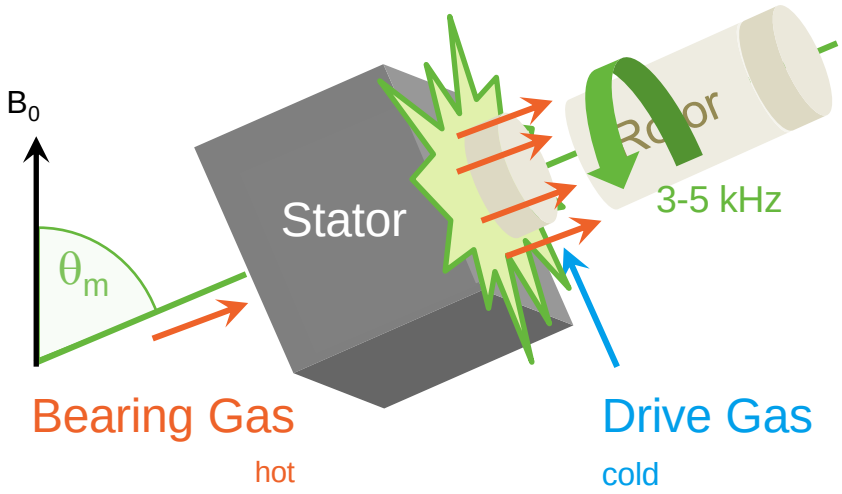
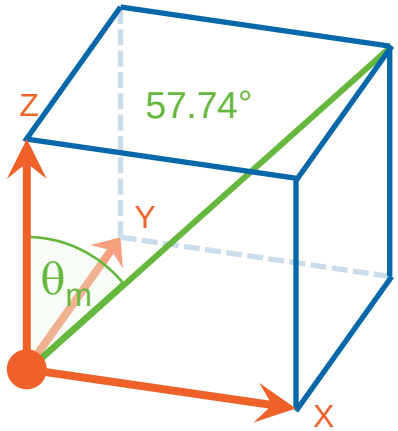
Melt-state Magic-Angle Spinning (MAS) stator



- Standard: solid-state NMR
  - Place bulk sample in 7 mm zirconia ceramic rotor
  - Seal using a ceramic cap with find (turbine)
  - Levitate on high-pressure gas bearing inside stator
  - Drive rotation to 4 kHz with high-pressure gas
- Non-standard: melt-state NMR
  - Melt-the sample 150-180°C
  - Keep sample in rotor while under MAS
    - complex, high risk = expensive (9 kEUR)



G. Hatfield, et al. Anal. Chem. **1995**, 67, 3082
K. Klimke, **2006** Ph.D. Thesis, University of Mainz, Germany
M. Pollard, et al. Macromolecules **2004**, 37, 813
K. Klimke, et al. Macromol. Chem. Phys. **2006**, 207, 382
M. Parkinson, et al. ACS Symp. **2011**, 1077, 24, 401

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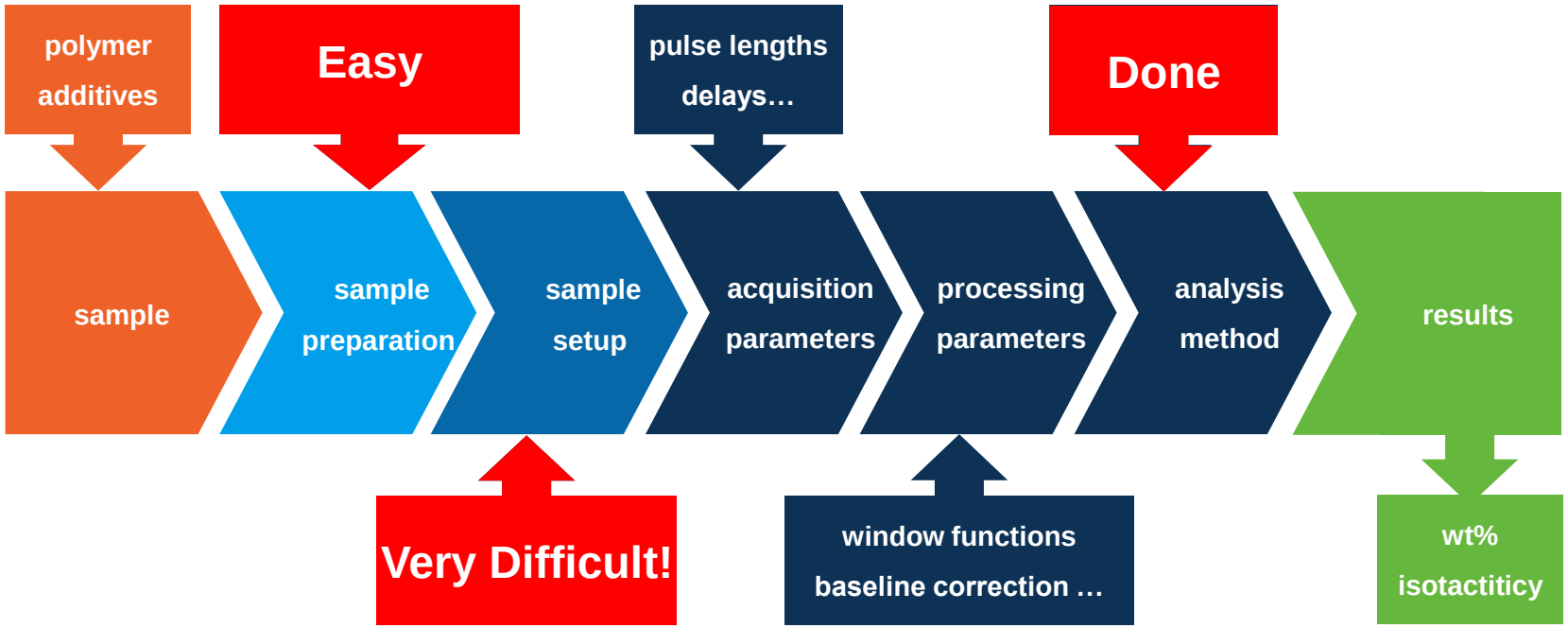
Quantitative Melt-State NMR Spectroscopy Process



- In the world of solid-state NMR spectroscopy
  - 7 mm rotor packing is difficult (symmetric weight distribution) but in melt no issue!
  - MAS spin-up automated but not stable for melt-state (crash)
  - sample exchange very rarely automated (long experiments, different setup needed)

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Major Challenges of Automating Melt-State MAS NMR

- Automated melt-state sample exchange: roadblock!
  - Very difficult: 2 years
- Automatic melt-state MAS Spin-up: roadblock!
  - Medium difficulty: 6 months
- Automatic tune/match (ATM) MAS probehead
  - Medium difficulty: 3 days (validated compromise)
- Automatic spectral analysis (Don’t measure what you can’t analysis)
  - Easy as already done! 1 day
- All solution also applicable to true solid-state NMR spectroscopy!

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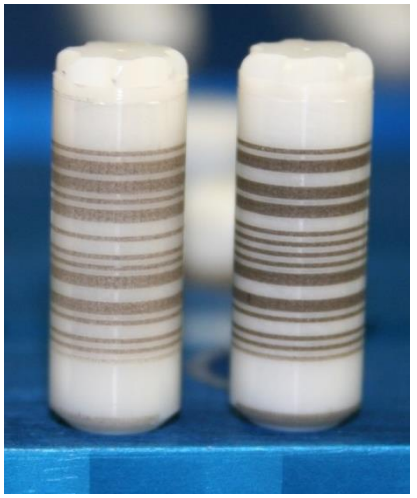
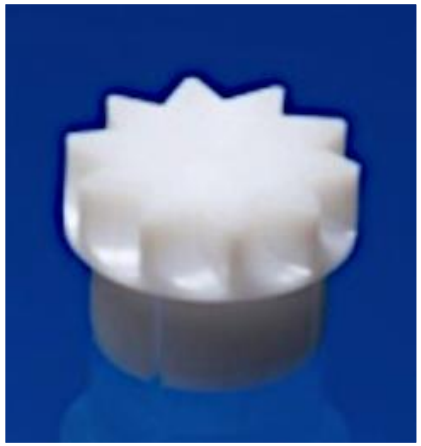
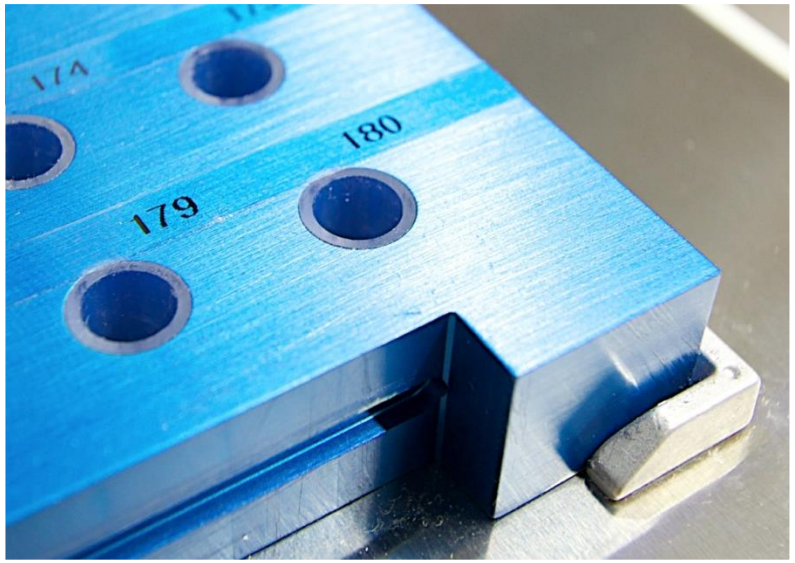
Automated Melt-State Sample Exchange

- Is there a current commercial solution available from Bruker Biospin?
  - 180 position sample changer for 7 mm MAS rotors capable of handling 180°C rotors
  - No: and was too complicated for in-house or automation specialist (ask vendor!)
- Can Bruker Biospin custom build hardware development
  - No: No market, non-standard setup, high-risk, little return on invested time/money (business)
  - However, did have large capacity changer for 4 mm MAS rotors designed for < 0°C!
    - Significant modification needed
  - True collaboration with Bruker co-hardware development with open knowledge sharing
  - Bruker agreed to modify hardware for 7 mm (no liability, very special SAT)
  - Borealis agreed to handle all hot/heavy rotor modifications and melt-MAS spin-up
- Why did vendor proceed?
  - We had the technical competence
  - Realistic expectations: we thought it might not work either!

Bruker Custom 7 mm SamplePro: Trays







- NOTE: rotors are **not pre-heated** and **not store hot**, just returned hot after measurement

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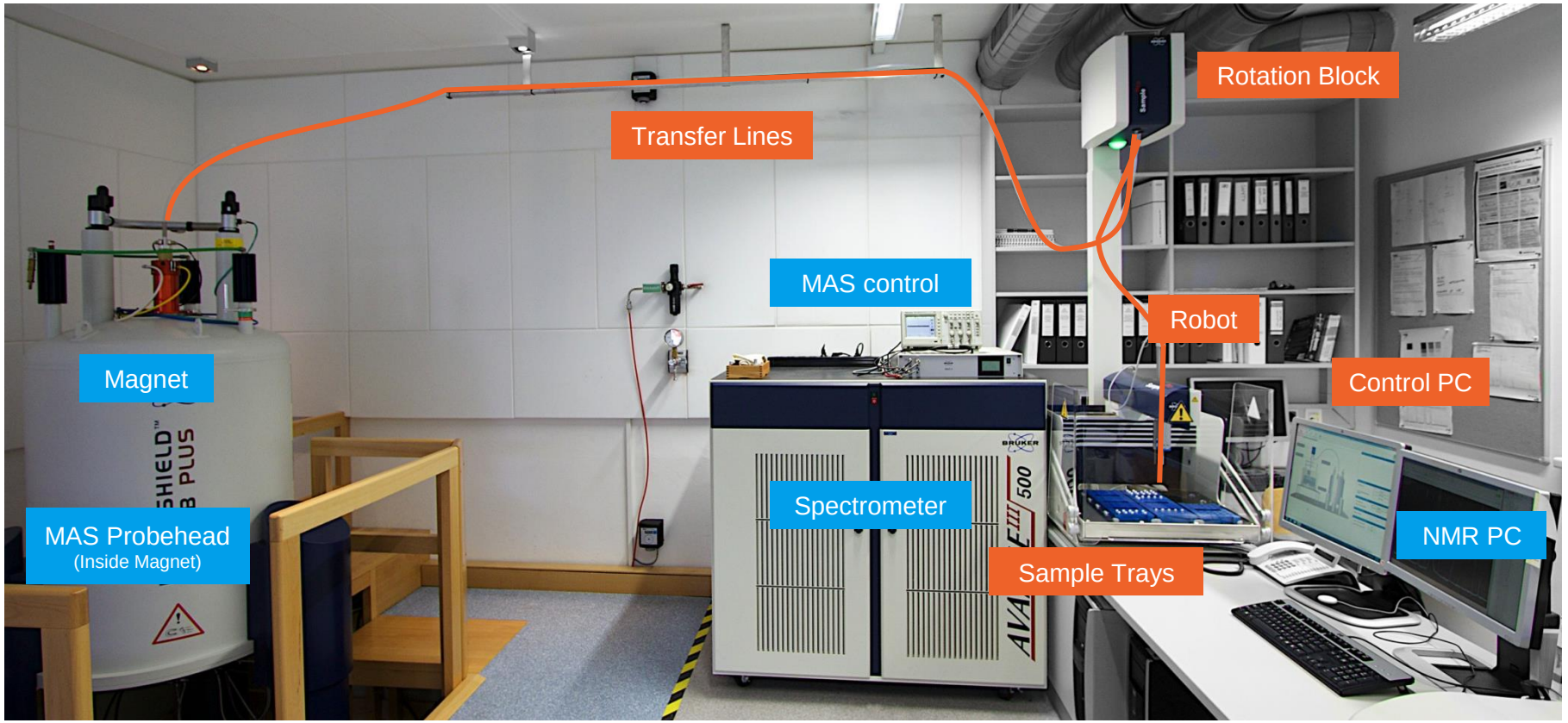
Bruker Custom 7 mm SamplePro: Overview



- In theory is simple, we just blow the rotor down plastic tube
- In practice very difficult to get to work

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Summary & Conclusions

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Automated Polyolefin NMR Spectroscopy: Positive

- Automated spectral analysis for quantitative polyolefin NMR (solution & melt-state)
  - Higher quality
    - Very high repeatability (most recent melt-state method had a CV 0.1%!)
    - Removal of user dependent results (no more manual phasing/baseline/integral bias)
    - Full version control of programs QM/QA compliant (continuous improvement)
  - Rapid method development via automated analysis (1-2 weeks with LIMS)
    - Directly comparable method (same logic) e.g. EB, EH, EBH
- Automated melt-state NMR
  - Higher throughput (20+ to 160 quantitative ^{13}C spectra/week @ same quality)
    - Faster delivery of project goals, new opportunities, all bench scale samples
    - all high-throughput Multi Modal Reactor (MMR) samples via ^{13}C (8x20 min = 3 hr / day)
  - Higher efficiency/hardware utilisation (60% to 96%)
    - NMR spectrometers need to run 24/7/365 to break-even

Automated Polyolefin NMR Spectroscopy: Negative

- Time: all automation was done in parallel to our daily work!
- Higher overhead!
  - More time is spent keeping devices working now combined with less time to think
- Rapid backlog generation
  - When things break-down sample stack up very quickly
- Forget the complexity
  - *Requestors:* get accustomed to high-quality rapid feedback
    unrealistic expectations regarding method development
  - *Laboratory:* over time you forget how your automation works (comment the code!)
    miss small things (need checklists)
  - *Specialists:* underestimate work between proof-of-concept and implementation!

Summary

- Implemented advanced automation for both solution-state and non-standard melt-state NMR spectroscopy of polyolefins
- Implemented modular system for automated polyolefin NMR spectral analysis
- Successfully automated non-standard melt-state MAS NMR technique
  - reached potential through full automation (long journey)
- Only possible with strong open vendor interaction
  - Custom hardware sample exchanger co-development (Bruker BioSpin IP)
  - Custom software melt-state MAS spin-up process (Borealis IP)

Acknowledgments

- InnoTech Operational Support (IOS) Management
  - Jochen Berrens, Jens Reussner

... the money & faith

- Bruker Biospin Solid-State NMR/automation
  - Steffan Steuernagel, Heiko Beiler, Jens Abromeit
    Michael Engelhardt, Rudolf Schöps

... the trust

- IOS NMR group
  - Gerhard Hubner, Lisa Steiner, Elena Pomakhina

... the hard work

- Polyolefin R&D groups
  - SPPR-PP, SPPR-PE, SPPR-HPPE, POLY, CAT-D, CAT-P

... the samples

Thank you

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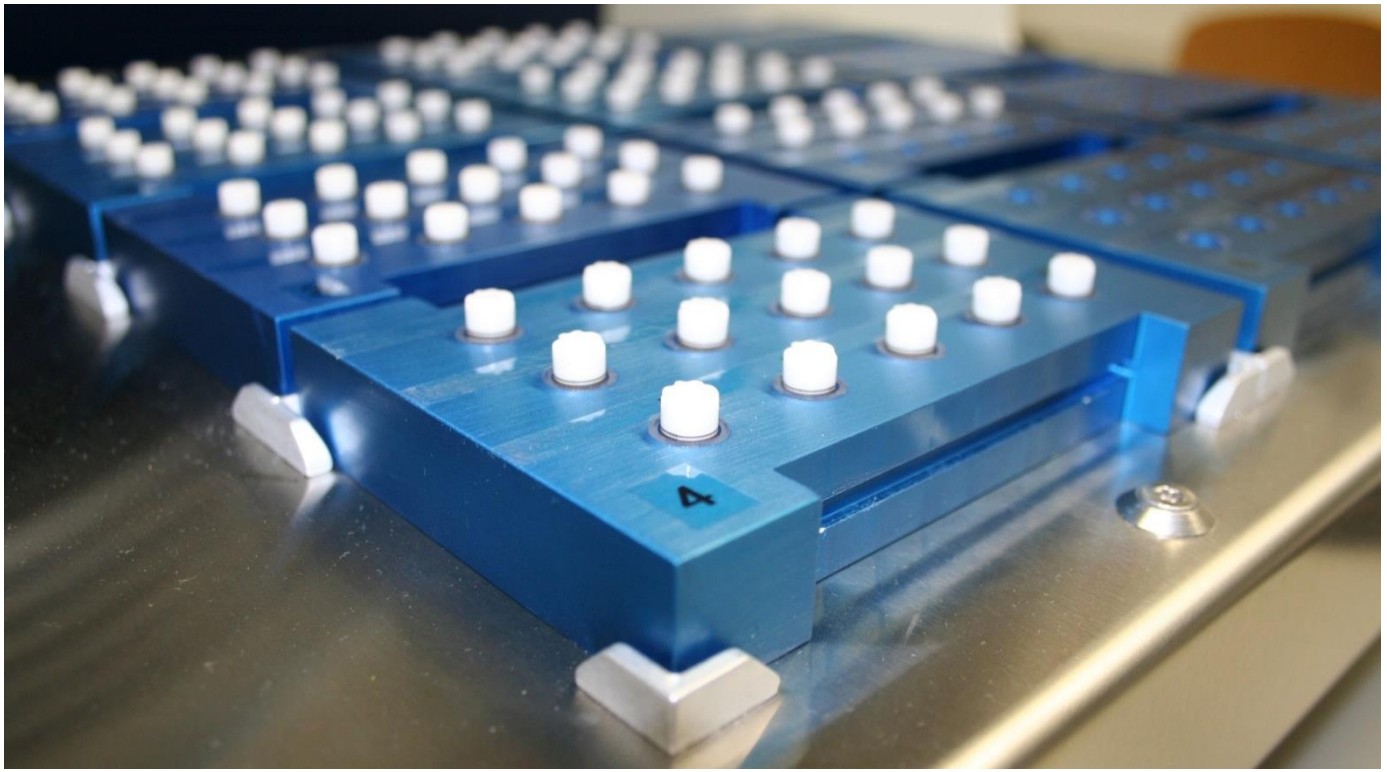
NMR Automation Humor

Q: What's worse than asking your management for money to automate a device?

A: Asking for four times that amount one year later just for sample containers to run the device at capacity!



7 mm zirconia MAS rotor/cap set = 1 kEUR each

Future Perspectives: Standardisation

- Standardisation of polyolefin quantification by ^{13}C NMR
  - currently no robust or universal standards (technically complex)
  - disconcerting when you consider how important tacticity of iPP is!

- Standardisation is in the interest of both industry and academia:
  - for Industry it would allows direct comparison for IPR/patent issues
  - for academia ensures repeatability/trust within academia and industry

- Technically and politically complex
  - need to standardise whole process on expensive heterogeneous equipment i.e. sample prep > measurement > processing> analysis > reporting
  - Sharing of proprietary knowledge/know-how from industry is complicated