



The (q)NMR-Cocktail

A recipe for Lithium-ion-battery analysis focusing the recycling process

„Why NMR, why this topic?“

The NMR cocktail allows a comprehensive look into the battery samples.

In routine analysis, ^1H -NMR and ^{13}C -NMR spectra are the most widely used, e.g. to easily quantify the purity and mixing ratio of the solvents in the liquid electrolytes with a measurement <5min using ^1H -qNMR. However, analysis is not limited to these two nuclei [1].

Especially for lithium-ion battery research, NMR-active nuclei such as ^7Li , ^{19}F and ^{31}P are of great interest to gain a comprehensive picture of the sample [1,2]. Therefore, lithium salts like LiPF_6 is to be investigated with the “NMR cocktail” of measurements using ^1H -, ^7Li -, ^{13}C -, ^{19}F - and ^{31}P -NMR to get the full qualitative and quantitative picture.

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ELECTROLYTE:

lithium salt e.g. LiPF_6 , LiClO_4 , LiBF_4

organic solvent e.g. ethylene carbonate, dimethyl carbonate, diethyl carbonat

POLYMER BINDER: Polyvinylidene fluoride (PVDF)

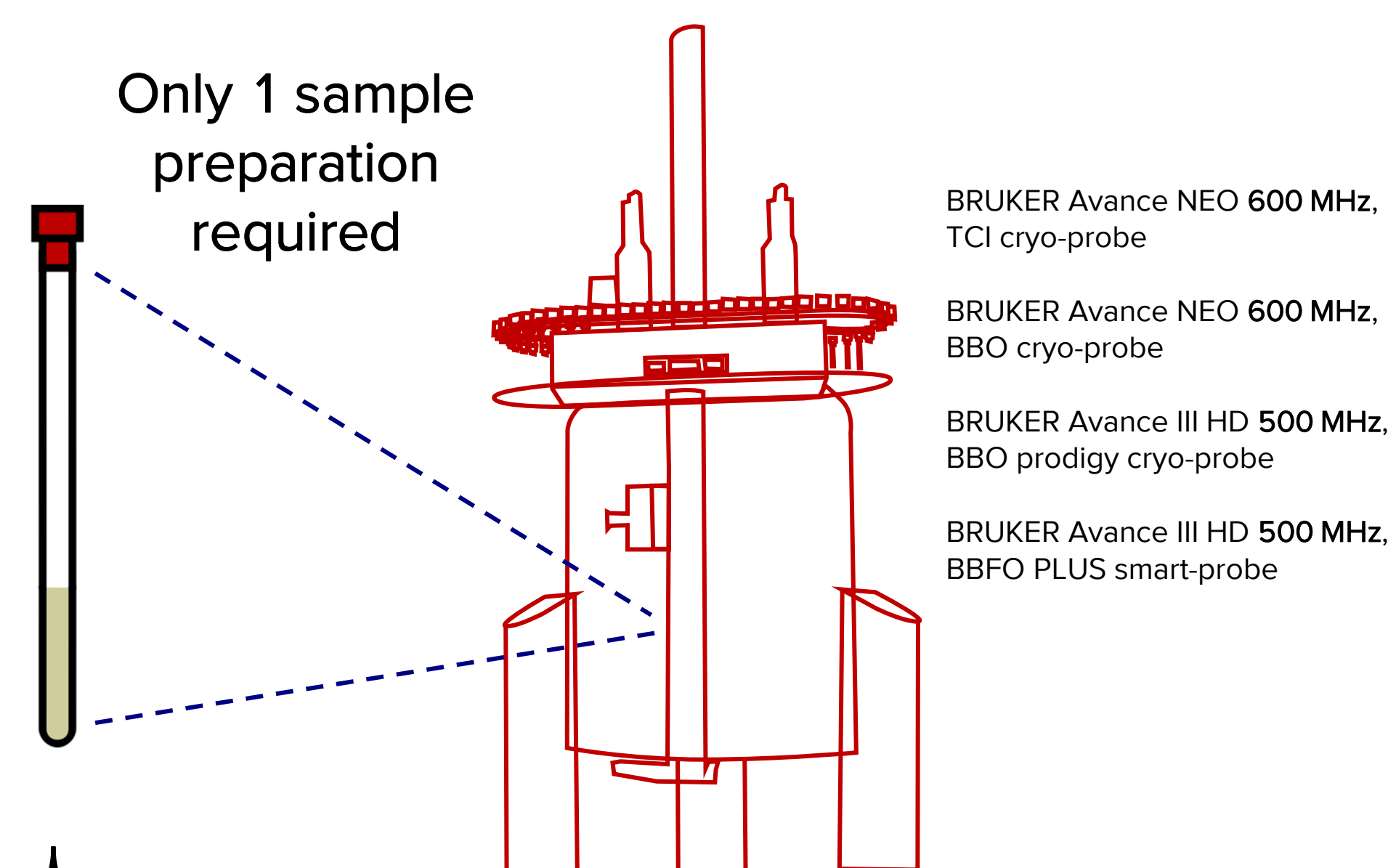
POLYMER FOIL: Polypropylene (PP), Peolyethylene (PE)

News in ^7Li -NMR

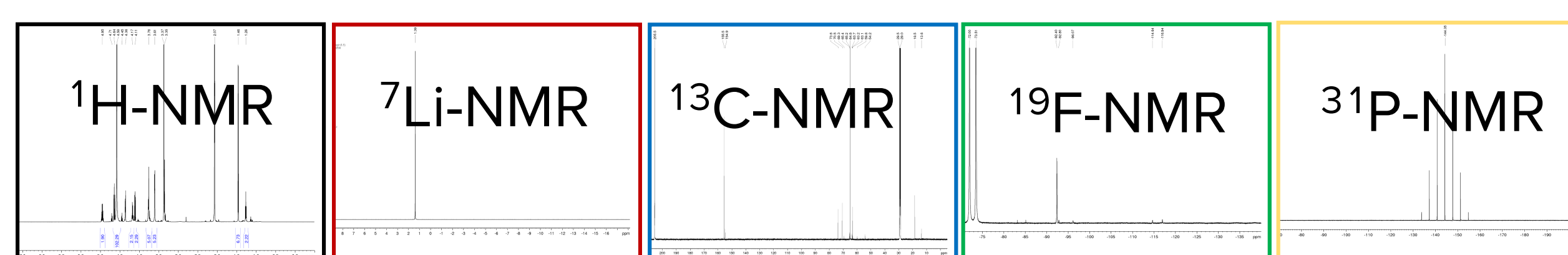
For determining the limit of detection (LOD) of $^7\text{Li}^+$ ions using NMR, a 5-point calibration of LiCl in D_2O was performed (SNR 3:1, on a 500 MHz spectrometer) and a LOD=0.44 ppm calculated (Fig 2).

Since ^7Li -NMR spectroscopy is a quantitative elemental analysis, this value can serve as an estimation for other Li-compounds such as LiPF_6 .

The absolute quantification of LiPF_6 is usually done by ^{19}F -qNMR spectroscopy, however we are working on the quantification of the total Lithium content in the sample using ^7Li -qNMR.



(Multi) NMR spectroscopy

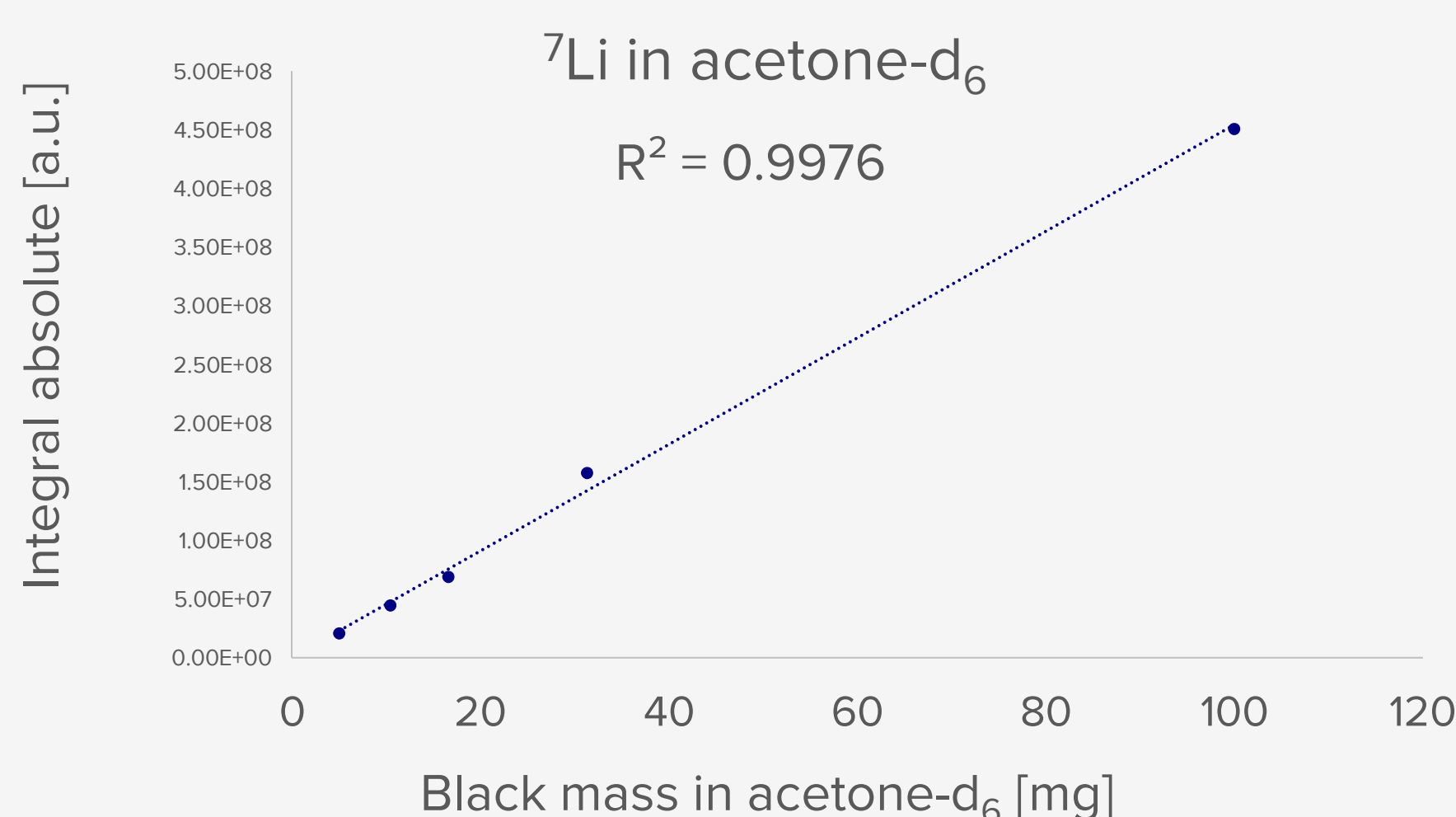


black mass
(5-100 mg) in 1.5 mL
acetone- d_6 + IS

30 sec
vortex

10 min
ultrasonic

centrifuge



	LOQ (SNR 10:1)
EC	0.45 μg
DMC	0.55 μg
PC	10.0 μg
EMC	4.0 μg
LiPF_6	4.1 μg
Li^+	1.5 μg

Figure 2: sample preparation procedure; 5-point-calibration curve of extraction of black mass in acetone- d_6 depending on the sample weight (5mg, 10mg, 15mg, 30mg, 100mg)

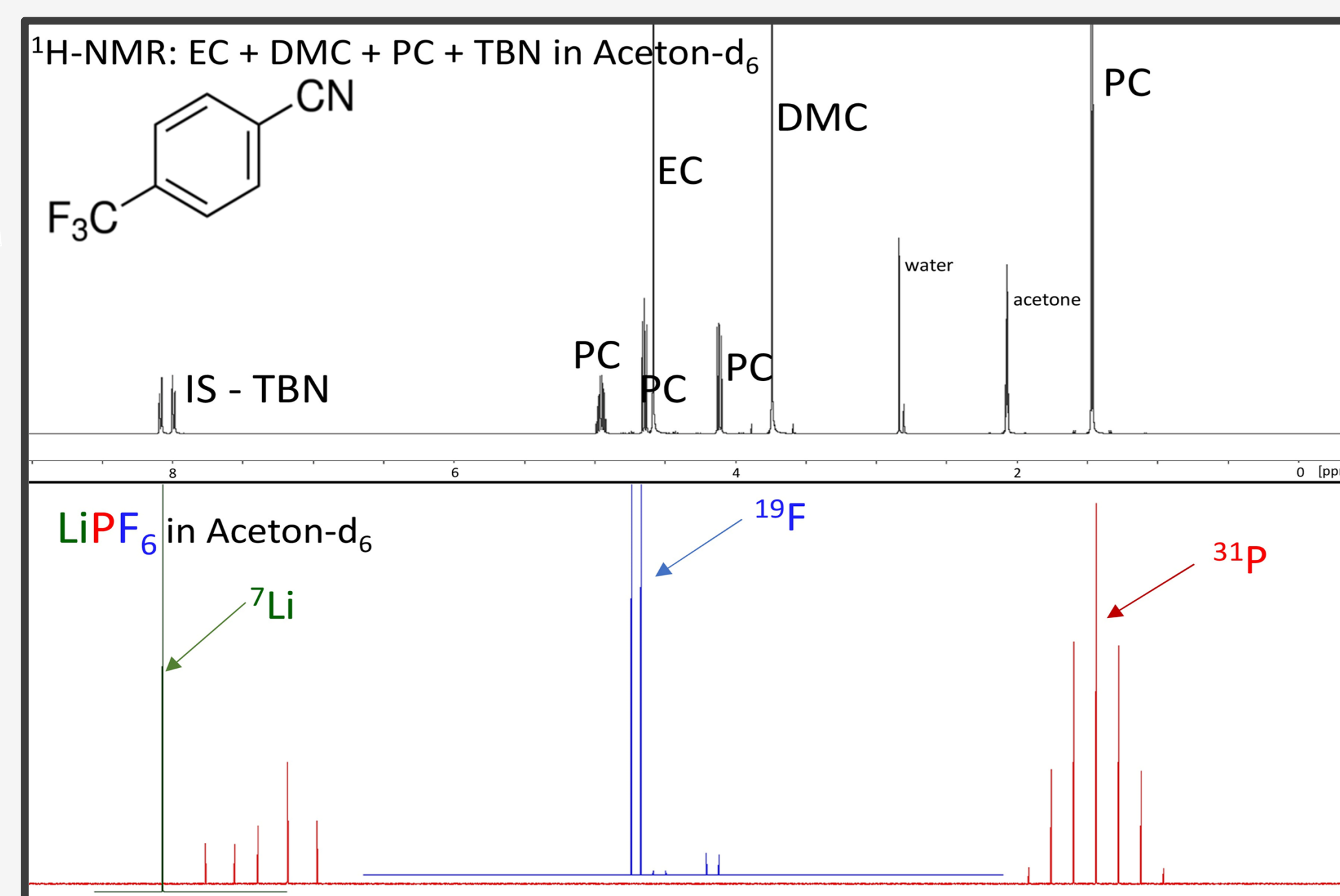


Figure 3: top) ^1H -NMR spectrum of EC, DMC, PC, TBN 1:1:1:1 in acetone- d_6 . bottom) ^{19}F -NMR (blue), ^7Li -NMR (green), ^{31}P -NMR (red) of LiPF_6 in acetone- d_6

Summary / Take-Home Message

Depending on the analytical question, the different nuclei can be investigated in a non-destructive way with only one sample preparation in a single NMR tube. Switching between nuclei is n problem for the NMR probe and a combination measurement of ^1H , ^7Li , ^{13}C , ^{19}F and ^{31}P only takes approx. 30 min. This provides a comprehensive picture, deriving both qualitative or quantitative statements, whichever is required - by means of qNMR spectroscopy, both are possible with low effort.

Analytical question

(q)NMR-Cocktail

High quality results

(All measurements were performed on a BRUKER Avance III HD 500 MHz, BBFO PLUS Smart probe).

[1] Diehl B, Holzgrabe U, Monakhova Y, Schönberger T. Quo Vadis qNMR? J Pharm Biomed Anal. 2020 Jan 5;177:112847.
[2] S.G. Patching, NMR active nuclei for biological and biomedical applications, J. Diagn. Imaging Ther. 3 (2016) 7–48.