

Determination of base oil content in lubricating greases by NMR

1 | INTRODUCTION

Lubricating greases are an important class of lubricants to reduce wear and friction in moving components.^[1,2] Greases consist of a thickener network which includes base oil and additives of typically low molecular weight. These latter two components are at least partially released on long time scales and under mechanical stress. They provide the tribological activity on the metallic surfaces. As a result, the base oil and additive concentrations in the grease decrease with use, and its consistency changes.^[1] When a critical level is reached, the functionality of the grease as lubricant is no longer given and either a lubricant change has to be carried out or—in the case of lifetime lubrication—the service life of the system has been reached. In addition to other parameters in grease analysis, the determination of the base oil concentration is therefore of decisive importance.^[3,4] In the Siemens ring method, a defined grease quantity of about 1 g is placed on a filter paper at 80°C for 6 h. The weight of the filter paper is measured before and after mechanical loading of the grease. The weight difference of the filter paper after the procedure describes the quantity of the separated base oil in the grease.^[4] This time-consuming method requires relatively large quantities of grease, which are irreversibly lost. It is also suspected that not only base oil, but also additives and thickener molecules are separated into the paper and thus influence the quantification.

NMR is well known in fundamental research of material characterization and in industrial process control and quality control (QC). Promising approaches are also known in lubricant analysis to routinely incorporate NMR into quality control.^[5,6] This application note will show how the problem of quantitatively measuring the residual oil content is solved via NMR spectroscopy. NMR spectroscopy, combined with transverse relaxation, provides the required sensitivity even in low field NMR, thus enabling this application in QC.

2 | SAMPLES

Four different greases were investigated: Greases 1–3 contain the same Li metal soap thickener and the same base oil, but vary in their additive amount and composition. Grease 4 is composed of a Li-Ca metal soap and a base oil with higher viscosity. The residual oil content was modified via the DIN 51817 standard test (“Oil Separation from Lubricating Grease Under Static Conditions”) for the four greases. This test is thought to predict the amount of oil that will separate during storage at room temperature. Test weights of up to 4 kg, contrary to the DIN standard, were used to enhance the oil separation in order to achieve a representative range of residual oil concentrations for calibration purposes. The residual oil content was calculated from the difference between the amount of grease claimed and the separated liquid fraction determined gravimetrically. The oil concentrations were known in the fresh greases.

3 | EXPERIMENTAL

¹H-NMR measurements were performed at 80 MHz (Bruker Fourier 80) at a sample temperature of 25°C. The transverse relaxation rate was measured by the CPMG pulse sequence.^[7] The repetition time T_R was 2 s, and 32 increments of echo time in the range $\tau_e \in [8, 960]$ ms and 8 scans were measured. The magnetization decays were modeled with the gamma distribution function^[8] and result in the mean transverse relaxation rate $\langle R_2 \rangle$ and the distribution width σ . Signal integrals were calculated by integration over a relatively large spectral range [0, 4] ppm because of the large linewidths. Subsequently, the ¹H-NMR spectrum was measured by a Hahn echo^[9] at $\tau_e = 40$ ms with $T_R = 2$ s and 8 scans. Quantification was performed by signal integration over the entire ¹H spectral range. ⁷Li and ³¹P spectra were measured at a ¹H Larmor frequency of 300 MHz to provide a

safe ground for the data interpretation. The instrument was a Bruker “SB Avance Nano Bay” with a 5 mm BBFO probe, 512 scans were acquired with a repetition time of 30 s for both nuclei.

4 | RESULTS

4.1 | Oil separation test: Composition of the separated fraction

The standardized oil separation test and in consequence the determined residual oil content assume that only base oil separates due to enhanced temperature and mechanical load. NMR spectroscopy on the separated fraction allows to check this assumption: ^{31}P -spectroscopy was used to check for additive separation, and ^7Li -spectroscopy was used to detect thickener molecules, at least fractions of them, in the separated fraction. The separated fraction of the greases and only this fraction is discussed in the following.

^{31}P signals of typical additives were detected at significant concentrations: zinc dialkyldithiophosphate (ZDDP) in the case of Grease 1 (Figure 1) and ZDDP and molybdenum dithiophosphate (MoDTP) in the case of Grease 2. At least these additives were separated during the DIN test. This observation agrees with other knowledge and expectations.^[6] In particular, the two mentioned additives act mainly as tribology improvers on metallic surfaces. A certain mobility within the grease thus is absolutely necessary.

During the formulation of lubricating greases, the mixture of base oil and thickener is often pre-fabricated.

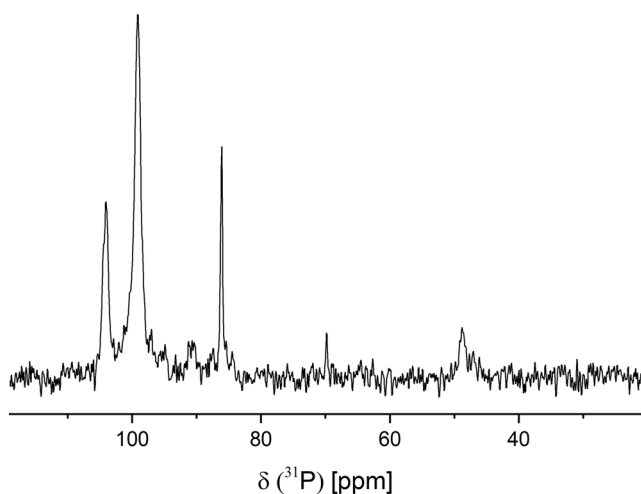


FIGURE 1 ZDDP (100 and 105 ppm) as well as aging products with low molecular weight such as thiophosphates were detected in ^{31}P -NMR of the separated fraction of Grease 1.

After this mixture has been heated and the thickener network has formed, some additives are added in a second step. These additives are dissolved in an oil – not necessarily in the same oil as the base oil. This workflow leads to the presumption that, in addition to the additives, the additionally added oil is also contained in the studied separated fraction.

^7Li -NMR signals were detected in the separated fraction of all greases (Figure 2). Most likely, thickener molecules that are not bound in the thickener network separate due to dipole–dipole, ionic or Van der Waals forces and are present as single molecules.^[2] The grease types differed with respect to the separation of thickener and oil molecules: The ^7Li concentration was roughly

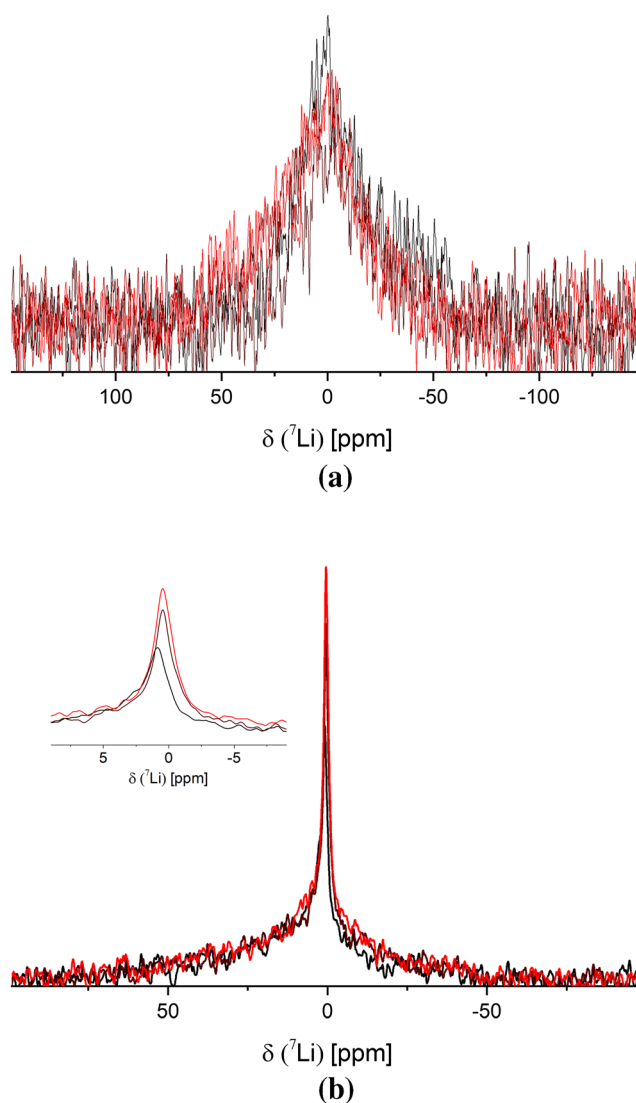


FIGURE 2 ^7Li -spectra of the separated fractions. Left: Grease 1, the signal integral is constant for all test weights (color gradient black \rightarrow red: increasing test weight). Right, Grease 4: in addition to the broad signal, a narrower line is observed with increasing intensity with increasing test weight (inset).

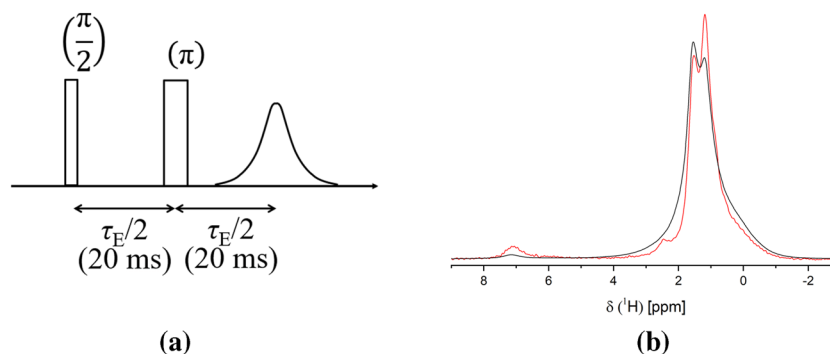


FIGURE 3 A Hahn echo was measured with $\tau_e = 40$ ms. Fourier transformation of the echo (right: red line) leads to a smaller line width compared with the FID-spectrum (black line).

independent of test weight for Greases 1–3. The signal ratios of oil to “thickener” remained constant in the separated fraction. Instead for Grease 4, the ^7Li fraction increased with test weight: the mechanical stress hence promoted the separation of “thickener”. The signature of the spectra also differed: Large line widths were observed in the ^7Li spectra for Greases 1–3. For Grease 4, this broad signal is overlaid by a signal with small linewidth at about 0 ppm attributed to mobile, unbound Li^+ -ions—an indication of different ^7Li -species in the thickener network.

The separation of thickener and additives influences the gravimetric determination of the separated base oil in the mentioned standard test. Thus, analytical approaches are desirable for an accurate quantification. The oil content generated and measured via the procedure described in DIN 51817 gives at least an estimate of the expected stability and potential bleeding. In order to classify the results of NMR spectroscopy and relaxation, the results are correlated with both the residual oil content and the test weights as a measure of mechanical stress to provide a complementary technique and procedure.

4.2 | Determination of residual oil content in greases: QC suitable NMR spectroscopy at 80 MHz

The greases themselves were investigated to measure the residual oil fraction in the stressed greases. As expected, signals from base oil molecules, thickeners and the alkyl chains of additives were clearly detected in the ^1H -NMR spectra at 80 MHz. The transverse relaxation rates of these components differ, however. In particular, the thickener molecules, which form a network, are restricted in their molecular mobility. In analogy to polymer networks, large $\langle R_2 \rangle$ values are therefore expected and tend towards values observed in macromolecular solids or gels. To answer the question whether a significant fraction of thickener signals had decayed already during the receiver dead time, FIDs were Fourier

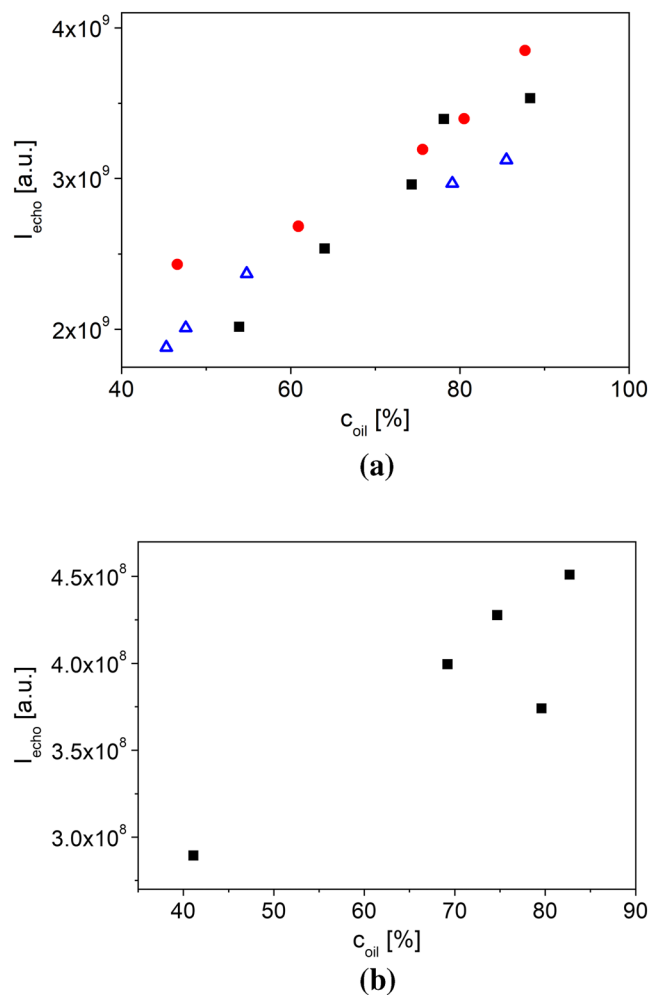


FIGURE 4 The residual oil content c_{Oil} in the stressed greases and signal integral I_{echo} correlate linearly in a first approximation. The correlation is influenced by thickener and additives and therefore depends on the base oil type (left, Grease 1: ■; Grease 2: ●; Grease 3: ▲, on the right: Grease 4). Deviations of individual samples are due to the limitations of accuracy in the oil separation test.

transformed, and the total spectrum was integrated. However, the integral normalized to the sample weight correlates neither with the residual oil content c_{Oil} nor

with the test weight m . Thus, significant thickener signals are present in the ^1H -spectra.

If, however, an echo with $\tau_e = 40$ ms is acquired and Fourier transformed, the signature of the spectrum changed compared with the spectrum measured via the FID: the broad signal disappeared, and the line widths were smaller (Figure 3). Although only a small part of the ^1H -magnetization of base oil and additives has decayed, little or no thickener signal was detected in this T_2 weighted spectrum.

The integral of the signal in I_{echo} now correlates with both, c_{Oil} and m (Figure 4). This provides the basis for calibration with the aim of determining c_{Oil} of samples taken from real applications. The correlation between c_{Oil}

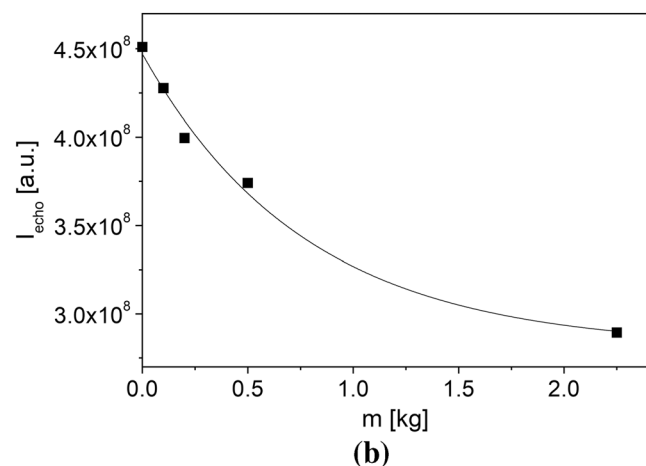
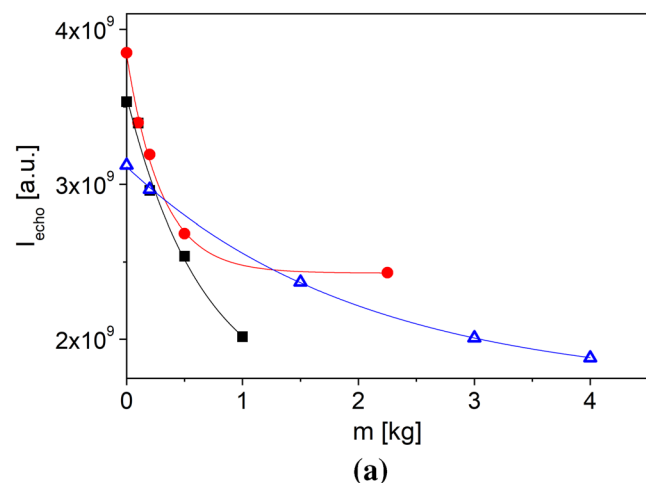


FIGURE 5 Disproportionately large test weights m are required for obtaining small I_{echo} during the production of low residual oil contents in greases (left, Grease 1: \blacksquare ; Grease 2: \bullet ; Grease 3: \blacktriangle , on the right: Grease 4). A non-linear relation between I_{echo} and m is found for all grease types. An empirical exponential decay results in a constant m_c which is specific for the greases (Grease 1 to 4: $m_c = 0.30$ kg, 0.66 kg, 2.0 kg and 0.77 kg).

and I_{echo} is approximately linear for all four greases. One limitation for accuracy of this calibration is that the determined c_{Oil} according to DIN 51817 is influenced by thickener and additives as discussed. This can also result in individual outliers, for example in the case of Grease 4 and $c_{\text{Oil}} \approx 80\%$ (Figure 4, right).

A different relation is found when correlating m and I_{echo} : disproportionately large loads are required for large oil reduction in the greases, i.e. small c_{Oil} or I_{echo} (Figure 5).

The results for Greases 1–3, which differ only in their additives, are comparable but with different dependence on load. The signal integrals are significantly smaller for Grease 4 with a different thickener and a base oil with a larger viscosity (400 cSt compared with 110 cSt for Grease 1–3). The correlation between I_{echo} and m , however, can empirically be described by an exponential decay with a constant m_c . Even for the greases with the same thickener and base oil type, m_c differs significantly in a range 0.30 kg ... 2.0 kg. This reveals that additives have a strong influence on the interaction of base oil and thickener and might also affect the thickener and its structure. Knowledge about the type of grease is required in a potential QC application of determination of residual oil content in greases with these approaches.

4.3 | Determination of residual oil content in stressed greases: NMR transverse relaxation

The base oil quantification is realized via “counting” the ^1H -nuclei in NMR spectroscopy, and a linear relation

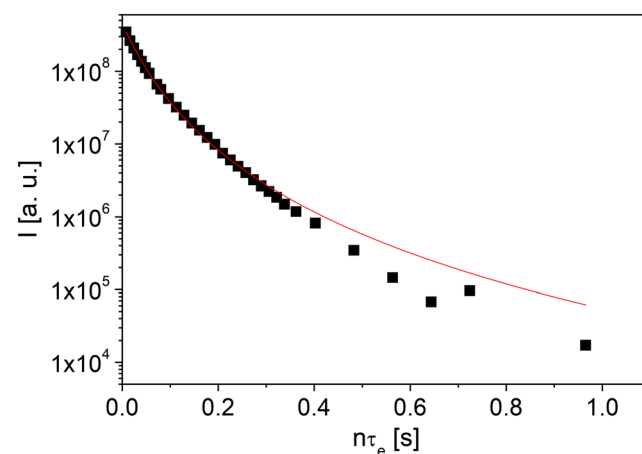


FIGURE 6 A magnetization decay was modelled using the gamma distribution function, which results in a mean transverse relaxation rate $\langle R_2 \rangle$ and a distribution width σ , on the example of fresh Grease 1.

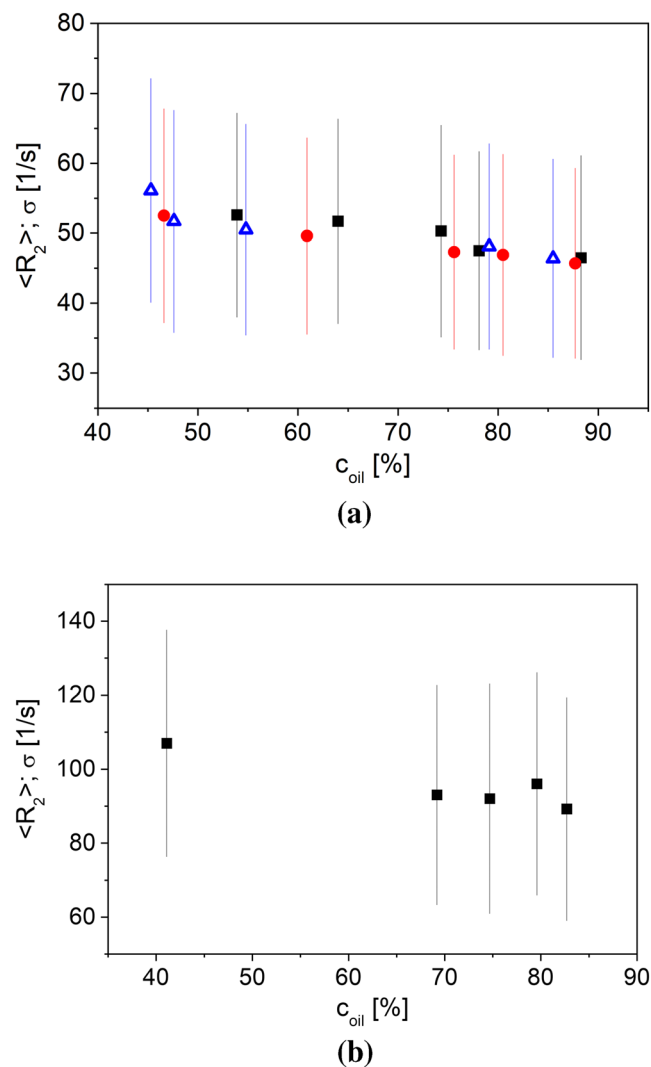


FIGURE 7 The mean transverse relaxation rate $\langle R_2 \rangle$ is sensitive to the residual oil content c_{oil} . Left: Greases 1–3, right: Grease 4. In addition, the distribution width σ is shown in form of vertical lines as a result of modeling the magnetization decays with the gamma distribution function.

between signal integral and residual oil concentration is expected and approximately found. $\langle R_2 \rangle$ instead addresses molecular dynamics and complements the spectroscopic approach (a typical magnetization decay and modelling in Figure 6). $\langle R_2 \rangle$ decreases with increasing residual oil concentration (Figure 7). This observation is in line with the macroscopic consistency of the greases—they become softer with increasing oil content. With regard to the analysis of aged greases, it is worth mentioning that $\langle R_2 \rangle$ increases as a result of paramagnetic relaxation enhancement (PRE) in the case of abrasion of (super-) paramagnetic materials containing for example iron or copper ions. The correlation between $\langle R_2 \rangle$ and c_{oil} is therefore obscured, and the residual oil content can only reliably be deduced when knowing

composition and concentration of abrasion or when separating the particles.

5 | CONCLUSION

NMR spectroscopy and NMR transverse relaxation are both sensitive to the residual oil content c_{oil} in stressed lubricating greases. This quality parameter c_{oil} is important in the analysis of lubricating greases. The two NMR approaches together allow for a correlation with the residual oil content determined via DIN 51817. The integral of the Fourier-transformed echo I_{echo} or the mean transverse relaxation rate $\langle R_2 \rangle$ correlate with c_{oil} . Especially the transverse relaxation depends on the base oil and thickener type, a calibration of the NMR quantities against the established standardized procedure is required. In contrast to other analytical methods, sample amounts as small as 10 mg are sufficient; moreover, the sample is not destroyed and can be reused. Both measurements, ^1H -spectroscopy and transverse relaxation can be performed on QC suitable low-field instruments. In addition, spectroscopy has shown that additives and thickener molecules also separated out in the standardized oil separation test DIN 51817. The residual oil content determined thereafter may include an offset which needs to be checked for each specific grease. This fact also influences $\langle R_2 \rangle$ and I_{echo} . In a future application, it will be possible for lubricant manufacturers to synthesize specific greases and characterize them according to the described procedure, whereas a calibration is easily established for defined base oil contents known during formation.

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CONFLICT OF INTEREST STATEMENT

The authors have declared no conflict of interest.

PEER REVIEW

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