Lube-Tech
PUBLISHED BY LUBE: THE EUROPEAN LUBRICANTS INDUSTRY MAGAZINE
No.147 page 1

Extended lubricant analysis using Nuclear Magnetic Resonance (NMR)

Dr. Christoph J. Rohbogner**, CLS, OELCHECK GmbH, Brannenburg, Germany* ***cro@oelcheck.de

The analysis of used oil samples is performed today by using a number of sophisticated techniques allowing a concise condition assessment.

A standard used oil analysis programme typically consists of more than 40 single values[1]. Among them:
- Kinematic viscosity
- Water Content
- Fuel Content (if applicable)
- Particle Counting (if applicable)
- Detection of Additive and Wear Elements using ICP or similar
- FTIR (Fourier transform infrared)

The results of these tests [2] are used for judging whether a lubricant has to be replaced or further use is possible without harming the machinery. The analysis of a sample does not only reveal the status of the lubricant but also of the machine or its lubricant wetted parts: Wear and debris found during the analysis allows one to decide whether normal or abnormal wear is present. Historically, the analysis of used oils began after the Second World War when major US railroad corporations were trying to monitor the health status of their diesel locomotives. Subsequently, it has been adopted by the armed forces leading to the JOAP (Joint Oil Analysis Program). [3]

The formation of such programmes was flanked by the application of existing analysis methods and fuelled the development of new analytical instruments.

Lately, such used oil analysis has gained more traction as the carbon footprint of lubricated equipment is more important due to climate and sustainability goals. It has become not only of financial interest extending the lifetime of a lubricant but also an imperative in terms of social and environmental responsibility.

However, it is not only the extension of the lifetime of the lubricant yielding carbon benefits. The condition of the machinery must also be part of the assumption. Thus, extending drain intervals may reduce component lifetime, leading to the opposite of a low carbon footprint as spare parts contribute enormously to carbon dioxide production during their manufacturing process and in the logistics chain.[4] [5]

Accordingly, the more knowledge the operator may obtain about the status of the lubricant, the better. Especially remote installations such as offshore wind farms or installations with large oil fillings and low sampling frequency as well as installations with restricted accessibility rely on in-depth information content in analyses, as possible abnormalities may be detected upfront minimising equipment downtime or damages. [6]

In addition, newer machinery will potentially have a different result from that of existing formulated lubricants, in terms of the additives used, the quantity of lubricant consumed and the resulting profit. Detailed analysis is required to determine the lifetime of the appropriate oil. [7]

As indicated above, standard used oil analysis is a viable tool for the safe and continuous operation of machinery. However, such an analysis does not necessarily reveal the state of anti-wear (AW) and/or extreme-pressure (EP) additives. The typically conducted ICP-OES analysis does yield a reliable statement about the concentration of typical elements present in AW and EP additive formulations, such as phosphorus, zinc and sulphur. Knowing the abundance of additive elements present in the lubricant allows to judge whether a lubricant must be refreshed or even exchanged if, for example the level of additives have fallen below a certain threshold. [1]

But, besides the concentration of additive elements, a structure-function-relationship is present. Thus, only certain structures of the molecules exhibit their engineered properties. As the additive structure is altered during use, changed molecules may fall back in their protective posture.[8] However, such alteration is not directly visible when using only spectroscopic methods. The concentration of additive elements may still be the same or only slightly lower than in the fresh product. As additives are typically surface active, surface wear may impact upon additive concentration whereas its effectiveness can no longer be expected at the same given percentage. Thus, knowledge about the structure and therefore the effectiveness of these additives is crucial for the prediction of the remaining useful lifetime of a lubricant, among the other parameters as for example the viscosity (class), water content or wear metals. FTIR spectroscopy allows, to a certain extent, the monitoring of such properties. [9] However, its application is limited due to interferences.

Subsequently, OELCHECK has developed together with the Karlsruhe Institute of Technology (KIT) a method that allows the determination of the concentration of active anti-wear and extreme pressure species based on Nuclear Magnetic Resonance Spectroscopy in the course of routine used oil analysis.

Nuclear Magnetic Resonance (NMR) is the most powerful analytical method known in organic chemistry today. The principle has been developed in the 1940s and their inventors have been awarded with the Nobel Prize for Physics in 1952. [10]

For more than 40 years, the technology has been used for the analysis of petroleum products. Numerous methods have been developed and standardised such as:
- Determination of hydrogen content in fuels (i.e. ASTM D7171, ASTM D4808, ASTM D3701
- Polyurethane Raw Materials (i.e. ASTM D4273, ASTM D4875)
- Determination of Aromatic Carbon content in Hydrocarbon oil according to ASTM D5292

Furthermore, NMR has its application in borehole analysis of crude oil reservoirs. [11] [12] [13]

As lubricants are comprised of organic and metal-organic compounds, it is reasonable applying NMR in lubricant analysis. [14] [15]

The principle of NMR relies on resonant adsorption and subsequent irradiation of magnetic energy in form of radio frequency. Only nuclei with a non-zero magnetic moment such as ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P and others are so- called NMR-active nuclei. The magnetic moment is responsible for the spin which is necessary for a successful NMR experiment. For a ^{1}H or ^{31}P atom, two possible spin orientations are known: α (+1/2) or

β (-1/2). For NMR analysis, the spins are oriented using an external magnetic field. By irradiating the sample with radio frequency ($h\nu_1$), the spins absorb (a) or emit (e) the energy and subsequently change their original orientation (Figure 1). [10]

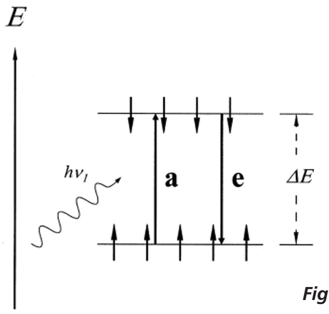

Figure 1: *Nuclei Spin Energy Levels. [10]*

Modern NMR spectrometers typically rely on the "pulse" principle, meaning that all nuclei of one type are simultaneously stimulated by the action of a high frequency pulse inducing resonances. These are directly related to the vicinities in situ. surrounding them. The resonances are detected as free induction decay (FID) which is converted into the NMR spectra by the action of Fourier Transformation. [10]

The magnetic field in modern NMR instruments is generated through super conducting magnets using liquid Helium as coolant. Thus, magnetic fields of 23.5 T with a 1H resonance frequency of 1 GHz are available today. Furthermore, modern instruments allow the observation of different nuclei and the possibility of multidimensional NMR experiments, showing direct spin-spin couplings between neighboring nuclei, facilitating molecule structure solving in R&D facilities. [16]

The concentration of the NMR active nuclei isotope is also of great relevance. A high concentration thereof leads to superior signal to noise ratio, yielding evaluable information and to acceptable measurement timing. [Lit] Usually several thousand high frequency pulses are used during the acquisition of an NMR spectra. Before the sample is subjected to a new pulse, the full relaxation of the spins must be ensured. [10] This may be affected by the viscosity of the lubricant. Thus, dilution with a NMR specific solvent is applied, leading to low viscosity of the resulting solution, ensuring spin relaxation within a reasonable timeframe. [15] [17]

As indicated above, the observed resonance of the nuclei is directly influenced by its environment. Thus, different neighboring structures lead to altered resonances. Additionally, only the resonance is specifically linked to the observed core, leaving other parts of the molecule mostly aside. Therefore, the resulting information is more precise as for other analytical methods where the whole molecule is brought into resonance, regardless of the contained elements (i.e. FTIR).

Thus, NMR allows the deliberate observation of different elements and their neighbouring chemical structures. This is used to observe the changes within the additive molecules in comparison with fresh oil references. It is a very versatile method as the specific observation of elements and structures is possible without disturbances of other compounds present in the lubricant mixture as described. [18]

Chemical Shift [ppm]	AW/EP-Species	Functional Group/31P Position
90 – 120	Mo-dtp	$(\mathrm{RO})_2\mathbf{P}(\mathrm{S})\mathrm{S\,Mo\,S}(\mathrm{S})\mathbf{P}(\mathrm{OR'})_2$
94 – 103	Zn-dtp	$(\mathrm{RO})_2\mathbf{P}(\mathrm{S})\mathrm{S\,Zn\,S}(\mathrm{S})\mathbf{P}(\mathrm{OR'})_2$
90 – 96	O,O,O-Trialkyl-dtp	$(\mathrm{RO})_2\mathbf{P}(\mathrm{S})\mathrm{OR'}$
86 – 96	O,O,S-Trialkyl-dtp	$(\mathrm{RO})_2\mathbf{P}(\mathrm{S})\mathrm{SR'}$
86 – 87	Dialkyl-Dithiophosphoric acid	$(\mathrm{RO})_2\mathbf{P}(\mathrm{S})\mathrm{SH}$
68	Trialkyl-Thiophosphate	$(\mathrm{RO})_3\mathbf{P}(\mathrm{S})$
54	Triphenyl-Thiophosphate	$(\mathrm{PhO})_3\mathbf{P}(\mathrm{S})$
53 – 55	O,S,S-Trialkyl-dtp	$(\mathrm{RO})\mathbf{P}(\mathrm{O})(\mathrm{SR'})_2$
28	Dialkylthiophosphate	$(\mathrm{RO})_2\mathbf{P}(\mathrm{O})\mathrm{O}$
-5 - +30	Aminophosphate	$(\mathrm{RO})_2\mathbf{P}(\mathrm{O})\mathrm{O}(\mathrm{NR_2}')$
-8 - +10	Phosphoric acids	$(\mathrm{RO})_2\mathbf{P}\mathrm{OOH}$
-18 - +16	Triphenylphosphate	$(\mathrm{PhO})_3\mathbf{P}(\mathrm{O})$

Table 1: *^{31}P-NMR Resonances of common AW/EP Additives.[19]*

It is known that AW and EP additives are structurally altered during their use. [8] [19] As their structures change, it is possible to track the concentration of the original and the aged AW/EP molecules (Figure 2).

As AW/EP additives are typically based on Phosphorus ^{31}P, the observation of the ^{31}P isotope with NMR is a preferable choice. Furthermore, it is possible to track the concentration of different additives such as thiophosphates, phosphates, phosphoric esters and amides as well as zinc-dialkyldithiophosphates due to their different moieties leading to different chemical shifts in the ^{31}P-NMR.

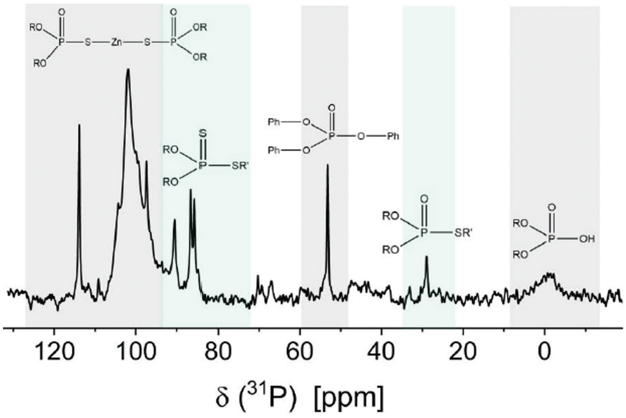

Figure 2: *^{31}P-NMR Spectrum of Common AW/EP Additives.[19]*

Results and Discussion

For reasons of simplicity, proofing the applicability of the method, the observation has been limited to the Phosphorus contained in Zinc dithiophosphate (Zn-dtp). Of course, Zn-dtp describes not a single compound but a class of different strain, optimised for the intended purpose. [20] It is a well-known AW additive class typically contained in any modern lubricant intended for the use in internal combustion engines. [21] [22] In addition to its proven anti-wear properties, Zn-dtp acts as a secondary anti-oxidant. Thus, it is subjected to depletion by two independent mechanisms of lubricant ageing. [23]

Accordingly, it is not possible to distinguish whether the Zn-dtp structure has been altered by tribological effects or other influences.

Lubricant samples of a light commercial vehicle have been drawn on a regular basis in the course of the field-testing of a newly designed 4-cylinder diesel engine. Samples of several field test vehicles have been submitted. The evaluation for this report is performed exemplary on the data gained from the specimen of one vehicle. The lubricant used in all vehicles was from the same brand and type, a market available oil in the SAE 5W-30 viscosity class with an ACEA C3 approval as well as holding the approvals of several OEMs at the time of the testing. It is intended for prolonged oil drain intervals (ODI), so called "long life", according to the relevant OEM specifications. A fresh oil sample is required as reference for the determination of the Zn-dtp degradation.

The used lubricant samples were drawn and subsequently submitted to OELCHECK for analysis. In addition to the standard analysis programme, ^{31}P-NMR has been measured to track the behaviour of the Zn-dtp concentration. The measurements were conducted using a 300 MHz Bruker SB Avance Nanobay NMR instrument with a BBFO sample head (5mm). The samples were diluted 1:1 using $CDCl_3$. Sample tubes have been sealed after dilution.

The initial measurement of the reference oil revealed that Zn-dtp decomposition products were already present in the fresh oil (Figure 3, blue curve, resonances at 80 ppm). The reason for this is not clear; it may result from the production process.

The sample data show, that Zn-dtp is fully consumed during the operating interval. According to the manual, 30,000 km is the intended oil operating time.

The conversion to so called poly phosphates which can be found in the NMR spectrum at around 0 ppm has been achieved. Intermediate or by-products of the conversion have also been detected in the samples submitted for analysis. However, no elucidation of the structure has been made.

The runtime of the lubricant was subsequently prolonged until a total of 70.000 km. During the remaining time, no active Zn-dtp has been found via NMR in the submitted lubricant samples. The typical decompositon route for Zn-dtp is the conversion to so-called polyphosphates. [23]

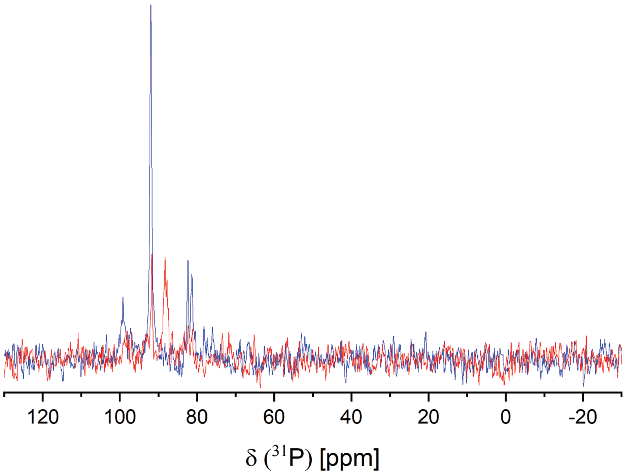

Figure 3: *NMR spectra of fresh oil (blue) and used oil (red) showing depletion of AW/EP Additives.*

The NMR spectra comparing the end-of-test sample with the fresh oil (Figure 6) clearly shows this conversion: no relevant resonances in the area of Zn-dtp (~90 ppm) but a rather broad signal in the area of 0 ppm, indicating the presence of the decomposition products.

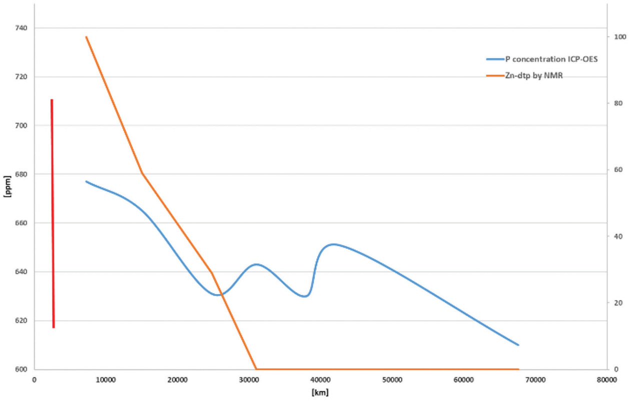

Figure 4: *Comparison of the Phosphorus concentration by ICP-OES vs. active Zn-dtp by ^{31}P-NMR.*

Surprisingly, the level of Phosphorus determined using ICP-OES remained nearly unchanged. Although it looks like a downward trend, differences among the samples were within the deviation of the standard, indicated by the red bar (Figure 4).

Moreover, no significant increase in wear metal concentration, indicating an abnormal wear situation, has been found after complete Zn-dtp consumption (Figure 5).

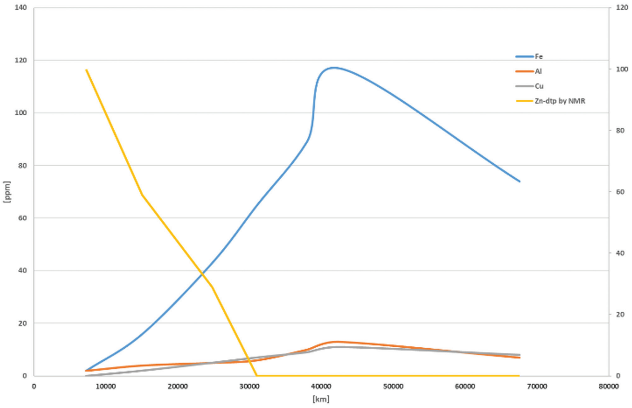

Figure 5: *Wear Metal concentration by ICP-OES compared to Zn-dtp concentration by ^{31}P-NMR.*

The determined concentration of wear metals show an increase, especially in the case of iron (Fe). However, considering the running time of the engine and lubricant as well as typical wear limit values for such applications, the determined iron concentration can be considered normal.

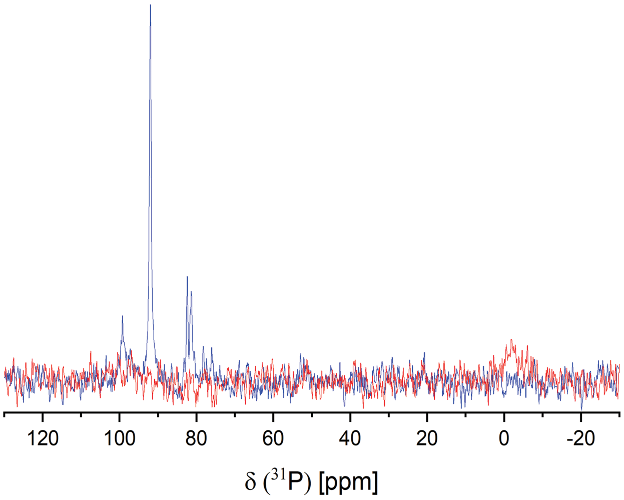

Figure 6: *NMR spectra of fresh oil (blue) and used oil (red) at the end of the ODI: Zn-dtp (~90 ppm) fully consumed, Polyphosphates (~0 ppm) present.*

Furthermore, no reports indicating unusual wear after dismantling of the engine are known.

NMR used as additional method in a used oil analysis programme yields more viable information about the status of the lubricant. It is even more beneficial when used in field-testing of new machinery or in situations where the structure-function relationship between additives and a machine is of great importance. The additional gained information about changes in additive structure allows a more in-depth judgment of the lubricant condition. This extra information may assist in prolonging the lifetime of a lubricant filling without compromising the safety of the machinery. This extended lube oil analysis may contribute to a more sustainable lubrication of machinery in operation. Further studies in applying magnetic resonance techniques for used oil analysis for other lubricant types (i.e. gear oils) are currently ongoing.

Acknowledgment

This work has been funded by ZIM (Zentrale Initiative Mittelstand) by the Federal Ministry of Economics of the Federal Republic of Germany

oelcheck.com

References

[1] Krethe, R. *Handbuch Ölanalysen*, expert verlag GmbH, 2020.

[2] Müller, R. Laboratory Methods for Testing Lubricants. In *Lubricants and Lubrication*, Vol. 2, 3rd ed.; Mang, T., Dresel, W., Eds.; Wiley-VCH, **2017**, pp 881-902.

[3] Poley, J.; Murphy, M. *The History of Oil Analysis*, Noria Corp. **2007**, **https://www.machinerylubrication.com/Read/1113/history-of-oil-analysis** (accessed 06/30/2023).

[4] Gustafsson, M., Svensson, N., Eklund, M., Möller, B. F., Well-to-wheel climate performance of gas and electric vehicles in Europe, *Transportation Research Part D*, **2021**, *97*, 102911 – 102928.

[5] a) Lomborg, B.; Welfare in the 21st century: Increasing development, reducing inequality, the impact of climate change, and the cost of climate policies, *Technological Forecasting & Social Change*, **2020**, *156*, 119981 – 120016.
b) Woydt, M.; Bock, E.; Hosenfeldt, T.; Bakolas, V.; Luther, R.; Wincierz, C. Effects of Tribology on CO2-emissions in the use phase of Products, 2023 {bold}, Gesellschaft für Tribologie e.V.

[6] Von Eberan-Eberhost, C. Motorölanalysen und ihre Aussagekraft. In *Schmierung von Verbrennungsmotoren*, 3rd Ed.; Bartz, W. J., Mesenholl, H.-J., Wippler, E. expert verlag GmbH, **2010**.

[7] *Lubricants and Lubrication*, 3rd ed.; Mang, T., Dresel, W., Eds.; Wiley-VCH, **2017**.

[8] Heuberger, R., Rossi, A., Spencer, N., Pressure Dependence of ZnDTP Tribochemical Film Formation: A Combinatorial Approach, *Tribology Letters*, **2007**, 28, 209–222.

[9] ASTM E2412-23: Standard Practice for Condition Monitoring of In-Service Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry, ASTM international, **2023**.

[10] Friebolin H. *Ein- und zweidimensionale NMR-Spektroskopie*, 4th ed.; Wiley-VCH, **2006**.

[11] Balle, B., Führ Dal’ Bó, P. Santos, J., Aguiar, L., Coelho, P., Favoreto, J., Arena, M., Hélisson, N. S., Ribero, C., Borghi, L. A new Method to improve the NMR log interpretation in drilling mud-invaded zones: A case study from the Brazilian Pre-salt, *Journal of Petroleum Science and Engineering*, **2021**, *203*, 108692 – 108715.

[12] Luo, S., Guo, J., Xiao, L., Prospects of borehole NMR instruments and application, *Magnetic Resonance Letters*, **2022**, *2*, 224 – 232.

[13] Ivashchenko, P. M., Bakai, E. A., Yurchuk, A. I. About the possibility of identification of hydrocarbon deposits with the help of NMR, *Geoscientific Instrumentation Methods and Data Systems*, **2016**, *5*, 551 – 559.

[14] Fraenza, C. C., Förster, E., Guthausen, G., Nirschl, H., Anorado, E. Use of 1H-NMR spectroscopy, diffusometry and relaxometry for the characterization of thermally-induced degradation of motor oils, *Tribology International*, **2021**, *153*, 106620 – 106648. (and references therein)

[15] Rudszuck, T., Förster, E., Nirschl, H., Guthausen, G. Low-field NMR for quality control on oils, Magnetic Resonance in Chemistry, **2018**, 1-17.

[16] Bruker Almanac **2012**.

[17] Rudszuck, T.; Zick, K.; Groß, D.; Nirschl, H.; Guthausen, G. Dedicated NMR sensor to analyze relaxation and diffusion in liquids and its application to characterize lubricants, Magnetic Resonance in Chemistry, **2021**, *59*, 825-834.

[18] Rudszuck, T. Charakterisierung von frischen Schmierstoffen und Detektion der Schmierstoffalterung mittels NMR-Methoden, Ph.D. Thesis, Karlsruhe Institut für Technologie, **2022**.

[19] Sharma, V., Doerr, N., Erdemir, A., Pranesh, A. B. Antiwear properties of Binary Ashless Blend of Phosphonium Ionic Liquids and Borate Esters in Fully Formulated Oil (no Zn), *Tribology Letters*, **2019**, *67*, 11249 – 11279.

[20] Braun, J. Additives. In *Lubricants and Lubrication*, Vol. 1, 3rd ed.; Mang, T., Dresel, W., Eds.; Wiley-VCH, **2017**, pp 117 - 151.

[21] Haperscheid, M. Lubricants for Internal Combustion Engines. In *Lubricants and Lubrication*, Vol. 1, 3rd ed.; Mang, T., Dresel, W., Eds.; Wiley-VCH, **2017**, pp 249 - 290.

[22] Huynh, K. K., Tie, K. A., Pham, S. T. Synergistic and Competetive Effects between Dialkyldithiophosphates and Modern Generation of Additives in Engine Oil, *Lubricants*, **2021**, *9*, 35 – 49.

[23] Matsumoto, K.; Yamakawa, S.; Yamamotoe, H.; Yamada, Y.; Beppu, Y.; Matsuoka, T.: Development of a Test Method to Evaluate the Life of Gear Oils for Heavy-Duty Vehicles, **2003** SAE International Spring Fuels&Lubricants Meeting; Published: 2003; Page 1– 8