

Automating the NMR analysis of base oils: Finding naphthene signals



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HIGHLIGHTS

- Automated analysis of base oil samples using quantitative ^{13}C NMR presented in detail.
- 2D NMR, including ^{13}C – ^{13}C NMR (INADEQUATE) used for detailed assignment.
- ImatraNMR and novel SimpeleNMR software used for automation, freely available at <http://vltr.fi/imatranmr/>.
- Napthenic structures detected directly from real base oil samples using NMR.

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ABSTRACT

Base oils, as many other oil products, are mainly analyzed with dedicated techniques designed to characterize the performance of these products in their intended use, along with suitable analysis techniques such as MS or GC to provide basic chemical information about the constituents. However, the physico-chemical properties of base oils are direct result of the chemical structures of the molecules present in the oil, from which these techniques provide limited information. NMR spectroscopy, while more complex and expensive than many other analysis techniques, provides unique insight to the chemical structures present in these complex hydrocarbon mixtures. Utilizing NMR for analysis of base oils is not straightforward, and in this paper we go through this process and demonstrate how our software designed for mass analysis of quantitative spectra (ImatraNMR) can be used to automate the analysis, especially with novel addition of SimpeleNMR processing software. Additionally, ImatraNMR and a novel 2D version of Q-INEPT-CT experiment are used to conduct statistical correlation analysis aiming to detect signals originating from naphthene (cycloalkane) structures present in base oil samples.

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1. Introduction

Lubricants are important products in modern society, as almost any mechanical device requires some sort of lubrication. The performance of the lubricant is important factor affecting the energy efficiency, wear and maintenance, leading to significant economical effects. In this article we concentrate on the analysis of lubricant base oils, which are used mostly as main components of automotive lubricants. While the analysis concentrates on these products, it should be applicable to any similar oil products as well.

Base oils are usually produced from vacuum gas oils, high boiling components ($>343\text{ }^\circ\text{C}$) of crude oil [1], which are significantly chemically modified via extensive refining processes during base oil production. Synthetic base oils are also being made, notably PAO oils (Poly Alpha Olephin) and via gas-to-liquid processes [2]. The final products contain molecules with >20 carbons, usually around 30 carbons. Most important properties of base oils are usually stable viscosity across wide temperature range (measured by

Viscosity Index, VI), viscosity itself (kinematic viscosity), ability to flow at low temperatures (measured by pour point, PP) and thermal and oxidative stability. These desired properties have lead modern base oils to be almost purely composed of various branched aliphatic hydrocarbons.

1.1. Base oils and NMR

Base oil samples are in several ways quite different samples compared to "regular" samples typically encountered in organic chemistry:

- *Low functionality:* Typical modern base oils are very pure aliphatic hydrocarbons, containing only trace amounts of aromatic or olefinic structures, or any structures involving other elements, such as oxygen, nitrogen or sulphur. Thus, the molecular structures are limited to variations in aliphatic hydrocarbon chain length and branching, including cyclic structures.
- *Complex mixture:* While the sample consist mostly of simple aliphatic hydrocarbons, the varying branching and chain lengths still lead to a complex mixture of many different, but very similar molecules.

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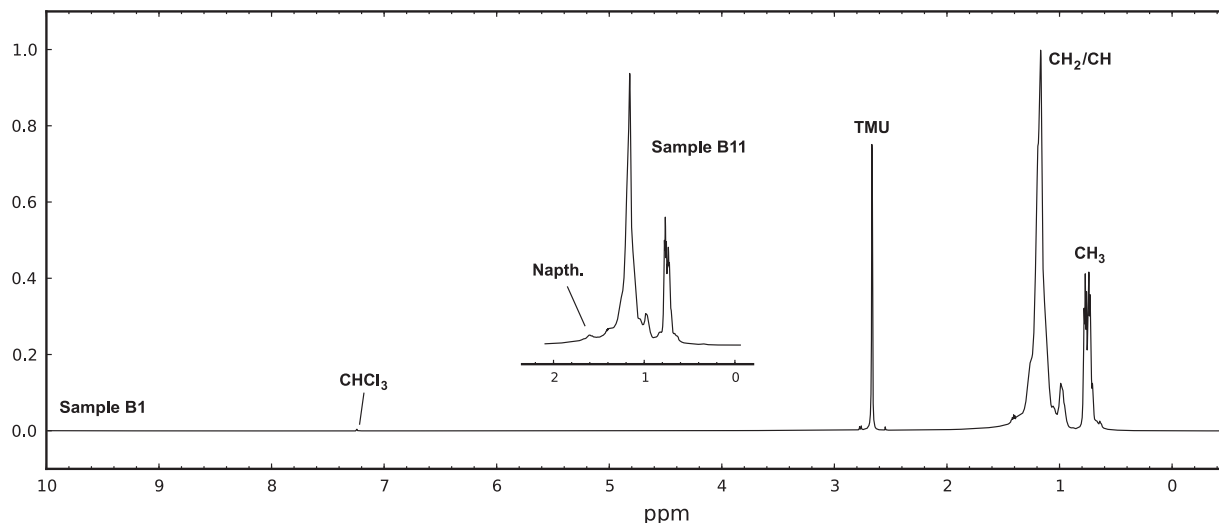


Fig. 1. Typical ^1H NMR spectrum of a modern base oil, obtained from sample B1, with 0–2 ppm region additionally shown from sample B11. No aromatic or olefinic signals can be seen. All oil signal is concentrated to 0.5–1.8 ppm causing heavy signal overlap, and only methyl signals can be clearly distinguished. In the sample B11 small hump caused by naphthene structures can be distinguished (analysis 2). TMU signal, used as an internal standard, can be seen at 2.67 ppm.

- **Sample availability:** As the samples are produced at industrial scale, virtually unlimited sample amount is available for analytic needs.

The first two points make the analysis of the oils challenging and quite unique, while the last point is large aid when using NMR, as the relatively low sensitivity of NMR greatly benefits from large amounts of sample being available.

1.2. Signal overlap

NMR is fundamentally based on observing the resonance frequencies of suitable atomic nuclei (commonly ^1H and ^{13}C) in strong external magnetic field, and relies on the slight variations of these frequencies to differentiate the nuclei depending on the chemical structure they are part of. This is possible because the magnetic field experienced by the nuclei is affected by the electron structure surrounding the nuclei, which again depends on the molecular structure which the atoms are part of. As the differences in the res-

onance frequencies stem for chemical structure, they are called *chemical shifts*.

Typical modern base oils contain almost exclusively aliphatic hydrocarbons, meaning that the nuclei have very similar electron environment, and consequently very similar chemical shifts in NMR. This in combination with the large amount of very similar molecules present cause to several signals being observed in narrow spectral region, which can lead to signal overlap. Indeed, in a typical ^1H NMR spectrum of base oil, all observed signals are concentrated on small chemical shift range and severe signal overlap renders individual signals undistinguishable (Fig. 1). Clearly, only limited amount of information can be easily retrieved from such spectra.

The chemical shifts of ^{13}C nuclei are fortunately more sensitive to the molecular structure, leading to significantly larger signal dispersion (Fig. 2). From a typical ^{13}C spectrum of a base oil, over ten intensive signals and tens or hundreds of smaller signals can usually be resolved. While carbon spectra clearly contains a significant amount of structural information, the chemical shifts are still only

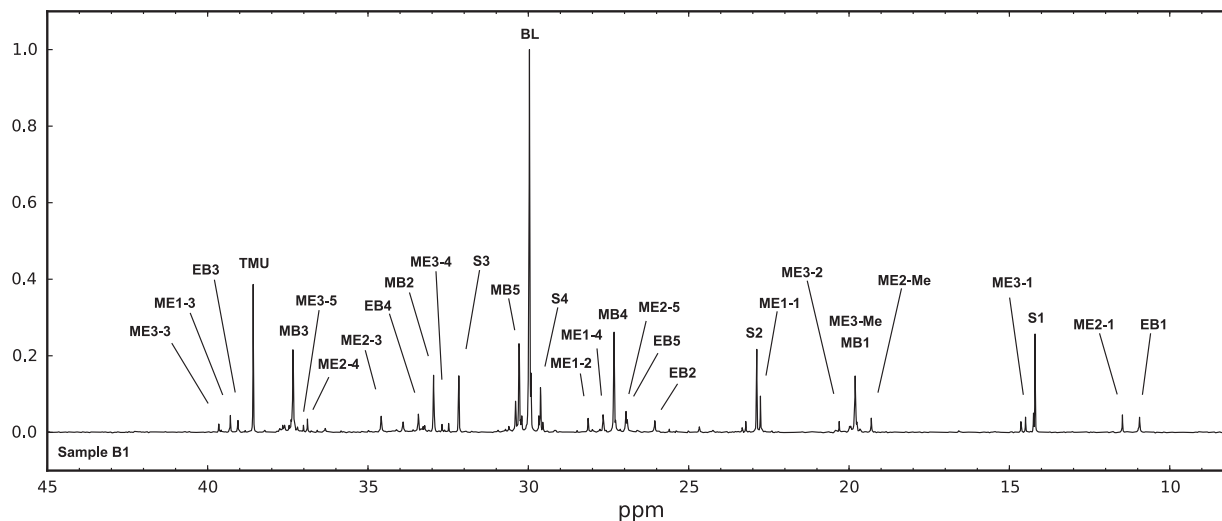


Fig. 2. Typical quantitative ^{13}C NMR spectrum of a modern base oil, obtained from sample B1. The assignments made during Analysis 1 are marked in the spectrum, corresponding structures can be found in Fig. 5.

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