

# Application of Quantitative Artificial Neural Network Analysis to 2D NMR Spectra of Hydrocarbon Mixtures

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Understanding relationships between the structure and composition of molecular mixtures and their chemical properties is a main industrial aim. One central field of research is oil chemistry where the key question is how the molecular characteristics of composite hydrocarbon mixtures can be associated with the macroscopic properties of the oil products. Apparently these relationships are complex and often nonlinear and therefore call for advanced spectroscopic techniques. An informative and an increasingly used approach is two-dimensional nuclear magnetic resonance (2D NMR) spectroscopy. In the case of composite hydrocarbons the application of 2D NMR methodologies in a quantitative manner pose many technical difficulties, and, in any case, the resulting spectra contain many overlapping resonances that challenge the analytical work. Here, we present a general methodology, based on quantitative artificial neural network (ANN) analysis, to resolve overlapping information in 2D NMR spectra and to simultaneously assess the relative importance of multiple spectral variables on the sample properties. The results in a set of 2D NMR spectra of oil samples illustrate, first, that use of ANN analysis for quantitative purposes is feasible also in 2D and, second, that this methodology offers an intrinsic opportunity to assess the complex and nonlinear relationships between the molecular composition and sample properties. The presented ANN methodology is not limited to the analysis of NMR spectra but can also be applied in a manner similar to other (multidimensional) spectroscopic data.

## INTRODUCTION

New traffic fuel and lubricants contain less aromatic compounds, less unsaturated compounds, and more aliphatic hydrocarbons. When oil fraction lacks aromatic and olefinic compounds, the product properties are determined purely by structural properties of the aliphatic compounds. The main influence on the product properties is therefore branching of the carbon chains. Some average structural parameters, e.g. n-paraffin to iso-paraffin ratio, has been used to describe this property.<sup>1</sup> However, there is no measure based on which accurate prediction of product properties would be possible. One reason for the complexity of the situation is, that the product properties, for example the viscosity index (VI) of aliphatic hydrocarbons, are not exclusively dependent on the amount of branching but also on the type of branches. Therefore, if the various substructures of the base oil could be reliably identified and quantified, the predictions of the product properties would considerably improve.

NMR spectroscopy has been widely applied in analytical studies of various hydrocarbon mixtures.<sup>2–5</sup> The studies of modern multicomponent base oils are challenging due to heavy signal overlap that makes both resonance assignment

and quantification difficult. Therefore, the modern two-dimensional (2D) NMR spectroscopy methods, enabling distinction of the methyl-, methylene-, and methine groups based on their proton and carbon chemical shifts, are increasingly applied in the field.<sup>6–8</sup> In fact, the heteronuclear 2D NMR methods have proven to be excellent tools to identify the substructures of oil fractions. However, quantification by heteronuclear 2D NMR spectroscopy is far from straightforward due to multiplicity, variation of couplings, and relaxation that all affect the volume of correlation peaks. Nevertheless, application of the knowledge of magnetization transfer calculations via product operator formalism,<sup>9</sup> new pulse sequences have been developed that provide quite accurate experimental basis for quantitative 2D NMR spectroscopy. Here the HSQC pulse sequence, the details of which are reported elsewhere,<sup>10</sup> was applied.

Artificial neural network (ANN) analysis is currently recognized as an effective and advantageous way to handle complex data not only in chemistry and spectroscopy<sup>11–15</sup> but also in various other scientific areas.<sup>16–18</sup> While the quantitative use of ANNs is a quite recent application in the field of NMR spectroscopy,<sup>14</sup> it is now well established that ANNs can offer a reliable and efficient way of spectral quantification in the case of 1D NMR spectra.<sup>15,19,20</sup> In the analysis of 2D NMR data we are not aware of any applications using ANNs.

In this work we have applied quantitative 2D NMR spectroscopy to study hydrocarbon based oil products. The

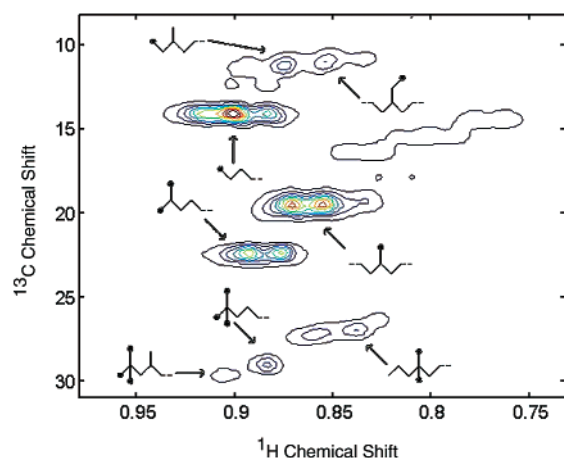
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**Figure 1.** The methyl resonance region of one typical 2D NMR spectrum of an oil fraction together with the main resonance assignments.

methyl resonances in the 2D NMR spectra were subjected to ANN analysis in order to correlate and study the relationships between the molecular structure as well as the sample composition and a product property, namely the viscosity index.

#### MATERIALS AND METHODS

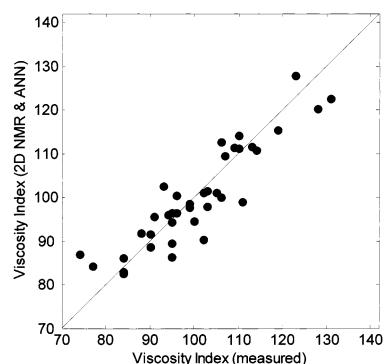
**Materials.** To have a wide range of VIs, the samples were taken from several test runs, microreactor, bench scale, and pilot scale oligomerization, and from production. Thirty-eight samples were selected for the current study. The samples had the VI within the range from 70 to 131.

**Sample Preparation.** The NMR samples of the oil fractions were prepared as 50 volume-% solutions with deuteriochloroform for the total volume of 0.6 mL in 5 mm NMR tubes.

**2D  $^1\text{H}$ - $^{13}\text{C}$  NMR Spectroscopy.** A Bruker DPX400 spectrometer with 5 mm broadband gradient inversion probe was used for the PFG HSQC measurements.<sup>21</sup> Experiment temperature was 35 °C. Quadrature detection was accomplished with gradient based echo-antiecho coherence selection. Spectral widths were 1.6 and 50 ppm for proton and carbon dimensions, respectively. Number of acquired points was 800 with acquisition time of 0.625 s with 128 increments and 2\*2 scans for each increment. Repetition rate was 5 s, giving the total experiment time of 22 min. Number of real points in the spectra was 1k\*256.

The spectra were phase-corrected and automatic baseline correction was applied in both dimensions. Shifted sine bell function was utilized in both dimensions. The methyl resonance region of these 2D NMR spectra (from 0.75 to 0.95 ppm for  $^1\text{H}$  and from 9.0 to 32.0 ppm for  $^{13}\text{C}$ , in total 19764 data points) is illustrated in Figure 1 together with the main resonance assignments.

**Artificial Neural Network Analysis.** The input data for the neural networks were obtained from the original methyl resonance region of the 2D NMR spectra (from 0.75 to 0.95 ppm for  $^1\text{H}$  and from 9.0 to 32.0 ppm for  $^{13}\text{C}$ , in total 19 764 data points) by taking every second point in the region. This resulted in 4941 data points to be used as inputs for the neural networks. The sum intensity for this spectral region for each sample was scaled to a constant value. The whole data set of 38 spectra was divided into four groups (10, 10, 9, and 9



**Figure 2.** The correlation between the measured viscosity index of the oil fractions and the one estimated by the ANN analyses of the 2D NMR spectra. The results are from the independent test sets in the ANN analyses, and the value for R is 0.903.

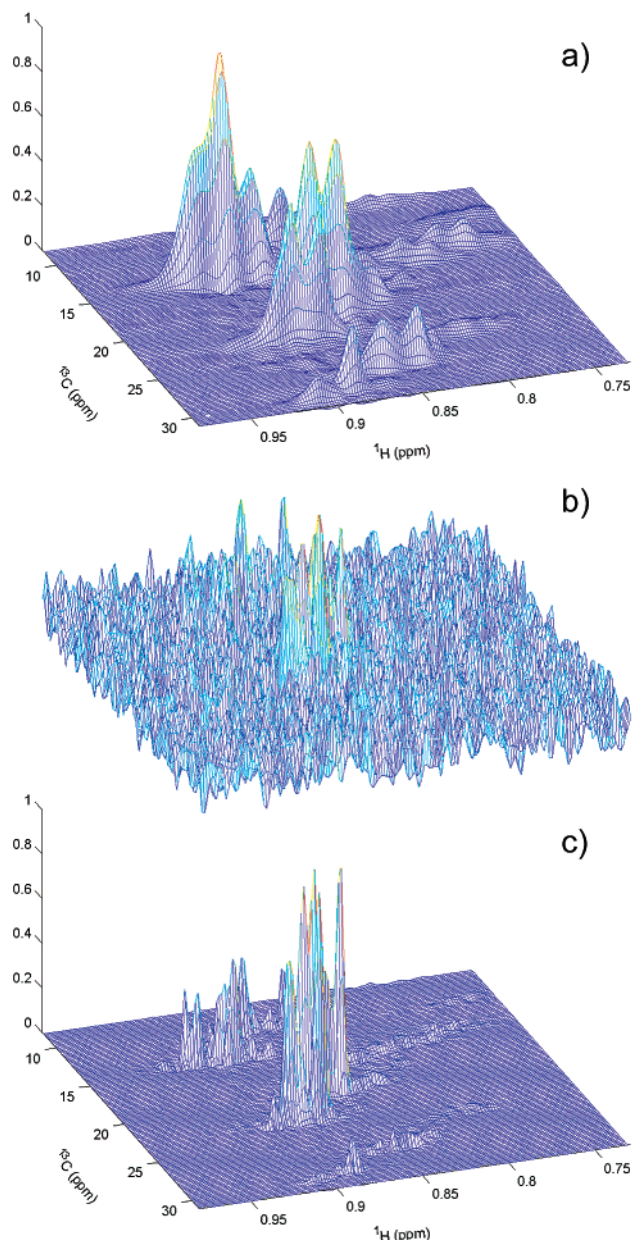
spectra) which were subsequently used in the four rounds of training and testing of the neural networks. Each time three groups represented the training set and one group was used as the test set. The results from the four different test groups were then combined leading to an effective use of the whole data set.

A feed-forward fully connected neural networks were used applying the back-propagation algorithm in the training.<sup>22</sup> The 4941 data points formed the input layer of the networks. In the hidden layer two neurons were used, and the output layer consisted of one single neuron representing the value for the viscosity index. Logistic functions were used both for the hidden and output neurons. The ANNs were thus trained to estimate the value of the viscosity index for each sample on the basis of the methyl resonance region of the 2D NMR spectrum. The training of an ANN results in a model in which each input data point is associated with a particular weight factor that can be used to calculate the relative importance of the inputs in the estimation of the output,<sup>22</sup> i.e., the viscosity index in this case. The NeuroShell 2<sup>23</sup> and MabLab<sup>24</sup> softwares were used in all the analyses. In the calculation of the relative weight factors the Contributions module of the NeuroShell 2 software was applied.<sup>23</sup> This model gives the best separation for the input variables when three layer nets are used with only few hidden neurons.<sup>23</sup>

#### RESULTS AND DISCUSSION

The results from the test sets when the ANNs were trained to estimate the value of the viscosity index based on the methyl resonances in the 2D NMR spectra are shown in Figure 2. The correlation coefficient between the measured viscosity index and the one estimated by the ANN analyses and 2D NMR spectroscopy was 0.903. While this correlation is reasonably good, it should be noted that only two neurons in the hidden layer were used. This compromises the ability of the networks to model nonlinear relationships but, on the other hand, will give a better representation when assessing the most important input variables in the estimation of the output.<sup>22</sup>

The relative contribution of the spectral inputs in the methyl region, when estimating the VI, is shown in Figure 3b. It is notable that only some of the resonances in the methyl region seem to contain information relevant in the estimation of the viscosity index. It is interesting to compare Figure 3a, which shows the methyl region for one of the



**Figure 3.** (a) The measured methyl resonance region of one typical 2D NMR spectrum of an oil fraction, (b) the relative contribution map of the spectral inputs in the methyl resonance region as a result of the ANN analyses for estimating the viscosity index, and (c) the measured spectrum multiplied with the relative contribution map. Note the relative intensity changes and the resolution enhancement.

original spectrum, and Figure 3c, which is this original spectrum multiplied with the relative contribution map of Figure 3b. The modified map in Figure 3c shows clear differences in comparison to the original map. For example, the most intensive resonance in the original is the normal paraffin terminal methyl resonance at 0.90 and 14.2 ppm. However, this resonance is remarkably reduced if the original spectrum is scaled according to the relative contributions of the spectral inputs when estimating the VI. In the latter case the two doublet resonances, namely the methyl branch and terminal isopropyl resonances at 0.86 and 19.8 ppm and 0.88 and 22.8 ppm, respectively, are much more pronounced. This nicely shows the importance of iso-paraffin substructures to the increase of VI.

Oil fractions are mixtures that consist of untold different hydrocarbon chains. In the NMR spectrum the chemical shift of the observed carbon is influenced by nearby chemical groups. The 2D NMR spectrum, however, cannot reveal the entire hydrocarbon chain, and thereby the obtained information can be considered more or less as the topology of the oil fraction, e.g., which kind of substructures are present in a particular hydrocarbon sample. The relative amounts of various substructures present in the oil sample can thus be estimated.

The results presented here illustrate some of the advantages of using neural networks in the analysis of complex spectroscopic data. There is no need to manually select or analyze the overlapping raw data, but it can directly be taken into the network.<sup>14,15,18–20</sup> Here it means that not all the substructures need to be identified, but the ANN analysis will automatically focus on the most relevant substructures of the compounds. If the experimental set up is such that quantitative aspects are incorporated in the data, the ANN analyses will also automatically make use of this information. Furthermore, the model generated by the training process of the network will allow for the assessment of the relative contributions of the different spectral resonances. This information can then supervise the research on the effects of these particular substructures. Indeed, in this work we have established such estimation for the viscosity index of the hydrocarbon based oil samples using the methyl resonances in the HSQC NMR spectra and concomitantly generated a 2D map for the relative contributions of the spectral data points. The ANN analysis revealed clear distinction in the relevance of the different methyl resonances in the estimation of the VI. An important demonstration here was that the ANN analysis, without a priori knowledge, pointed out the importance of the iso-paraffin substructures to the VI.

The analyses presented here illustrate that quantitative ANN analyses have apparent advantages in the case of complex spectral information and complicated associations. Moreover, the resulting assessment of the relative importance of the input variables will help in aiding the understanding of the relationships between the molecular structure as well as the composition and the (macroscopic) properties of the samples.

#### ACKNOWLEDGMENT

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