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Quantitative Analysis of Constituents in Heavy Fuel Oil by ^1H Nuclear Magnetic Resonance (NMR) Spectroscopy and Multivariate Data Analysis

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Characterization of heavy fuel oil (HFO) is highly important to ensure technically, economically, and environmentally proper operation of the engines and power plants that use this source of energy. This applies in particular to the shipping industry. Here, we demonstrate that the combination of standard ^1H nuclear magnetic resonance (NMR) spectroscopy and multivariate data analysis can be employed for quick and accurate extraction of parameters pertaining to the physical and chemical properties of complex suspensions, such as HFO. For 82 HFO samples of known origin, good prediction models were obtained for a large number of characterization parameters, including the calculated aromaticity index, the density, gross and net calorific values, and water and sulfur contents, as well as micro-carbon residue.

Introduction

There is a substantial need for analytical methods that can provide information about the constituents in complex mixtures of industrial interest. Such mixtures include all sorts of oil, such as crude oil, petroleum and derivatives thereof, biodiesel, and mixtures of vegetable oils. Our specific focus will be on heavy fuel oil (HFO), for which the need for characterization is urgent because of environmental concerns and the risk of engine failure in cases of inferior quality fuel. HFO is widely used in maritime shipping to power large marine and other vessels. Other uses for this black, low-grade fuel of tar-like consistency include the production of electricity and to fire blast furnaces in industry. HFO is derived from the distillation process of crude oil as a byproduct or residue, along with asphalt. Other commonly used names for this substance are residual fuel oil or bunker C.

HFO is a complex, highly heterogeneous mixture of saturated, unsaturated, and aromatic hydrocarbons, containing a number of additional elements, such as sulfur, vanadium, nitrogen, etc. The molecules contained within this mixture range from simple hydrocarbons to complex macromolecular structures.^{1–3} Because of the high level of complexity and the staggering number of individual, structurally different components, the complete qualitative and quantitative characterization of each constituent in the oil is beyond reach. This means that the primary aim of the analysts has been to find suitable physicochemical parameters that adequately characterize the oil sample at hand in the most time- and cost-efficient way. A number of such parameters has been developed and is currently in use in the shipping industry. These parameters include physical measures, such as the viscosity, density, calorific value, and sediment potential,

as well as the chemical content of elements, such as sulfur, aluminum, silicon, nickel, lead, and water. The procedures of extracting such data are often time-consuming and include the handling of organic solvents detrimental to the environment and the analyst. An alternative way of obtaining the required information is therefore highly desirable.

Fourier transform infrared (FTIR) and near infrared (NIR), in conjunction with multivariate data analysis, have been demonstrated to yield accurate, reliable, and fast results with respect to properties of middle distillate fuels, crude oils, and hydrocarbon mixtures.^{4–10} NIR and FTIR have proven useful to identify several important oil quality markers with reasonable spectral resolution and very high sensitivity. However, because of the requirements of clean surfaces and environments for the infrared light-based techniques, other spectroscopic techniques, such as mobile low-field nuclear magnetic resonance (NMR) spectroscopy, may be an attractive alternative candidate for an *in situ* installation (for immediate analysis) in the hot, dirty environment of the machine room on a large marine vessel. In comparison to NIR, NMR typically offers very good spectral resolution, which may be taken into advantage for qualitative and quantitative determination of a broader range of oil-quality markers. Different functional groups resonate in unique, well-resolved spectral regions, and this fact has established NMR as a highly discriminative and quantitatively reliable analytical technique.

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NMR is a nondestructive technique that can be integrated in a flow-through system and thus requires only a minimum of experimental handling. NMR is well-suited for the identification and quantification of different types of hydrocarbon and can provide information on the relative content of aliphatic, olefinic, and aromatic components. Several studies have been reported in which NMR has been used for the structural studies of petroleum constituents.^{11–16} Recently, ¹H NMR spectra of five different crude oils and one mixture in conjunction with multivariate statistical analysis were correlated to a number of physicochemical properties and standard distillation cut yields.¹⁷

In the present study, 83 HFO samples taken during the actual tanking of the oil have been analyzed and data from their ¹H NMR spectra, recorded using standard high-resolution, high-field NMR spectroscopy, have been evaluated statistically. The objective was to develop a chemometric model that allows for the easy prediction of physical and chemical properties of unknown HFOs with a minimum of sample handling in the present case using standard laboratory NMR equipment. This is a first important step toward our final goal to develop *in situ* mobile NMR analysis of oil constituents using mobile NMR equipment based on low-field NMR equipment.

Experimental Section

Sample Details. A total of 83 different HFO samples were evaluated in this study. The fuel oil samples were collected during the bunkering of the oil in various ports around the world and sent to Lloyd's Register's Fuel Oil Bunker Analysis and Advisory Service (FOBAS) for detailed physicochemical characterization. All of the physicochemical measurements were performed according to the available American Society for Testing and Materials (ASTM) standards.

Vessels containing the oil samples were heated in an oven kept at 55 °C. Prior to the transfer to NMR tubes using disposable syringes, the containers were manually shaken to improve homogeneous distribution of constituents over the full sample volume. The samples were used undiluted, and the total sample volume was approximately 1 mL in 5 mm standard NMR sample tubes. The samples were numbered consecutively from 1 to 83 in the random order in which NMR spectra were recorded.

Of the 83 samples, 1 sample (number 48, San Nicolas) was identified as an outlier and was consequently excluded from the data set. The remaining 82 samples were randomly divided into a training set of 72 samples and a test set comprising 10 samples.

NMR Measurements. The ¹H NMR measurements were performed on a Bruker Avance 400 MHz (9.4 T) spectrometer (Bruker BioSpin, Rheinstetten, Germany) at 50 °C. The NMR samples were preheated for at least 1 h in an oven kept at 52 °C. The temperature never exceeded 55 °C, and the samples were confined to an airtight container. The individual samples were swiftly transferred to the NMR spectrometer and left for at least 15 min to achieve thermal equilibrium before data acquisition. The magnetic field homogeneity was optimized by manual shimming on a standard dimethylsulfoxide (DMSO) sample prior to recording spectra for a series of HFO samples, and the same shim setting was used for all subsequent samples.

One-dimensional ¹H NMR spectra were recorded with a spectral width of 10 000 Hz, 16 384 points, and 16 scans, using a repetition

delay of 2.3 s. The longitudinal relaxation time, T_1 , of the protons in the individual samples was estimated to be in the range of 0.4–0.6 s at 50 °C, on the basis of inversion recovery measurements of three randomly chosen oil samples (sample numbers 23, 27, and 38). To monitor the effect of spectrometer drift and provide a means of correcting for this, spectra of a standard DMSO sample were recorded in between subsequent HFO samples. The free-induction decays (FIDs) were multiplied by an exponential weighting function corresponding to a line broadening of 5 Hz prior to Fourier transformation.

Data Analysis. Each spectrum was individually phased and manually baseline-corrected, although we envisaged no problems using automated procedures for these purposes. All spectra were aligned using the peak with the highest intensity (typically a group of overlapping CH₂ or CH₃ signals in the aliphatic region) to compensate for the distinct and reproducible shift that was observed. This shift, which differed from sample to sample, may be attributed to concentration effects,¹⁸ the presence of paramagnetic centers in the oil,^{19–21} or bulk magnetic susceptibility effects.²² It should be noted that this alignment can be performed automatically.^{23–25} For the present study, the alignment on the largest peak was considered adequate, fast, and reliable. In the chemometric analysis, the spectral area between 9 and –1 ppm was subdivided into 100 bins, each spanning 0.1 ppm. Small individual shifts related to pH, polarity, and concentration effects were found to be well-encountered by the binning procedure. Each data point was mean-centered and scaled to unit variance.

With the aim of establishing optimal conditions for extraction of quantitative information about HFO constituents with high accuracy and reliability, we performed a multivariate calibration, relative to the test set in Table 1. A multivariate calibration refers to the construction of a mathematical expression relating a property, such as content or physical parameter to the experimental data set, e.g., the absorbance as a function of the wavelength in a set of ultraviolet (UV) or IR spectra or, as in this case, the intensity as a function of chemical shift in a set of NMR spectra. One of the more popular ways of constructing this mathematical model is PLS. PLS stands for projections to latent structures by means of partial least-squares regression and is a method for relating two data matrices, X and Y , to each other by a linear multivariate model.²⁶ In the present case, the X matrix consists of the NMR spectra for all of the HFO samples in the calibration set, while the Y matrix consists of the associated physicochemical data sheet obtained from the laboratory analysis. Cross-validation was performed by systematically omitting parts of the data in the training set such that each data element is kept out once and only once. The number of cross-validation groups was 7. The multivariate data analysis performed during the present investigation was carried out using the SIMCA P 11.5 software (Umetrics, Sweden).

Results

The NMR spectra of the HFO samples showed fairly broad lines without many distinguishing features even at 50 °C. The

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Table 1. Values of Selected Physiochemical Parameters in the Test Set^a

sample	port of origin	CCAI	density (kg/L)	GCV (MJ/kg)	NCV (MJ/kg)	MCR (% w/w)	water (% v/v)	sulfur (% w/w)
10	Tanjung Pelepas	853	0.989 ± 0.0015	42.76	40.45	12.6 ± 1.3	0.4 ± 0.04	1.8 ± 0.16
20	Rotterdam	836	0.9756 ± 0.0015	43.24	40.88	12.14 ± 1.3	0	1.56 ± 0.14
36	New York	847	0.9858 ± 0.0015	42.55	40.26	15.89 ± 1.5	0.25 ± 0.025	2.8 ± 0.24
44	Kingston	827	0.9655 ± 0.0015	43.23	40.85	10.33 ± 1.2	0	2.08 ± 0.18
52	Fujairah	848	0.9864 ± 0.0015	42.59	40.29	17.8 ± 1.7	0.15 ± 0.015	2.76 ± 0.24
56	Ras Tanura	831	0.9657 ± 0.0015	42.61	40.27	12.9 ± 1.3	0.25 ± 0.025	3.62 ± 0.31
60	Kali Limenes	849	0.9883 ± 0.0015	42.34	40.05	16.4 ± 1.6	0.65 ± 0.065	2.7 ± 0.23
63	Kerch	831	0.961 ± 0.0015	43.26	40.87	8.15 ± 1	0.05 ± 0.005	2.2 ± 0.19
71	Dangjin	827	0.9574 ± 0.0015	42.99	40.62	9.59 ± 1.1	0	3.16 ± 0.27
83	Vlissingen	849	0.99 ± 0.0015	42.82	40.51	13.4 ± 1.4	0.1 ± 0.01	2.16 ± 0.19

^a The following abbreviations were used: CCAI, calculated carbon aromaticity index; GCV, gross calorific value; NCV, net calorific value; and MCR, micro-carbon residue. The uncertainty is given in the form of reproducibility.

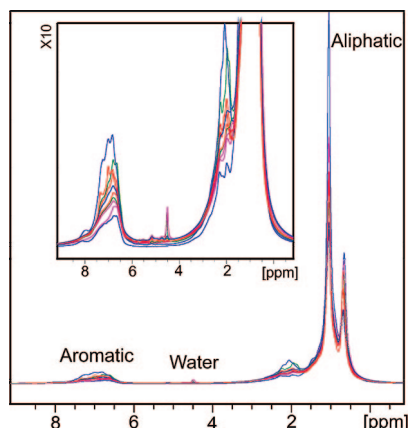


Figure 1. Overlay of 10 representative ¹H NMR spectra of HFO samples (recorded at 50 °C) with an indication of typical spectral components.

spectra were comparatively similar at a first glance, but closer inspection revealed a large variation in intensities of the different parts of the spectra. Figure 1 shows an overlay of 10 representative spectra after alignment of the most intense peak.

Because of the crowded and highly overlapping nature of the NMR spectra, it is not possible to perform any detailed atomic or molecular assignments. It is, however, possible to assign distinct structural regions to different functional groups in the HFO.^{16,17} The region with the lowest chemical shift originates from aliphatic hydrogen atoms. The peak at around 0.5–1.0 ppm can be ascribed to aliphatic CH₃ groups and is as such related to the molar amount of aliphatic constituents in the oil. The aromatic region spans from 6.5 to 8.5 ppm. The signals in the higher end of this scale originate from aromatic protons in higher aromatic systems, such as naphthalene rings. The aromatic signal intensity has a high degree of correlation to the intensity in the region between 1.5 and 2.5 ppm, where CH₃ groups attached to aromatic ring systems resonate. One of the interesting components in the HFO is water. Ideally, the oil should not contain any water because it is detrimental to the engine or furnace and does not have any fuel value. Water gives rise to a resonance near 4.5 ppm in the central region of the spectrum at 50 °C. The exact position of the water resonance is highly sensitive to pH, polarity of the medium, and temperature,²⁷ and the water peak is indeed the peak showing the largest variability with respect to position after the alignment of the spectra. This variability is well-accounted for by the binning and thus does not disturb the analysis.

The distinct, characteristic shift of each spectrum necessitating the alignment was investigated with respect to possible cor-

relations with the 20 measured parameters. It was found to correlate strongly with the calculated carbon aromaticity index (CCAI),²⁸ with a correlation coefficient of $\rho = -0.92$. That is, the larger aromatic fraction in the HFO, the larger shift of the spectrum. This lends credibility to the idea that this effect is due to the different bulk magnetic susceptibilities of the differently composed liquids or perhaps to a lesser extent the presence of paramagnetic systems in the form of free radicals stabilized by the aromatic compounds in the HFO. The shift of the spectra was included along with the spectral intensity data as an experimental variable in the following data treatment.

Data Analysis. The available laboratory reference data for the HFO samples included information on the content of aluminum, silicon, lead, calcium, iron, nickel, phosphorus, sulfur, vanadium, sodium, zinc, and water, in addition to data on the calculated carbon aromaticity index (CCAI), the density at 15 °C, gross and net calorific values (GCV and NCV, respectively), the viscosity at 50 °C, ash content, total sediment accelerated, and micro-carbon residue (MCR). Of these parameters, the chemometric investigation revealed a good predictive correlation between ¹H NMR spectra and CCAI, density, GCV and NCV, MCR, and sulfur and water contents. Values of these parameters for 10 samples comprising the test set are shown in Table 1, while a more extensive overview of the parameters for all 83 samples can be found in the Supporting Information.

Principal Component Analysis (PCA). To obtain an overview and a deeper understanding of the data set, PCA was performed on both the NMR and physicochemical data. The statistically significant number of principal components is assessed by cross-validation.^{26,29} PCA on the X block (i.e., NMR spectra for all 83 samples) returned 12 significant components. Inspection of the distance to model for the X block, called DModX, indicated that one sample (number 48, San Nicolas) was different from the rest of the data set and was thus a possible outlier. Spectroscopically, the distinguishing feature of this sample was the presence of a large water signal. This sample was found to have a detrimental effect on the prediction model and was therefore removed in the further data treatment. A second round of PCA on the remaining 82 samples returned five significant principal components, among which the first two components described 77% (50.2% PC1 and 26.4% PC2; Figure 2a) of the variation, while the least dominant component (PC5) accounted for 3.1%. The loading plot for the two first components (Figure 2b) reveals that these factors reflect the relative amounts of aromatic and aliphatic proton signals in the NMR spectra.

It is evident from Figure 2 that the two components describing the largest variation in the data set offer a good discrimination

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(28) $CCAI = D - 140.7 \log(\log(V + 0.85)) - 80.6 - 483.5 \log((T + 273)/323)$, where D is the density (kg/m³) at 15 °C and V is the viscosity (cSt) measured at T (°C).

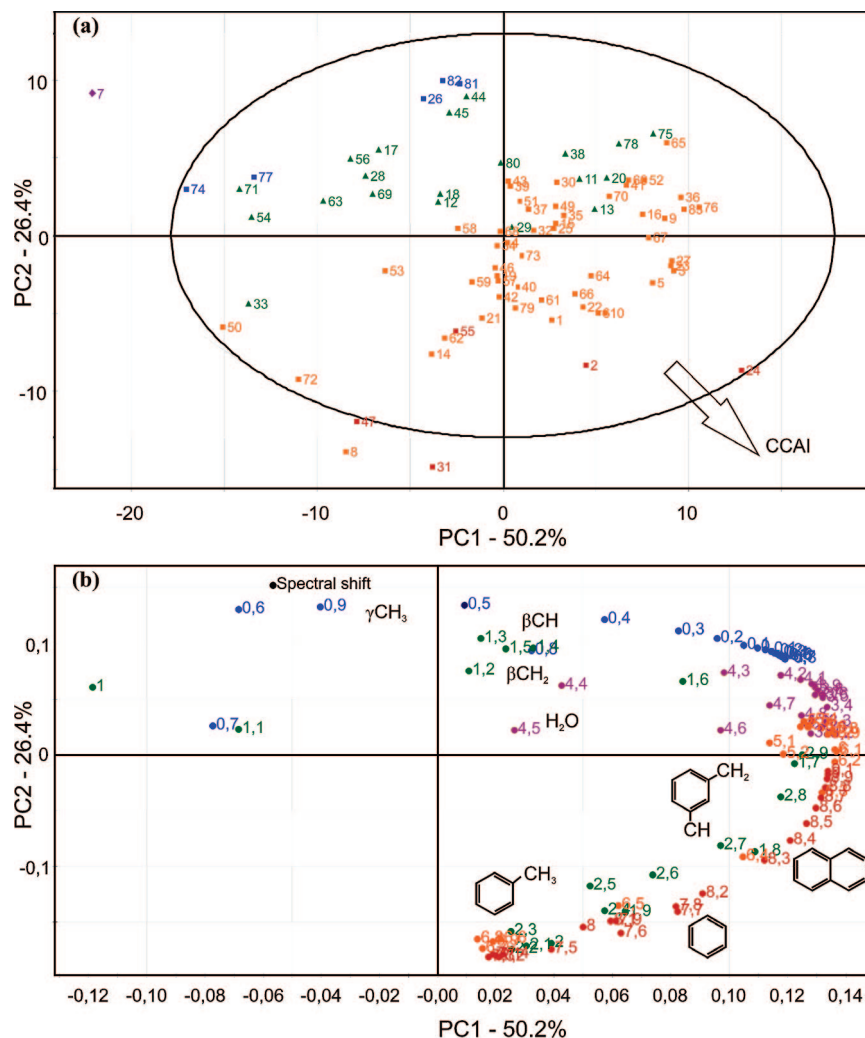


Figure 2. (a) Score plot of 82 HFO samples analyzed by NMR. The samples are colored according to their calculated carbon aromaticity index (CCAI): 794–810, purple; 810–825, blue; 825–840, green; 840–855, orange; 855–871, red. The number refers to the sample number. (b) Loading plot corresponding to the score plot shown in a. The numbers denote chemical shifts, which furthermore are grouped by colors according to their values: -8 – 1 ppm, blue; 1 – 3 ppm, green; 3 – 5 ppm, purple; 5 – 7 ppm, orange; 7 – 10 ppm, red. Assignments of some of the chemical-shift regions are indicated.

between samples with a high content of aromatic compounds and more aliphatic-containing samples. Sample 7 (Benghazi) is positioned well outside the Hotelling T2 ellipse delineating the 95% confidence interval. This sample is characterized by having the lowest aromatic content and is concomitantly the sample with the lowest CCAI, lowest density, lowest sulfur content, and the highest calorific value. Accordingly, this sample was further examined with respect to it being a possible outlier. No further sign of sample 7 being an outlier, however, was discovered when inspecting the distance of the observation in the training set to the X model plane or hyperplane (DmodX) or in the T2 range plot, which displays the distance from the origin in the model plane. Furthermore, it was found that omitting this sample had a detrimental effect on the predictive power of the subsequent PLS model. Sample 7 was therefore kept as an important delimiting member of the training set.

PCA on the Y matrix (i.e., the laboratory analysis data set) resulted in three significant components that in total describe 55% of the variation among the 20 measured parameters. A 3D loading plot (Figure 3) revealed tight correlations between the physicochemical parameters measured in the HFOs. It was found that aluminum and silicon are tightly correlated. The amount of these elements in the HFO is predominantly due to the remainder of catalysts from the cracking procedure during

the refinement of the crude oil. CCAI and density are closely correlated, which is to be expected because CCAI is calculated from the density and viscosity. Gross and net calorific values are almost perfectly correlated. This is also quite understandable because the net calorific value is calculated on the basis of the gross calorific value.

Less tight correlations were also found. The amount of sulfur and the calorific value are positioned opposite each other in Figure 3 and thus indicate that sulfur and the calorific values are anticorrelated. Phosphorus and zinc are loosely correlated, and finally, nickel and vanadium show a common trend.

The PCA analysis of both matrices also indicated that the data set is homogeneous without any distinct groupings.

Projections to Latent Structures by Means of Partial Least-Squares. The samples were subsequently divided into a training set and a randomly chosen test set consisting of 10 samples (see laboratory analysis of the test set in Table 1). The 72 samples in the training set were subjected to a preliminary PLS run, in which all 20 physicochemical variables were included. It was immediately evident that some of the parameters could not be described in terms of the NMR data. These include the total sediment accelerated as well as

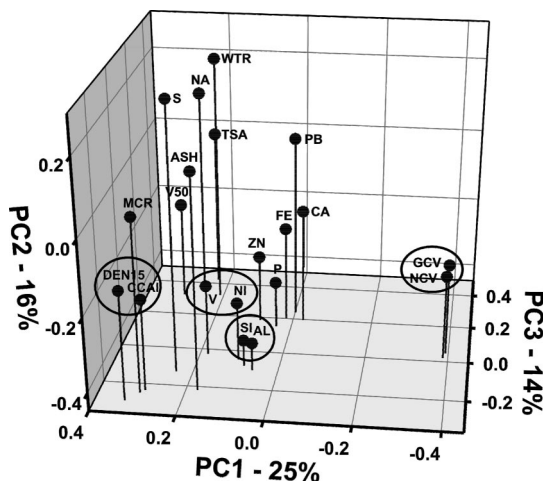


Figure 3. Three-dimensional loading plot of the laboratory data set of the 82 HFO samples. Pair-wise correlated parameters are indicated by circles. In addition to the quantities defined in Table 1, the figure contains the following parameters: ASH, content of ash; V50, viscosity at 50 °C; TSA, total sediment accelerated; FE, content of iron; PB, lead content; AL, aluminum content; P, phosphorus content; SI, silicon content; ZN, zinc content; NA, sodium content; CA, calcium content; NI, nickel content; and V, vanadium content.

Table 2. Description and Statistical Summary of the PLS Model Constructed on the Basis of NMR Data

parameter	$R^2Y(\text{cum})^a$	$Q^2Y(\text{cum})^b$	RMSEEC ^c	RMSEP ^d
CCAI	0.92	0.86	3.44	1.39
density at 15 °C	0.90	0.86	0.004	0.002
GCV	0.84	0.69	0.22	0.08
NCV	0.84	0.68	0.21	0.07
MCR	0.73	0.63	1.61	0.81
sulfur	0.72	0.60	0.53	0.29
water	0.88	0.75	0.20	0.13

^a $R^2Y(\text{cum})$ = the cumulated fraction of the variance in the parameter explained by the model. ^b $Q^2Y(\text{cum})$ = the cumulative predicted fraction of the variation of the parameter as determined by cross-validation. ^c RMSEE = root-mean-square error of the fit for the observations in the training set. ^d RMSEP = root-mean-square error of the prediction for observations in the test set.

the calcium, lead, phosphorus, sodium, and zinc contents because the predictability of these parameters in terms of $Q^2Y(\text{cum})$ turned out negative. The criteria that $Q^2Y(\text{cum})$ should be above 0.50 ruled out the contents of ash, aluminum, iron, nickel, silicon, and vanadium as predictable parameters. However, a number of properties were found to be quite well-predicted from the NMR data, and a further refinement of the PLS model was performed for these. The selected parameters included CCAI, density at 15 °C, GCV and NCV, MCR, and the sulfur and water contents. A refined model consisting only of these seven physicochemical parameters was constructed. The calculated PLS model contains six significant PLS components describing in total 92% of the spectral variation [$R^2X(\text{cum})$] and explaining 72–92% [$R^2Y(\text{cum})$] of the variation in the seven physicochemical parameters (Table 2).

The performance of the chemometric prediction model was tested against 10 samples not used during the construction of the model. All 10 samples were shown to be well-described by the model as gauged by their DModX values. The actual

versus predicted values for the test set can be seen in Figure 4. A good prediction of the unknown values was demonstrated.

Discussion

It is evident from the analysis above that ^1H NMR allows for fast and reliable determination of numerous parameters of importance for the quality of HFO. Among these range in particular the CCAI, the density at 15 °C, the MCR, and the sulfur content, while valuable information may also be obtained for the water content and gross and net calorific values. ^1H NMR was unable to predict the content of calcium, lead, phosphorus, sodium, zinc, and the total sediment accelerated. Weak correlations were observed for the contents of ash, aluminum, iron, nickel, silicon, and vanadium. In a previous NMR study of crude oils, correlations were found between the NMR data and the content of vanadium and nickel.¹⁷ It was speculated that this effect is due to the paramagnetic properties of these atoms, affecting neighboring protons and thus, indirectly, affecting the entire ^1H NMR spectrum. This seems like a plausible explanation, which in this study can be extended to also account for the weak correlations observed for iron and aluminum.

Addressed in more detail, it is apparent that the CCAI and the density measured at 15 °C displayed tight regression curves (Table 2 and Figure 4) with a goodness of fit, R^2Y , above 0.9. The cumulated Q^2Y for both parameters is over 0.85, indicating a very high degree of predictive power as gauged by cross-validation. CCAI is calculated on the basis of the density and viscosity and is used as an indicator of the ignition quality of the fuel. The NMR method offers a fast and less cumbersome way of measuring this property.

Further investigation of the coefficients calculated by the PLS procedure revealed which parts of the NMR spectrum are important for the prediction of the various chemical and physical parameters. Figure 5 depicts the coefficients important for the determination of the density at 15 °C. As seen in the figure, the intensity in the aliphatic region contributes negatively to the predicted value, whereas the aromatic region around 7.5 ppm gives a small positive contribution. A positive contribution is also seen for the region containing aliphatic protons attached to aromatic ring systems. These effects mean that highly aromatic oils are predicted to have a high density and oils containing a high fraction of aliphatic compounds tend to have a lower density. The same trend is observed for the CCAI. That is, the more aromatic content of the oil, the higher predicted the CCAI.

The gross and net calorific values as well as water content displayed goodness of fit values above 0.8. These parameters also relay information on the quality of the fuel. The regions most important for the determination of these entities were found to be positioned around 1.5, 0.7, and 0.5 ppm, with a negative contribution from the region around 2.5 ppm.

The MCR is an important parameter that is related to the propensity of the oil to form carbon deposits.^{1,30} MCR is correlated with the content of asphaltene and is therefore connected to the stability of the fuel oil. The stability of the fuel oil is an important factor when two different fuel oils are mixed. The mixture of two incompatible fuels leads to extensive formation of solid material, with devastating effects in the case where the precipitation takes place in the engine or tank of a HFO-powered ship or power plant. The prediction of incompatibility between two HFOs is, however, not straightforward and relies on many other factors than MCR

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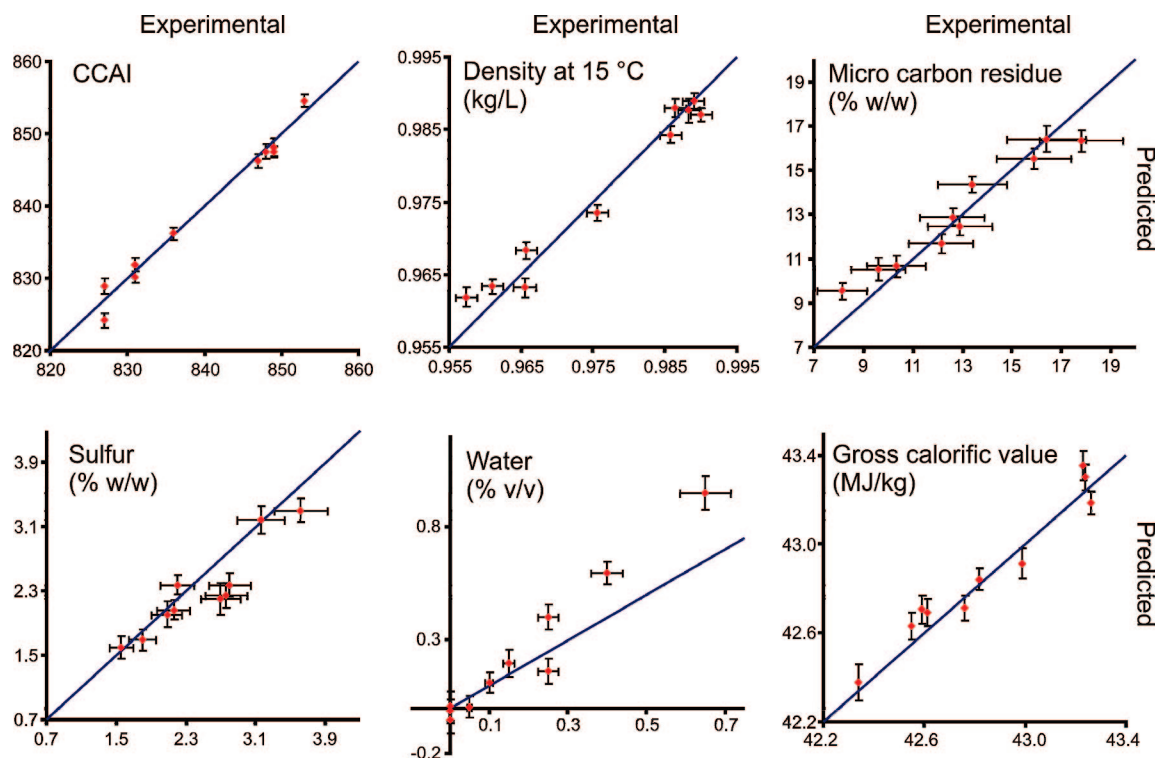


Figure 4. Predicted values for the test set obtained by the NMR-PLS method plotted against experimental values determined using traditional methods. The predicted values are plotted with standard error bars, and the experimental values are plotted with reproducibilities, where available. The plot for NCV strongly resembles that of GCV and is therefore omitted.

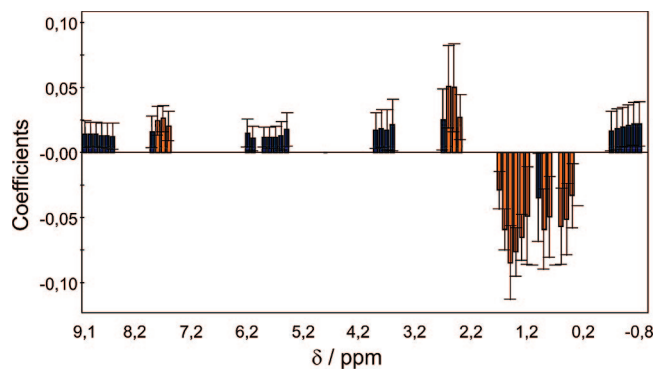


Figure 5. Coefficients used to predict the density at 15 °C. Nonsignificant coefficients have been deleted for clarity. The most important coefficients as judged by their magnitude in conjunction with their error bars are indicated in orange. Error bars represent 95% confidence intervals.

alone. The MCR shows a goodness of fit of 0.72 and a cumulated Q^2Y of 0.63. The important parts of the NMR spectrum to predict this parameter is the region from 4.7 to 6.2 ppm, as well as small contributions from the 3.2–3.7 region and small negative effects from the aliphatic region around 1 ppm.

Somewhat surprisingly, the content of sulfur could to a fairly good degree of certainty be quantified using just the ^1H NMR spectrum. The reason for this correlation can be speculated to stem from the characteristic types of sulfur compounds typically found in crude oil. These compounds have been demonstrated to primarily consist of alkyl sulfides and thiols, thiophene, benzothiophene, and dibenzothiophene.³¹ An inspection of the important coefficients used to construct the prediction model for sulfur revealed that the content of this element was primarily determined by signals in the chemical-shift region between 2.1

and 3.0 ppm. Interestingly, protons in alkyl groups close to the sulfur atom in sulfides typically resonate in this spectral region.

The model for the water content in the HFO was the least well-determined. As can be gauged from Figure 4, water was overpredicted for the two samples containing the largest amount of water. This may be rooted in the fact that very few samples in the data set had high values of water, and as such, the calibration was less good for samples containing more water. It may also be a consequence of the mixing procedure prior to sampling of the data. In any case, the present experimental procedure used to measure the water content in HFO samples is quite laborious and time-consuming, which makes NMR an attractive alternative. Inspection of the coefficients returned by the PLS show that the only significant contribution from the spectrum to the prediction of water comes from the chemical-shift bins centered around 4.5 ppm, which is in perfect agreement with the resonance frequency for water at this temperature.

Conclusions

^1H NMR spectroscopy in combination with chemometrics provides a fast and reliable way of obtaining physicochemical data on HFO. Furthermore, the use of this technique abolishes the need for extensive handling and sample preparation, which more than compensates for the higher cost associated with an NMR spectrometer. In the present study, good predictive models were obtained, relating physical properties and chemical content of HFO to ^1H NMR spectra. These models can be used on unknown oil samples to predict properties, such as the ignition quality (CCAI), the propensity to form carbonaceous deposits (MCR), the content of water, which may be a key component in the corrosion of the engine, and the content of sulfur, which is a cause of environmental

concern, as well as an idea of the energy content stored within the fuel (GCV and NCV).

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Supporting Information Available: Data on all 20 physico-chemical parameters for the 83 samples investigated in this study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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