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The characterization of heavy fuel oils (HFOs), used as fuel for boats, requires the analysis of various properties that are essential for engine optimization and pollution control. For some time, near-infrared (NIR) spectroscopy combined with chemometric treatment of the spectra was used for on-line analysis. This preliminary study included 61 heavy fuels from Europe, America, and Asia with different specifications according to their geographical origin; their refining process; and their physicochemical properties, including density, flash point, viscosity, and sulfur content. We have developed a new method for sampling heavy fuels on a fiberglass cell support. This support offers the advantages of speed, easy implementation, repeatable results, and freedom from problems associated with tank cleaning. Two sample presentations, an integrating sphere and an optical fiber, were used to collect the NIR spectra. A theoretical study of the choice of the value of resolution, scan number, and spectral region was conducted. The best conditions were chosen as a function of the quality of quantitative analysis results on viscosity, sulfur content, flash point, and density. The two collecting methods were compared on the same criteria.

Index Headings: **Fuel; Near-infrared; NIR; Calculated carbon aromaticity index; CCAI; Sulfur content; Soft independent modeling of class analogy classification; SIMCA; Partial least squares; PLS.**

INTRODUCTION

Heavy fuel oils (HFOs) are products of crude oil refining after a distillation process. According to the nature of the refined crude oil, 10–20% of it is separated out as HFOs. These heavy fuels are mainly used in boats and power stations. Very complex matrices consisting of chains of hydrocarbons, HFOs have degrees of alkylation between 25 and 200 atoms of carbon. These samples also contain high levels of heteroatoms, such as sulfur, nitrogen, and oxygen, as well as metals, including nickel and vanadium. The characterization of HFOs requires the analysis of selected chemical and physical properties. The properties of HFOs depend on the geographical origin of crude oil and on the refining processes. For example, Venezuelan crude oil is known for its high ash content, whereas crude oils from the Middle East generally have low sulfur content. The HFOs obtained from those crude oils will present different physicochemical characteristics. For an engine to run optimally, it is essential to have a basic understanding of such fuel characteristics and properties as viscosity,[1] carbon residue, vanadium content, calculated carbon aromaticity index (CCAI), and flash point, and such contaminants as nitrogen and water,[2] which affect fuel handling and fuel treatment systems. Although heavy fuels must be in accordance with the specifications required in all countries, the complexity of the refining of crude oils influences the variability of the quality of finished products. Recently, infrared and fluorescence measurements have been used in petroleum development. Investigations studied tank continuity[3] and evaluated thermal maturity.[4,5] Among several methods of spectroscopic data interpretation, we highlight the studies of Kister et al.[6,7] wherein indexes have been calculated from areas of absorption bands to describe the global structure of oils by Fourier transform infrared spectrometry (FT-IR) and their aromatic structures by synchronous excitation–emission ultraviolet fluorescence. Fourier transform infrared spectrometry was used to determine aliphatic, aromatic, and functionalized compounds for each oil, whereas the condensation degree of aromatic rings has been evaluated by synchronous ultraviolet fluorescence analysis.[8–10] Traditionally, spectral analysis by chemometrics proved their relevance to analysis of crude oils,[11,12] petroleum fractions such as gasoline,[13] and lubricant oils.[14] Near-infrared spectroscopy[15] was used to control the oil refining process. In this work, a new methodology for heavy fuels analysis is proposed, with a new sampling method for heavy fuels. This new sampling technique was tested to develop calibrations for some physicochemical parameters of the fuel samples to determine whether they could be recognized as conforming to international standards. Simultaneously, the same analysis could be done on the spectral data to confirm the diagnostic obtained on the physicochemical parameters. Then, the main parameters, such as density, CCAI, and viscosity, and nitrogen, vanadium, sulfur, and carbon residue contents, could be predicted using chemometric treatment of spectra. Furthermore, these data are relevant to combustion parameters.

MATERIALS AND METHODS

New Diffusing Support. A fiberglass cell support (Fig. 1) was tested in this study. This commercial product (provided by the Duran Group) has the following characteristics: a 15 mm diameter, a porosity of 2, and 10 St/pcs. Different tests were carried out to define the optimal volume of sample to be used, by considering HFOs with lower and higher viscosities. This support allowed the collection of repeatable NIR spectra of HFOs, by using the constant volume of HFO of 340 μL to be impregnated.

Near-Infrared Spectra. The NIR heavy fuel spectra were recorded with a Nicolet Antaris spectrometer,

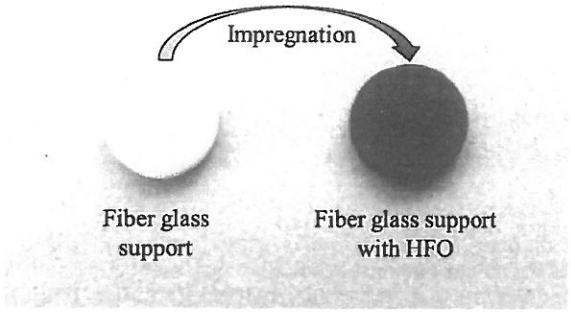

FIG. 1. Fiberglass support before and after impregnation with HFO.

equipped with an indium gallium arsenide detector, an I_2 NIR source, and a calcium fluoride/Ge beam splitter. The measurements were carried out in an air-conditioned room at 21 °C. Fourier transform NIR spectra were recorded by collecting the NIR energy that scatters on the surface of sample, by using an integrating sphere with an accumulation of 64 scans and an optical fiber with an accumulation of 800 scans, with the surface of the fiber end directly in contact with the surface of the sample to be analyzed. All spectra were computed with a 4 cm^{-1} resolution, between 4000 and 10 000 cm^{-1} (1100–2500 nm), using Result Integration 2.1 software (Thermo Nicolet). A background spectrum was collected under the same conditions before each batch measurement.

Sampling for Near-Infrared Spectroscopy. Sixty-one samples of HFOs were collected from several countries; the reference analyses were conducted by Société Générale de Surveillance (SGS). For each sample, 340 μL of HFO was placed onto a fiberglass support. Each spectrum used for the classification was the average of two independent spectra obtained with two different fiberglass supports.

Principal Component Analysis (PCA). Principal component analysis is an "unsupervised" method describing a data set without any a priori knowledge of the data structure.[16] PCA is oriented toward modeling the variance–covariance structure of the data matrix into a model that is based on the significant differences (significant scores) and considers noise as an error. Data are first centered and reduced, and principal components (PCs) are all orthogonal to each other. The number of PCs depends on the model complexity, but the scores have to represent the best of variance of data and explain a large part of the total variance. The first component extracts the largest source of variance. The scores and loadings of the individual PCs are recovered from each PCA model. Scores describe the variation in the samples compared with the dataset, whereas loadings describe the correlations among variables. Each vector of stone features can be considered in the space defined by the PCs as values called component scores.

Soft Independent Modeling of Class Analogy Classification (SIMCA). Soft independent modeling of class analogy (SIMCA) is the most supervised pattern recognition used of the class-modeling techniques.[17] SIMCA classification is based on disjoint PCA modeling realized for each class in the calibration set. Unknown samples are then compared to the class models and assigned to classes according to their analogy with the calibration samples. A new sample will be recognized as a member of a class if it is similar enough to the other members; otherwise, it will be rejected. Each class is modeled using separate PCA models. A model distance limit called *Smax* is used for classifying new samples, and *Smax* is calculated for the class model *m* as follows:

$$Smax(m) = S_0(m)\sqrt{F_c} \qquad (1)$$

where S_0 is the average distance within the model and F_c (Fisher criterion) is the critical value provided by the Fisher–Snedecor tables. The F_c value depends on the percentage of risks and is generally set to 5%.[11] Class membership is defined at a significance level of 2.5% of *Smax*. Mean centering is applied before modeling. The number of samples used in PCA is 29, and the prediction set was formed by 32 samples.

Partial Least Squares (PLS) Regression. This supervised analysis is based on the relation between the signal intensity and the Y variable.[18] Interference and overlapping of the spectral information may be overcome by using a powerful multicomponent analysis, such as PLS.[19] This method is a sophisticated statistical approach using the full or partial spectral region rather than unique and isolated analytical bands. The algorithm is based on the ability to mathematically correlate spectral data to a property matrix of interest while simultaneously accounting for all other significant spectral factors that disturb the spectrum. It is thus a multivariate regression method that uses the full spectral region selected and is based on the use of factors. Models were built with a full cross-validation method during the calibration developments. The evaluation of the errors in the calibration was carried out by computing the standard error of calibration (*SEC*) after comparing the real concentration with the computed concentration for each component. The formula for the *SEC* is as follows:

$$SEC = \sqrt{\frac{\sum_{i=1}^{N}(C_i - C'_i)2}{N-1-p}} \qquad (2)$$

where C'_i is the known value, C_i is the value calculated by the calibration equation, N the number of samples, and p is the number of independent variables in the regression optimized by cross-validation. The standard error of prediction (*SEP*) gives an estimation of the prediction performance during the step of validation of the calibration equation below:

$$SEP = \sqrt{\frac{\sum_{i=1}^{N}(C_i - C'_i)2}{M}} \qquad (3)$$

where M is the number of samples in the prediction set.

All models were built by full cross-validation.

TABLE III. Results obtained using integrating sphere in the spectral range 6500-5000 cm^{-1}.

NIR2[a]	Range	R^2	RMSEC[b]	LV[c]	r^2	RMSEP[d]
CCAI (a.u.)	867–789	0.96	3.53	8	0.87	8.78
Density (kg/m^3)	1007–941	0.82	10.97	4	0.72	9.39
Carbon residue % (w/w)	16.7–7.7	0.89	1.07	7	0.68	1.29
Sulfur % (w/w)	0.22–3.49	0.82	0.51	6	0.81	0.55
Vanadium (ppm)	2–365	0.83	50.87	7	0.7	59.89
Nitrogen (ppm)	5175–1959	0.60	543	4	0.66	667
Net energy (MJ/kg)	41.82–39.81	0.89	0.20	7	0.84	0.24

[a] NIR2, ; a.u., arbitrary units; ppm, parts per million.
[b] RMSEC, root mean square error of calibration.
[c] LV, latent variable.
[d] RMSEP, root mean square error of prediction.

TABLE IV. Results obtained using fiber optic in the spectral range 4000-5000 cm^{-1}.

NIR1'[a]	Range	R^2	RMSEC[b]	LV[c]	r^2	RMSEP[d]
CCAI (a.u.)	867–789	0.82	7.52	5	0.69	15.37
Density (kg/m^3)	1007–941	0.79	8.62	5	0.73	14.97
Carbon residue % (w/w)	16.7–7.7	0.80	1.24	5	0.80	1.39
Sulfur % (w/w)	0.22–3.49	0.67	0.66	5	0.62	0.71
Vanadium (ppm)	2–365	0.92	32.05	9	0.74	63.86
Nitrogen (ppm)	5175–1959	0.55	590	4	0.27	741
Net energy (MJ/kg)	41.82–39.81	0.78	0.26	5	0.73	0.35

[a] NIR1', ; a.u., arbitrary units; ppm, parts per million.
[b] RMSEC, root mean square error of calibration.
[c] LV, latent variable.
[d] RMSEP, root mean square error of prediction.

TABLE V. Results obtained using fiber optic in the spectral range 6500-5000 cm^{-1}.

NIR2'[a]	Range	R^2	RMSEC[b]	LV[c]	r^2	RMSEP[d]
CCAI (a.u.)	867–789	0.79	8.22	4	0.7	15.26
Density (kg/m^3)	1007–941	0.80	8.82	4	0.70	15.42
Carbon residue % (w/w)	16.7–7.7	0.86	1.05	6	0.77	1.58
Sulfur % (w/w)	0.22–3.49	0.95	0.27	10	0.81	0.52
Vanadium (ppm)	2–365	0.78	54.48	6	0.71	67.59
Nitrogen (ppm)	5175–1959	NC	NC	NC	NC	NC
Net energy (MJ/kg)	41.82–39.81	0.91	0.17	8	0.81	0.32

[a] NIR2', ; a.u., arbitrary units; ppm, parts per million.
[b] RMSEC, root mean square error of calibration.
[c] LV, latent variable.
[d] RMSEP, root mean square error of prediction.

analyser must have to be as cheaper as possible, what induces a right choice of spectral range.

Two spectral ranges were compared using the two sampling methods: 4000–5000 cm^{-1} attributed to the combination of C–H or C–O and 6500–5000 cm^{-1}, corresponding to the first overtone. The optimal factor was chosen as a function of the quality of quantitative analysis results on the viscosity, sulfur content, flash point, and density using a full cross-validation. For the integrating sphere, in the 4000–5000 cm^{-1} spectral range, the results (Table II) were very good for CCAI, density, nitrogen content, and energy and good for carbon residue and sulfur and vanadium contents. Concerning vanadium content, NIR enables to study interactions between vanadium and other functional groups, but not metal absorption directly. It should be noted that sulfur is much more concentrated in heavy fuels than in other fuels, such as gasoline and diesel, with a wide range according to the known origins. In the 6500–5000 cm^{-1} range, the results (Table III) were very good for CCAI, density, nitrogen content, and energy and good for carbon residue and sulfur and vanadium contents. It was possible to see a slight degradation of the results in this range compared with the previous analyses.

For the fiber optic in the region 4000–5000 cm^{-1}, the results (Table IV) were good, but the precision of values predicted decrease compared to the results obtained from spectra collected with the integrating sphere. The impact of the loss of scattering was visible. With the fiber

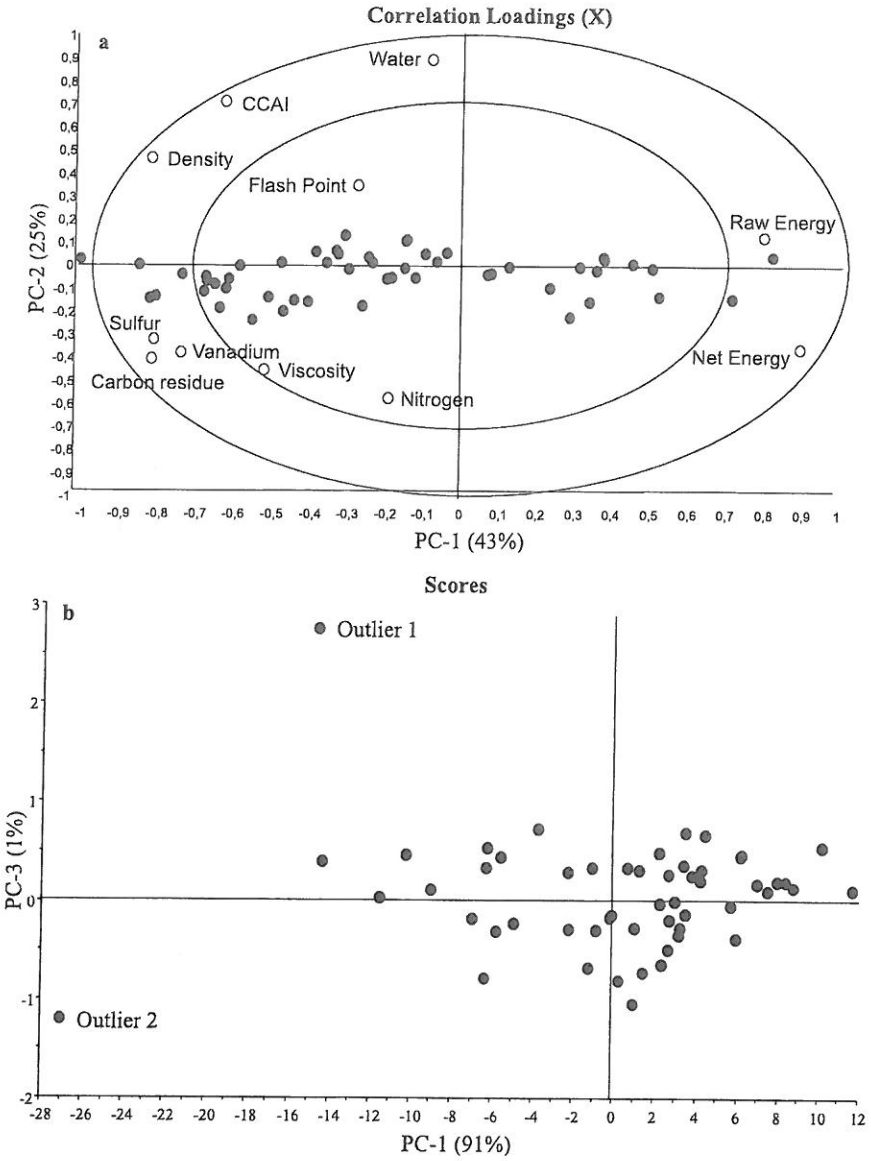

FIG. 4. PCA results on reference data (**a**) and NIR data (**b**).

?11 **TABLE II. Results obtained using integrating sphere in the spectral range 4000–5000 cm^{-1}.**

NIR1[a]	Spectral range (cm^{-1})	R^2	RMSEC[b]	LV[c]	r^2	RMSEP[d]
CCAI (a.u.)	867–789	0.91	5.61	4	0.85	5.75
Density (kg/m^3)	1007–941	0.84	10.43	4	0.72	9.04
Carbon residue % (w/w)	16.7–7.7	0.88	1.14	7	0.82	1.02
Sulfur % (w/w)	0.22–3.49	0.91	0.37	7	0.91	0.38
Vanadium (ppm)	2–365	0.74	61.93	5	0.7	57.26
Nitrogen (ppm)	5175–1959	0.77	426	8	0.75	510
Net energy (MJ/kg)	41.82–39.81	0.90	0.20	7	0.89	0.20

[a] NIR1, ; a.u., arbitrary units; ppm, parts per million.
[b] RMSEC, root mean square error of calibration.
[c] LV, latent variable.
[d] RMSEP, root mean square error of prediction.

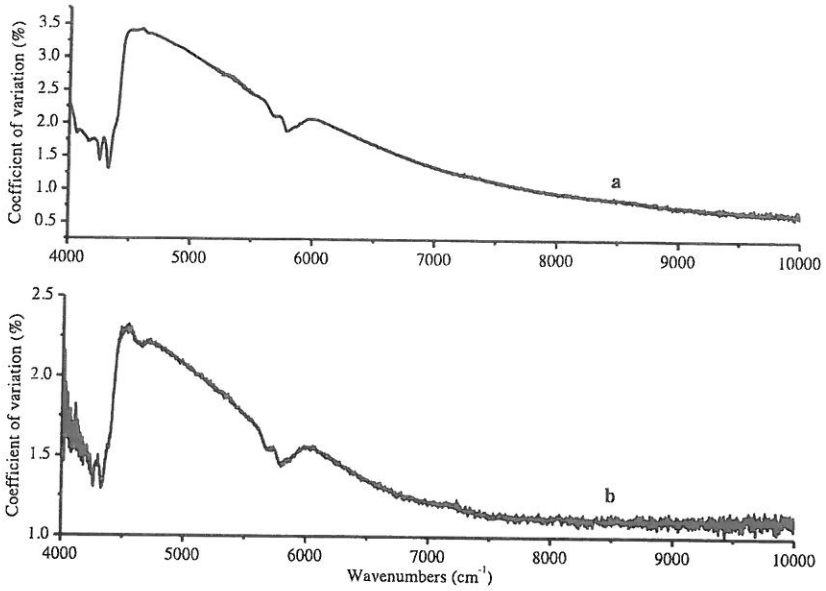

FIG. 3. Coefficient of variation for spectra of HFO collected using an integrating sphere (a) and optical fiber (b).

in the Fig. 4a for the reference data and in Fig. 4b for the integrating sphere data. For the reference data, the two first PCs represented 68% of the total variance (43 and 25%, respectively). Two samples were outliers: Outlier 1 and Outlier 2. The examination of the correlation loadings given in Fig. 4a showed that Outlier 1 presented high water content and Outlier 2 low viscosity and high energy values. For the NIR data, in the space of the first and third PCs, corresponding to 92% of the spectral variance, the same samples could be reported as outliers. Similar results were obtained for spectra collected with the optical fiber. Given that the same samples could be excluded by the two methods, discriminant analysis could be used to explore the conformity of heavy fuels samples. Twenty-nine samples with good-quality results, from several countries, were used to control the conformity of all the other samples by using SIMCA analysis. The 32 other samples were classified by using the model built from the first set of 29 samples. Identification allows assigning new objects to the class to which they show the most similarity. The results obtained for all the samples used in the prediction set show that two samples were rejected, again the same samples as those in the PCA step, whereas all the other samples are accepted as "conforming" samples. The total number of samples used in the study was 59. These physicochemical parameters are important for the fuel combustion process. The corresponding NIR spectra were pretreated by SNV correction to eliminate drift in baseline variation[24] before the construction of the PLS models. For the fiber optic sampling, the impact of the spectral resolution was studied on the carbon residue data (Table II). The calibration coefficient of determination appeared to be best at an 8 cm^{-1} resolution, but the predicted results were very poor; thus, 4 cm^{-1} resolution was selected for further analysis.

Different spectral ranges were studied to evaluate the ability to predict properties values, taking into account the purpose of the study—to develop an NIR analyzer. In particular, the detector that will be chosen to design this

TABLE I. Characteristic values of HFO used.

	Minimum	Maximum	Mean	Specification range	SD
Density (kg/m³)	920	1007	975	≤1010	20.2
Viscosity (mm²/s)	120	619.6	315	≤700	133.7
Carbon residue	7.7	16.4	12.8	Not specified	2.73
Sulfur % (w/w)	0.34	3.49	1.51	≤4%	0.91
Flash point	61	135	87	Not specified	19
Vanadium (ppm)[a]	2	283	104	Not specified	89
Nitrogen (ppm)	2260	4852	3584	Not specified	826
CCAI (a.u.)[a]	789	867	839	≤880	23
Energy (MJ/kg)	42.0	44.0	43	Not specified	0.6
Net energy (MJ/kg)	39.8	41.5	40.6	Not specified	0.5
Water % (w/w)	0	3.1	0.1	≤0.1	0.4

[a] ppm, parts per million; a.u., arbitrary units.

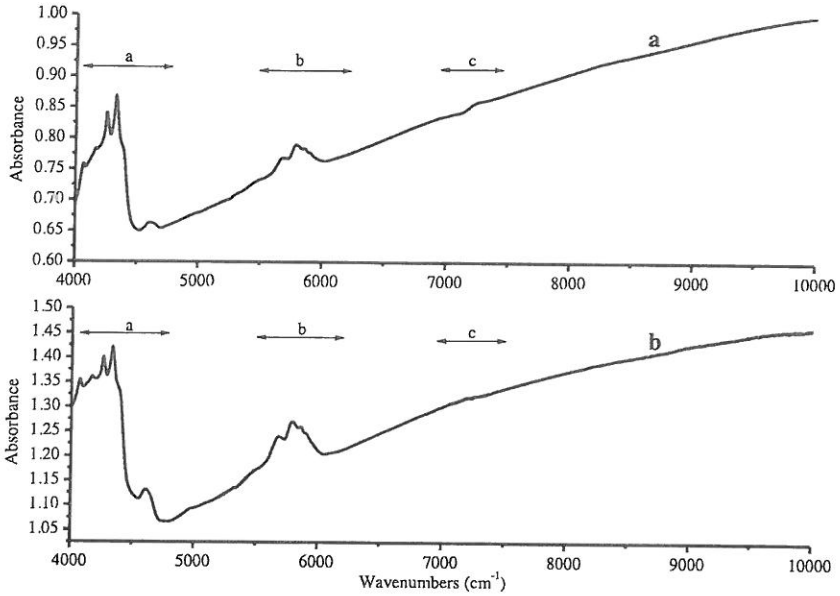

FIG. 2. NIR spectrum of HFO obtained using fiber optic (a) and an integrating sphere (b).
(line a) Combination of the CH stretching vibration with other vibrational modes.
(line b) First overtone of CH stretching vibration (methyl, methylene, and ethylene groups).
(line c) Combination of the CH stretching vibration.

Standard Normal Variate (SNV). During the data processing, the SNV correction pretreatment was used. This pretreatment is a row-oriented transformation that removes scatter effects from spectra by centering and scaling each individual spectrum.

Software. Chemometric applications are performed by The Unscrambler version X10.2 (Camo Software, Trondheim, Norway).

RESULTS AND DISCUSSION

Usually, for spectroscopic analysis, heavy fuels are placed into transmission cells with a short optical path as, for example, described by Laxalde et al.,[20] who used a 0.5 mm heated cell. This study was a part of a project whose objective was to develop an NIR analyzer, at line to control HFO quality. The use of solvents and the need to clean the transmission cell were not acceptable in terms of specifications in various cases (e.g., coal-fired power stations, boats). We developed a new method for the analysis of heavy fuels on a fiberglass support (Fig. 1). The use of fiberglass supports offered the distinct advantages of being fast and easy to implement and it provided repeatable results. The volume of sample was optimized to obtain a totally impregnated support without HFO oozing. In our case, 340 µL represented an appropriate compromise. Even if this value is not ideal, it is the same scale of size as the value used by Laxalde et al.[17] Two methods were used to collect the FT-NIR spectra:[21,22] an integrating sphere and an optical fiber. For the fiber optic method, the number of scans (800) accumulated to record the spectra was high to obtain a good signal-to-noise ratio. The spectra of the same sample obtained by both ways (Figs. 2a and 2b) showed some variations. The spectrum obtained using the fiber optic appeared to be less specific in the 4000–4500 cm^{-1} range, but the general aspect was similar: (1) combination of the CH stretching vibration with other vibrational modes, (2) first overtone of CH stretching vibration (methyl, methylene, and ethylene groups), and (3) combination of the CH stretching vibration.[23] To evaluate the repeatability of the sampling, the standard deviation was calculated on 10 spectra of a same sample (Figs. 3a and 3b). For each sample, two glass fibers were used to include the variability of the fiberglass support in the model, and five spectra were collected on each support using the integrating sphere and fiber optic. The results showed that the standard deviation is less than 2.5% for all the wavenumbers and that there was no significant variation between the two sampling methods. The spectral range that presented the highest variation corresponded to the lower absorption zone, 4900–4600 cm^{-1}. Thus, the use of a fiberglass support is a suitable means for heavy fuel analysis. The use of the classical cell involves problems of cleaning with an organic solvent and regulating temperature. Physicochemical properties, such as density, CCAI, viscosity, flash point, energy, and net energy, and the nitrogen, vanadium, sulfur, water, and carbon residue contents of samples were measured using reference techniques by the SGS laboratory. Table I shows minimum and maximum values of each parameter for the samples in the database and the ranges of values. Clearly, some samples were outside the limits, especially for water content.

To check whether the sample presentation maintains sample composition of the HFOs, PCA was applied to reference data and to NIR spectra. The results are given

optic in the region 6500–5000 cm^{-1} (Table V), the results obtained were good for CCAI, vanadium content, net energy, and density; correct for sulfur content; but poorer for carbon residue and nitrogen content.

CONCLUSIONS

This preliminary study showed the feasibility of analyzing heavy fuels by NIR spectroscopy. The use of a diffusing support allowed freedom from cleaning of the tank. The classification of samples as "conforming " or "not conforming" can be done on reference data (e.g., CCAI; density; viscosity; flash point; sulfur, vanadium, and nitrogen contents; energy and net energy) as well as on spectral data. Thus, the physicochemical characteristics were successfully predicted by chemometrics treatment from spectral data. The accuracy of analysis depends on the sampling, but with a fiber optic in the range of first overtone, the principal physicochemical data were correctly predicted. This point is very important for a better environmentally friendly use of these fuels.

ACKNOWLEDGMENTS

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