Determination of Asphaltene and Resin Content in Venezuelan Crude Oils by Using Fluorescence Spectroscopy and Partial Least Squares Regression

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The predictive ability of partial least squares regression (PLSR) as calibration technique in fluorescence spectroscopy with regard to asphaltene and resin content was explored in some medium and heavy Venezuelan crude oils. These samples dissolved in toluene exhibited significant fluorescence signal at very low concentrations due to fluorophores associated with asphaltenes and resins. Additionally, crude oils spectra presented small shifts in the maximum peak position and small differences in the full width at half-maximum. This fact made the simple linear calibration technique meaningless for quantification purposes. Accordingly, multivariate calibration was applied to establish the relationship between the nonselective fluorescence spectra and the hydrocarbon content. Results confirmed that fluorescence spectroscopy with PLSR is a very promising method to predict the asphaltene and resin content of the crude oil in a fast and reliable way. Prediction results are comparable to those obtained by very cumbersome methods such as traditional SARA fractionation procedure.

Introduction

Crude oil components are grouped into four chemical classes based on differences in solubility and polarity: saturates, aromatics, resins, and asphaltenes (SARA). When dealing with solubility aspects for crude oils, most of the studies are focused on the heavy components: asphaltenes and resins. The former correspond to the most aromatic portion and are defined in terms of their solubility as the fraction that precipitates when an excess of low molecular weight paraffin is added.[1] Resins are considered as homologous to asphaltenes, with lower molecular weights and less condensed structures, and therefore are soluble in solvents where asphaltenes precipitate.[2]

The knowledge of asphaltene and resin contents in the crude oils represents a major concern due its negative impact in exploration, production, transportation, and refinement of crude oil. In general, asphaltenes can: (i) Alter the flow phase of the reservoir, (ii) plug the wellbore, (iii) precipitate and eventually clog up the pipelines, and (iv) hinder the refining yield.[3–5] On the other hand, it is well-known that resins play an important and complex role in the aggregation and flocculation process of asphaltenes from the crude oils.[6,7]

There are significant numbers of methods for the determination of SARA components, and they can be found in the literature.[8] Generally, these methods make use of liquid chromatographic techniques that are simple but time-consuming. Also, it is well-known that the accuracy of the analytical results is subjected to the skill of the analyst.

Molecular spectroscopic techniques such infrared and fluorescence are new alternatives for the prediction of chemical and physical properties of crude oil.[9–16] Infrared spectra of crude oil are dominated by C–H bonds absorptions, making this technique a sensitive, reliable, faster, and nondestructive analytical method for the analysis of crude oil and their products. Infrared and near-infrared spectroscopies have been used for the determination of SARA fractions, API gravity, and octane number in gasoline.[9–13]

Fluorescence emission of crude oils is mainly produced by the aromatic ring system from unsaturated organic compounds. The excitation of these molecules causes π–π* transitions, and their energies are related, in a general sense, to the physical size of the aromatic ring system; the larger the size, the lower the transition energy.[17–23] This fact has been used to investigate

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Table 1. Origin and SARA Distribution for the Venezuelan Crude Oils Used To Get the PLSR Model

crude oil	origin	SARA fractionation results (RSD 10%)			
		saturates, wt %	aromatics, wt %	resins, wt %	asphaltenes, wt %
1	Boscan	10	23	48	19
2	CNS	21	27	37	15
3	Merey	23	25	36	16
4	Sur Mediano	25	28	35	11
5	Furrial	35	24	32	9
6	Hamaca	11	19	54	16
9	Bachaquero	21	23	42	11
10	Lagunilla	28	25	51	13
7	PTZL[a]	35	33	28	4

[a] Light crude oil used for comparison purposes.

and characterize crude oils and their fractions. In most cases, the spectra of a crude oil can be obtained in seconds with high sensitivity. Fluorescence spectroscopy was used to study the asphaltenes aggregation process, crude oil concentration at oil spills in water, correlation with source rocks, and maturity and prediction of physical and chemical properties of crude oils such as API gravities.[6,14–16] The setup of the instrument is very simple and less expensive than other optical spectrometers. Additionally, this is a noncontact, nondestructive, low sample consumption, and minimum waste generation technique.

Spectroscopic techniques are very sensitive for crude oil analysis. However, the lack of selectivity and precise chemical information represents a significant limitation for quantification purposes. In this case, only chemometric methods have proved to be efficient tools for analyzing correlations between the spectral information and crude oil composition and their properties.[13–19] In this connection, this work presents the use of partial least squares regression (PLSR) and fluorescence spectroscopy as an alternative for a fast and reliable determination of the asphaltene and resin content in medium and heavy Venezuelan crude oils.

Experimental Section

Fluorescence Spectrometer. The instrument used to obtain the fluorescence spectra was elaborated in our laboratory. The excitation source was an LED having a nominal wavelength of 386 nm. The power was 3 mW, which is significantly lower than those used by laser instruments. Both incident and emitted radiation was transported from the sensor through optic fiber connected to collimating lenses. Emission radiation was collected at a right angle from the excitation beam. The solution sample cell was contained in a 1.00-cm path-length glass cell. The detection system was a diode-array spectrophotometer (model EPP2000, Stellar Net, Inc.), which allowed us to acquire and process the fluorescence spectra in the spectral region within 350–750 nm. Fluorescence potency was detected through a photodiode (Melles Griot) coupled to an amplifier (Melles Griot). All measurements were taken at room temperature.

Samples. Venezuelan crude oils used in this work are listed in Table 1 together with their SARA composition. All the samples

are medium or heavy crude oils (API gravities lower than 22). PTZL sample was included in this work to compare the fluorescence behavior of light, medium, and heavy crude oils. SARA composition was obtained by precipitation of asphaltenes with *n*-heptane and thin-layer chromatography with flame ionization detector (IATROSCAN TLC-FID).[24]

Experimental Methods. The fluorescence spectral data were obtained by dissolution of the appropriate amount of sample in 50 mL of toluene. The use of this solvent does not affect the behavior of the signal and allows the easy manipulation of the heavy crude oils. Three independent studies were conducted. First, crude oil solutions having 10–750 mg L^{-1} were used to study the behavior of the fluorescence as a function of the concentration in toluene. The idea was to characterize the fluorescence spectra of crude oil at different concentrations. This could help in the selection of the appropriate sample concentration to construct the calibration model. The second study involved the analysis of the fluorescence of each SARA fraction to understand their contribution to the fluorescence of the total crude oil. The experiments were carried out by measuring the signal of the Hamaca crude oil and its SARA components. The latter were obtained following the ASTM method.[1] SARA solutions were prepared according to the values reported in Table 1: Saturates, 55 mg/L (11%); aromatics, 95 mg/L (19%); resins, 270 mg/L (54%); and asphaltenes, 80 mg/L (16%).

Finally, the fluorescence emission of toluene-diluted crude oils was obtained. These data were used to build the calibration model by using PLSR. Fundamentals of the PLSR technique are well-known.[25] In summary, this is a very attractive calibration technique for modeling the relationship between dependent (**Y**) and independent (**X**) variables when many covering variables are present. In this study, the data matrix **X** is the crude oil fluorescence spectra while the response **Y** is the observed asphaltene and resin contents. Regression models were obtained by using Unscrambler (version 9.1, CAMO ASA, Norway) multivariate analysis software package. Full cross-validation was employed to validate the prediction models because of the limited number of training samples. The method works by leaving out one sample, then conducting a calibration on the remaining samples, after which the calibration is used to predict the left out sample. The quality of the model was estimated by using the root-mean-square error of calibration (RMSEC), which measures the error in the calibration model data points, and the root-mean-square error of prediction (RMSEP), which measures the uncertainty of the model on future predictions from the calibration model data points. Correlation coefficients for plots between spectral variable and hydrocarbon contents were also calculated with Unscramble software.

Results and Discusion

Fluorescence Spectra of the Crude Oils. Venezuelan crude oils present a high content of resins and asphaltenes (see Table 1), and thus significant collisional quenching effects are expected.[6] Figure 1 presents the fluorescence spectra of the Hamaca crude oil as function of the concentration. It can be appreciated that the fluorescence signal presents a maximum signal around 100 mg/L. Above this concentration, the fluorescence signal decreases and the spectra lose definition with a maximum shift to the red. The initial increase can be attributed to an increase in the number of chromospheres as a function of concentration until reaching a level for which collision energy transfer processes between species begin to be significant. At this point, changes in the solution related to asphaltenes aggregation processes lead to a nonradiative loss of the fluorescence signal.[6,17–23] Accordingly, it is important to select the appropriate crude oil concentration to avoid loss of accuracy

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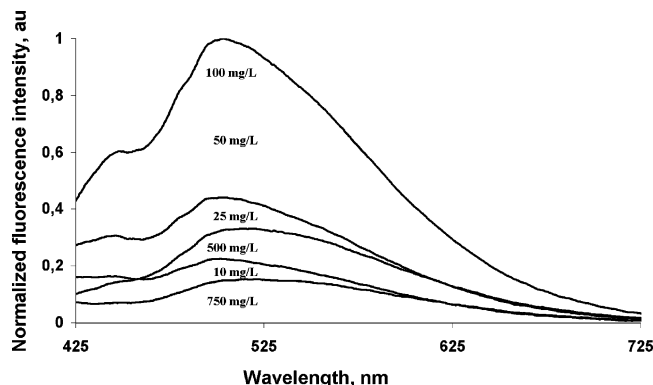(25) Martins, H.; Naes, T. *Multivariate Calibration*; Wiley & Sons: New York, 1998.

Figure 1. Fluorescence signal for Hamaca crude oil in toluene solutions as a function of the concentration.
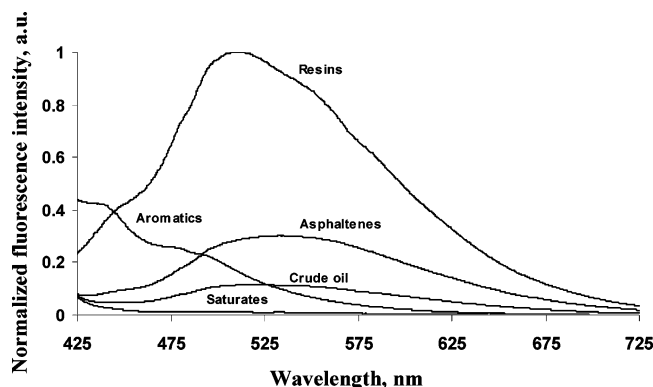

Figure 2. Fluorescence spectra of Hamaca crude oil and its fractions in toluene. The concentration of the crude oil is 500 mg/L. The concentration of each SARA fraction follows the values reported in Table 1 for Hamaca crude oil: Saturates (11%); aromatics (19%); resins (54%); and asphaltenes (16%). All fractions were separated by using the ASTM method.[1]

in the calibrations model and to diminish the quenching effects produced by fluorophores present in the sample. A crude oil concentration of 500 mg/L was selected in the next sections. Crude oil did not exhibit the higher fluorescence signal at this concentration. However, it can allow us to work with a low dilution of the sample and minimum quenching effects. This concentration is far away from the zone where the changes in solution, such as asphaltenes aggregation processes, begin to affect the signal.[6,17−23]

Fluorescence Spectra of the Crude Oil Fractions. Figure 2 shows the fluorescence spectra for Hamaca crude oil and its SARA in toluene. It can be appreciated that asphaltenes and resins present a strong fluorescence signal between 350 and 650 nm when compared to the aromatic spectra. The maximum signal of each fraction is obtained at small differences in wavelengths. Asphaltenes exhibit a broad band (higher full width at half-maximum) and less fluorescence signal than resins. In contrast, aromatics present a very narrow fluorescence signal and saturates give negligible fluorescence signal, as was expected for the lack of fluorophores species. Additionally, it can be observed that crude oil exhibits lower florescence intensity than resins. This is mainly produced by the association of all molecular species presented in the crude oil. This phenomenon is not present in each SARA fluorescence spectra. It is evident that the fluorescence of the crude oil responds to its SARA content in a complex way.

Relationship between Asphaltene and Resin Content and Fluorescence Spectra of Crude Oil. Figure 3 presents the fluorescence spectra of toluene-diluted Venezuelan crude oils:
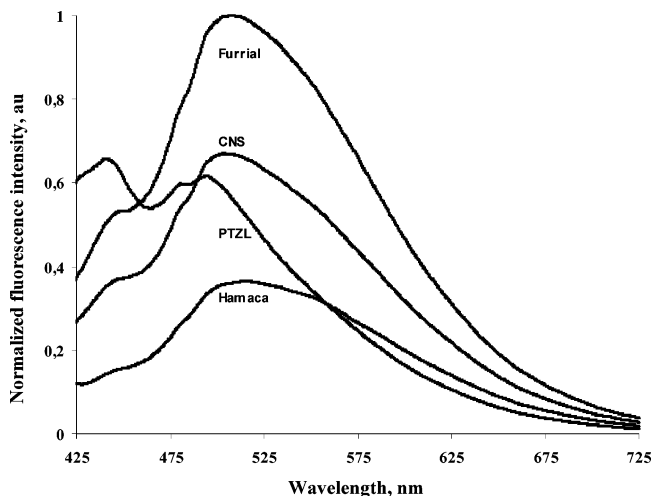

Figure 3. Fluorescence spectra of toluene-diluted Venezuelan crude oils. The concentration sample was 500 mg/L.
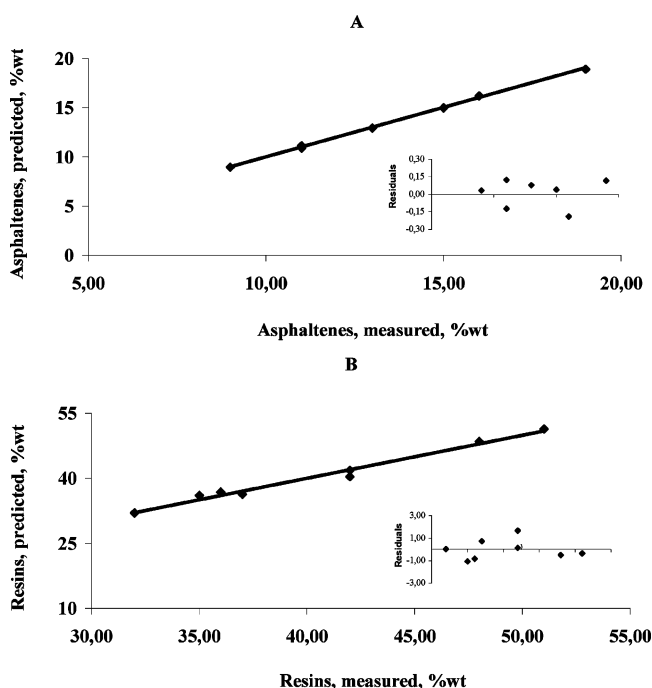

Figure 4. PLSR prediction model for asphaltenes and resins for Venezuelan crude oils from fluorescence spectra.

Hamaca, Cerro Negro, Furrial, Meza, and PTZL at 500 mg/L. It can be appreciated that these crude oils present different fluorescence intensity according to their differences in SARA content (see Table 1). Specifically, the signal intensity decreases as the resin and asphaltene content increases in the crude oil. Again, this is produced by the quenching effect observed in our previous experiments. All medium and heavy crude oil shows similar shapes in the fluorescence spectrum. In contrast, PTZL sample, a light crude oil such, exhibits a different behavior because of its high aromatic content. Fluorescence signal responds to the resin and asphaltene content of the crude oils (the signal increases as resin and asphaltene content decreases), and this fact can be used to predict them. However, the simple calibration method using a single wavelength cannot be recommended for prediction purposes, because the spectra of the crude oil have a poor selectivity. In this case, multivariate calibration techniques should be recommended to elaborate the prediction model. It is important to state that light crude oil was not considered for calibration purposes because it presents signifi-

Table 2. PLSR Data for Fluorescence Calibration for Venezuelan Crude Oils

	asphaltenes	resins
calibration range, wt %	9−19	32−54
X explained, %	100	100
Y-explained, %	99.98	99.85
latent variables	4	4
regression coefficient	0.9920	0.9836
RMSEC	0.30	1.30
RMSEP	0.44	2.75

cant differences in the fluorescence spectra when compared to heavy crude oils.

Asphaltene and resin contents were correlated with fluorescence spectra of the medium and heavy crude oils by using PLSR. The spectra data were used as *X*-data, while the response *Y* in the two models was the asphaltene and resin content. Table 2 presents PLSR data for fluorescence calibration of crude oils. Figure 4 shows the predicted values as a function of the measured ones for asphaltenes and resins together with their residuals. It can be appreciated that four latent variables explain the variability in data *X* and variable *Y* and the prediction model presents good correlation coefficients. It is evident that the asphaltenes model is better than the resins model as can be appreciated by the lower prediction error value. The efficiency of the fluorescence prediction models is similar to those obtained by NIR.[16] Calibration and prediction errors can be improved by increasing the number of samples in the training set. Unfortunately, it was not possible in this work.

Conclusions

Fluorescence spectroscopy can be used to predict the asphaltene and resin content of the crude oil in a fast and reliable way. The fluorescence spectra can be obtained with a high analytical sensitivity using a simple spectrometer based on an LED source. Venezuelan crude oils dissolved in toluene exhibit a significant florescence signal at relatively low concentrations due to the high fluorophore content. In addition, a multivariate calibration method can be used to satisfactorily correlate the nonselective fluorescence spectra with resin and asphaltene content. Prediction results obtained with the proposed method are comparable to those obtained by traditional SARA procedures and infrared spectroscopy.