DETERMINATION OF ASPHALTENE CONTENT IN CRUDE OIL BY ATTENUATED TOTAL REFLECTANCE INFRARED SPECTROSCOPY AND NEURAL NETWORKS ALGORITHMS

Silvia Colaiocco M. and Manuel Farrera
PDVSA INTEVEP
Analytical Chemistry Department
Caracas, Venezuela

INTRODUCTION

The asphaltene content of a crude oil is defined as the percentage weight of insoluble constituents in a paraffinic solvent, mostly n-heptane, under specific test conditions. The determination of the asphaltene content is part of the crude oil evaluation used in its commercialization. Also, the asphaltene content influences the stability and compatibility of crudes, as well as its processability during production and refining.

Standard methods for determining the asphaltene content of a crude oil are laboratory techniques, highly laborious and time consuming and requiring its preparative scale separation. Wilt and Welch[1] in 1998 worked on the prediction of the asphaltene content in petroleum crude oil using Fourier Transform infrared spectroscopy with an attenuated total reflectance tunnel cell and partial least squares (PLS) regression. The PLS model needed nine factors to obtain a good relation between actual and predicted values[1]. However, for low asphaltenic crude oils (0 to 2 wt %) the determined error (1 wt %) is much higher than the standard laboratory method precision[1]. In 2001, Aske et al.[2] presented the determination of saturate, aromatic, resin, and asphaltenic components in crude oils by means of infrared (IR) and near-infrared (NIR) spectroscopy using PLS regression. IR and NIR asphaltene model data had seven and eight factors respectively, with prediction errors also higher than standard laboratory methods[2]. It is well known that one of the limitations of PLS is that it tries to handle the non-linearities by including additional factors in the model, but this is unsatisfactory for reasons that have been already addressed[3,4]. Neural network algorithms are one option for the fitting of non-linear data[5].

This paper describes an alternative method for a rapid estimation of the asphaltene concentration in crude oils, using Fourier Transform infrared spectroscopy with an attenuated total reflectance cell kit (ATR-IR) and neural network algorithms (NNA)[6]. Comparisons between the predicted ATR-IR asphaltene content and the measured values from reference method IP-143[7] are presented. The predicted asphaltene values reported are better than those of the studies previously referenced, particularly for crude oils with low levels of asphaltenic compounds.

EXPERIMENTAL

Sample Set

Nineteen Venezuelan crude oil samples of different quality were used for developing the asphaltene content prediction models. Due to the small number of samples, just three samples were randomly selected out of the 19 to establish the test set. The remaining 16 samples were classified as the calibration samples, to be used to train the neural network.

The reference values for asphaltene content in the samples were obtained by IP-143 standard method[7].

FTIR Instrumentation

Spectra of the crude oil were taken on a Fourier Transform infrared spectrometer Nicolet model Magna 750 (Series II), with a KBr beam splitter and a liquid nitrogen cooled MCT-B (Mercury-Cadmium-Tellurium) detector. The spectral range acquired was from 10,000 to 650 cm^{-1}, with an accumulation of 128 scans and resolution of 2 cm^{-1}. The acquisition time of the spectra was approximately 80 seconds. An attenuated total reflectance kit (ATR) from Spectra-Tech model 0055 was coupled to the instrument, with a Zinc Selenide (ZnSe) crystal and 40° angle of incidence (14 reflections). The ATR kit is shown in Figure 1.

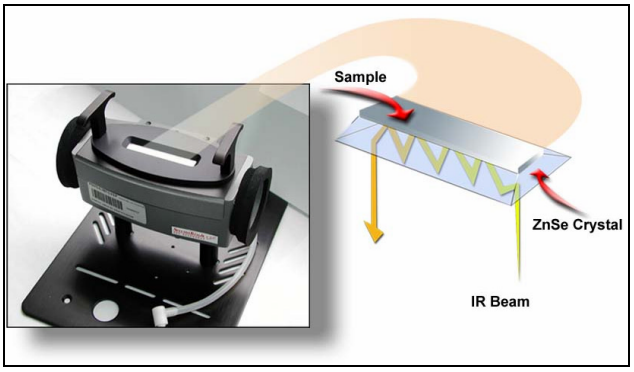

Figure 1. Attenutated Total Relectance (ATR) cell kit.

Only the spectral range from 1,800 to 685 cm^{-1} with an 8 cm^{-1} step was used in this study; spectra were baseline corrected at 2,000 cm^{-1}. The spectral region covered includes aromatic C=C stretching vibrations, CH_2 and CH_3 bending modes, bending vibrations of ethers or esters, and aromatic CH out of plane bending vibrations, among others. Figure 2 shows ATR-IR spectra of three of the crude oils.

Neural Networks Algorithms (NNA)

Commercial software QwikNet V2.20 was used for modeling the asphaltene content in crude oil by a three layer neural network (NN) configuration (Figure 3). The number of neurons in the input layer depends on the number of variables (absorbances) used to train the net. The output layer contained a single neuron for the target asphaltene concentration. The number of neurons in the hidden layer is adjusted according to the complexity of the relationship between input and output vectors. In the presented application, the configuration of the NN was 150:5:1. Delta-Bar-Delta back-propagation of the errors was the training rule employed for the three layers neural network[8]. Detailed information about NN can be found elsewhere[9,10]. The NN was trained using the calibration set of samples. Excessive training of the NN can cause memorizing and it might not be useful to predict cases not included in the calibration set. This NN memorization would correspond to overfitting in regression. To avoid that situation, the three-sample test set was presented to the NN throughout the training, to check the performance of the NN, and to detect the stop moment in the training step.

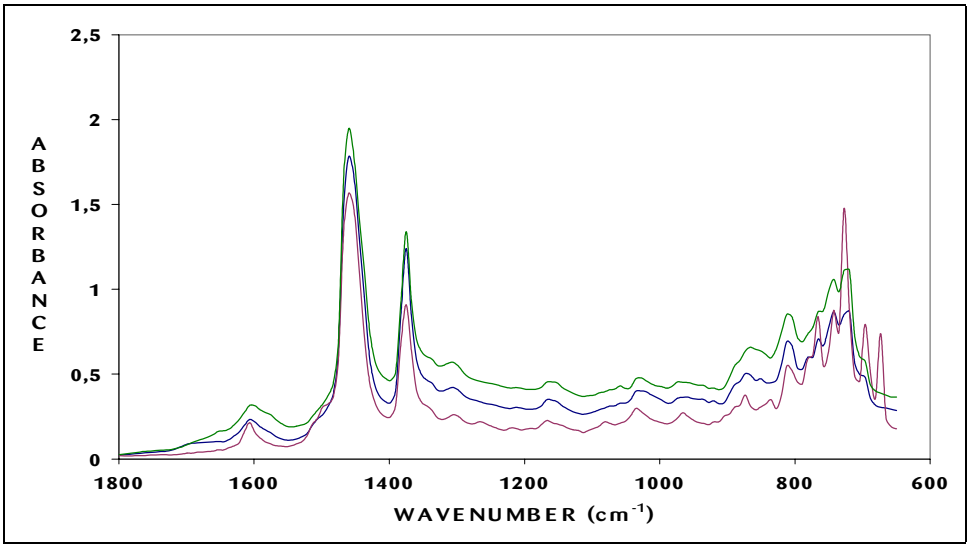

Figure 2. ATR-IR spectra of three selected crude oil samples.

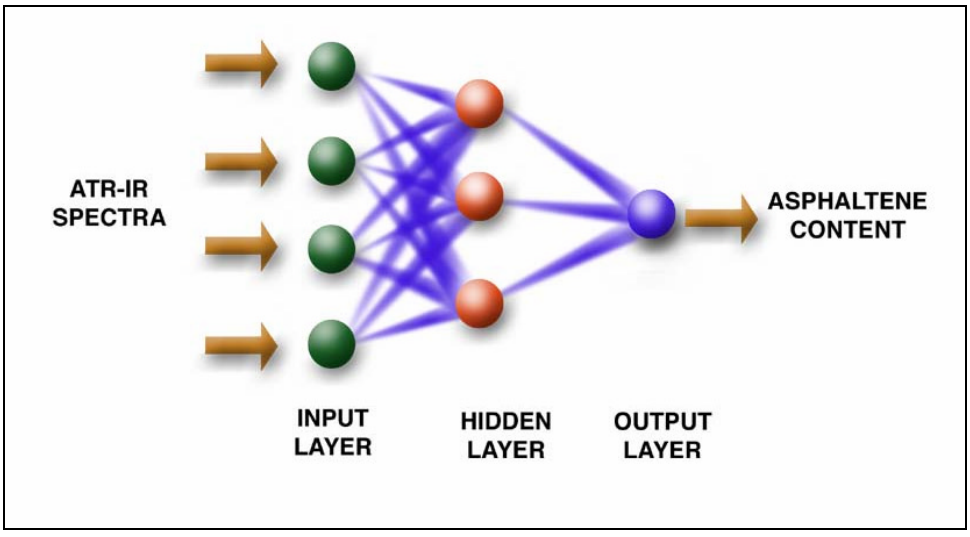

Figure 3. Generic neural network schematic.

RESULTS AND DISCUSSION

Table I shows the actual and predicted asphaltene values along with the residuals for the 19 samples. The agreement between the calibration and test sets is excellent.

Figure 4 is a plot of the ATR-IR-NNA predicted asphaltene concentration versus the actual values obtained by the IP-143 method. There is a correlation between both results, with an R^2 value of 0.996. A slope of 1.017 ±0.030, and an interception of -0.06 ±0.25 indicate no statistically significant differences between predicted and actual values. The standard error of calibration was 0.37 wt %.

Figure 5 is the absolute residuals plot showing a random distribution, with no bias, across the entire range of asphaltene content. Moreover, differences between actual and predicted values are similar to laboratory standard method precision.

Table I Actual and Predicted Asphaltene Values in Wt %
(C=Calibration, T=Test)

Sample	Actual	Predicted	Residual
1-C	0.2	0.3	0.1
2-C	6.1	6.1	0.0
3-C	3.9	3.9	0.0
4-C	1.0	0.8	-0.2
5-C	0.5	0.7	0.2
6-C	9.9	10.4	0.5
7-C	6.1	6.0	-0.1
8-C	16.4	15.7	-0.7
9-C	10.4	11.0	0.6
10-C	0.2	0.2	0.0
11-C	7.8	7.8	0.0
12-C	4.8	4.1	-0.7
13-C	17.8	17.1	-0.7
14-C	13.6	13.6	0.0
15-C	7.4	7.3	-0.1
16-C	0.2	0.2	0.0
17-T	0.7	0.8	0.1
18-T	9.7	9.7	0.0
19-T	1.4	1.4	0.0

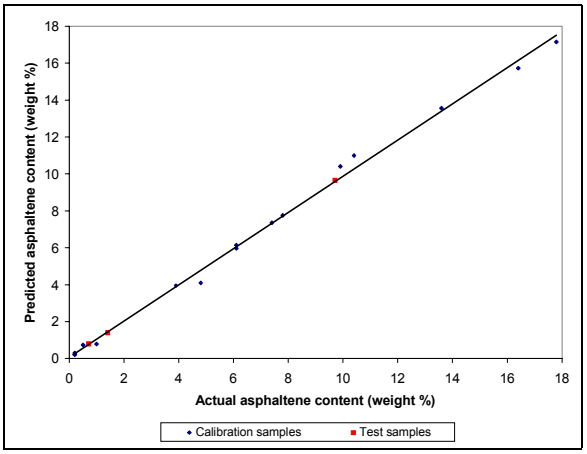

Figure 4. Predicted versus actual asphaltene values in weight %.

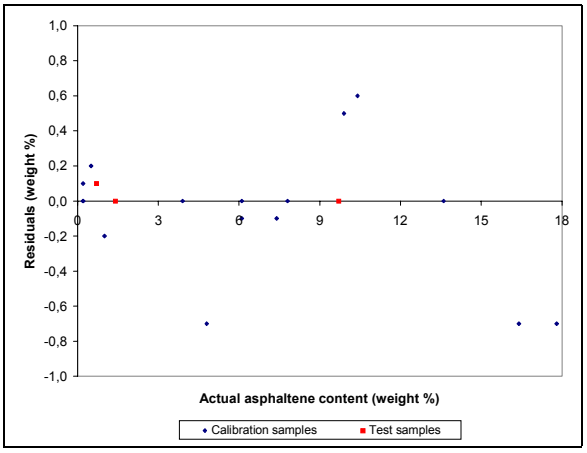

Figure 5. Absolute residual versus actual asphaltene content in weight %.

CONCLUSIONS

It is possible to determine the asphaltene content of crude oils by ATR-IR using neural network algorithms across a wide range of content and crude oil types.

The method is much less time consuming than standard laboratory methods, analytical scale, does not require solvents, and could be applied to other asphaltene-containing petroleum products.

The high absorbances obtained encourage the evaluation of ATR cells with a smaller number of reflections, as well as detectors that are less sensitive but operate at room temperature.

ACKNOWLEDGMENT

Thanks are given to PDVSA for providing the funds to conduct this work and to Miguel Orea and Mario Lattanzio for their collaboration in the determination of the asphaltene content in the crude oil samples.

REFERENCES

1. B.K. Wilt, W.T. Welch, and J.G. Rankin, *Energy Fuels*, 12, 1008-1012, (1998).
2. N. Aske, H. Kallevik, and J. Sjöblom, *Energy Fuels*, 15, 1304-1312, (2001).
3. B.R. Kowalski and M.B. Seasholtz, *Journal of Chemometrics*, 5, 1290-145, (1991).
4. H. Martens and T. Naes, Multivariate Calibration, (John Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore, 1989).
5. M.B. Seasholtz and B.R. Kowalski, *Analytica Chimica Acta*, 277, 165-177, (1993).
6. S. Colaiocco M. amd M. Farrera, *Fifteenth International Forum Process Analytical Chemistry* (IFPAC), Amelia Island, Florida, USA, (January 2001).
7. Institute of Petroleum. Method IP-193. *Asphaltene (Heptane Insolubles) in Petroleum Products*. London, 1990.
8. B.L. Wythoff, *Chemometrics and Intelligent Laboratory Systems*, 18, 115-155, (1993).
9. J.R.M. Smits, W.J. Melssen, L.M.C Buydens, and G. Kateman, *Chemometrics and Intelligent Laboratory Systems*, 22, 165-189, (1994).
10. W.J. Melssen, J.R.M. Smits, L.M.C. Buydens, and G. Kateman, *Chemometrics and Intelligent Laboratory Systems*, 23, 267-291, (1994).