

X-ray spectrometry allied to chemometrics in the determination of petroleum parameters

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In the whole world, the petroleum demand is increasing whereas light oils reserves are deeply decreasing. In this scenery the exploration of offshore heavy oils in coastal deep waters is urgent. This alternative strongly alters the standard procedures in petroleum refineries and requires fast and reliable sample characterization methods. The main features of heavy oils are low API degrees, high viscosity, high asphaltene, carbon, sulfur, nitrogen and metal residual contents. To fill a part of this blank, this work shows the development of a new analytical method, nicely applicable to routine, based on the correlation of X-ray Spectrometry (XRS) and some of the parameters mentioned above, as the determination of API degree and of asphaltene and metal contents. The correlations are reached through chemometric modeling between the spectra and data obtained by standard reference methods. All the standard methods are inadequate for routine analysis, since they are laborious, extremely reagent- and time-consuming, besides generating toxic residuals. The use of X-ray scattering as analytical signal to determine oil parameters is fundamental to open a new perspective in X-ray Spectrometry, showing better performance than reference methods. The models were obtained by applying chemometric tools, as PCA (*Principal Component Analysis*) and PLS (*Partial Least Square Regression*), with correlation coefficients above 0.9 between measured and previewed values.

1. Introduction

Nowadays, heavy crude oils are being processed extensively since the presence of light ones are deeply decreasing. Heavy oils are characterized by several undesirable parameters, namely high asphaltene contents and low API degree values, parameters that are extensively correlated with high metal contents. The standard method for oil

classifications as light, medium or heavy ones is based on the API degree, obtained through the density (ASTM D 5002-99 (2005)). It expresses the fluid behavior inside reservoirs and pipes. The API degree is inversely correlated with density, at 15.6 °C, as equation 1.

$$^{\circ}\text{API} = (141,5/\rho) - 131,5 \quad (1)$$

Light oils present API degree higher than 34; medium oils, between 25 and 34; heavy ones, in the 10 to 25 range and ultra-heavy, lower than 10.

Asphaltenes are high molar mass compounds that occur in heavier and polar fractions of petroleums and their residuals. These compounds are in higher concentrations in heavy samples and precipitate in the presence of light alkanes, as n-pentane, n-hexane or n-heptane. They are soluble in aromatic solvents, as toluene and benzene. The asphaltenes appear as vitreous solids, in brown and black colors. They are formed by paraffinic, naphthenic or aromatic hydrocarbons and also present functional groups containing oxygen, nitrogen, metals and sulfur. The n-heptane soluble fractions correspond to the resins, aromatics and saturated compounds (Sjöblom et al, 2003). Organic deposits can be formed in the petroleum environment by the precipitation of heavy fractions (asphaltenes and resins) due to alterations in temperature, pressure and oil composition. It can occur in either these locations: reservoir rock, production piping, refining equipments or stocking tanks. These occurrences may prejudice the petroleum fluidity and cause appreciable expenses to remove these solid deposits (Mohamed and Ramos, 1999). In this context, the determination of asphaltene contents in crude oil is an important task to be done before oil processing since it will dictate how it will be performed. This work shows a new, fast, reliable, non residue-generating procedure to determine their API degrees and metal and asphaltene contents based on their direct X-ray irradiation followed by multivariate calibration via PCA (Principal Components Analysis) and PLS (Partial Least Square Regression) (Geladi, 2003). The alliance of X-ray spectrometry and chemometrics is being explored successfully by one of the authors (Bueno et al, 2005).

2. Experimental

Pure petroleum samples were collected and mixtures of them were prepared. So, standard reference methods were applied to determine their API degrees (ASTM D5002-99) and asphaltene content (IP 143/84 (1989) and/or ASTM D6560-00). Both methods are inadequate for routine analysis, since they are laborious, extremely reagent- and time-consuming, besides generating toxic residuals. Table 1 shows the obtained results.

Table 1 – API degrees and asphaltene contents obtained by standard methods ASTM D5002 and IP 143, respectively.

Sample	API degree (ASTM D-5002-05)	Asphaltenes (% w/w) (IP143-84)
1	25.2	1.33
2	25.0	2.04
3	29.2	1.21
4	23.1	1.13
5	25.6	1.43
6	20.0	1.11
7	23.6	1.43
8	20.5	1.33
9	22.6	1.32
10	30.4	1.27
11	23.2	0.14
12	31.6	1.43
13	22.6	0.97
14	22.7	1.66
15	31.3	1.51
16	24.0	1.75
17	32.0	1.07
18	21.0	2.30
20	19.7	1.62
21	22.0	1.60
22	36.4	0.05
23	18.7	1.90
24	17.8	2.50
25	18.0	5.71
26	18.8	3.06
27	20.4	3.52

To proceed with the chemometric analysis, all samples were simply weighted (2.500 \pm 0.001 g) in appropriate cells for irradiation (Chemplex[®]), mounted with their bottoms with 2.5 μ m thick Mylar[®] films. All spectra were registered after 300 seconds of irradiation, in Helium atmosphere, with a 550 μ m collimator, a Ge diffraction crystal and a flux detector. The used spectrometer is a PW 2400, from PAN analytical, equipped with a rhodium X-ray tube. The considered spectrum region for the chemometric analysis was $2\theta = 96.64^\circ$ to 108.64° , where rhodium $L\alpha$ Compton and Rayleigh are manifested, besides the characteristic sulfur $K\alpha$ line ($2\theta=100.72^\circ$). Each spectrum is composed by 458 points.

3. Results and Discussion

In the specific case of API degree, the pretreatments applied to spectra were normalizations by each spectrum intensity media. However for the asphaltene determinations, Savitzky-Golay first derivative was considered. PLS method with internal validation was considered to obtain the results presented in Figure 1 (API degree) and Figure 2 (% asphaltene), considering the data measured by the standard reference methods from Table 1.

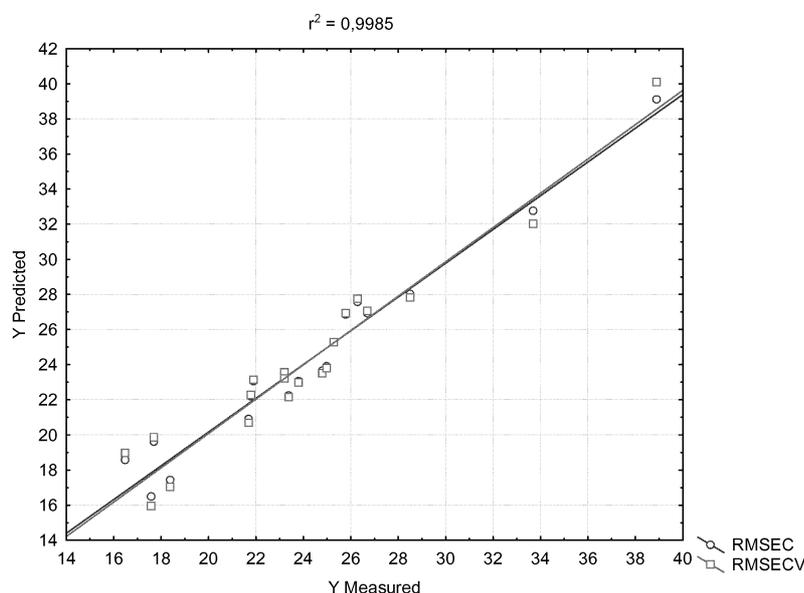


Figure 1 – PLS calibration and internal validation curves for API degree, using the reference method (Y measured) and the data obtained by the chemometric model (Y predicted), using three latent variables

An external validation was also performed and the relative errors were from 0.005 to 0.977 for API degree, whereas, for asphaltene contents, they varied from 0.008 to 0.287.

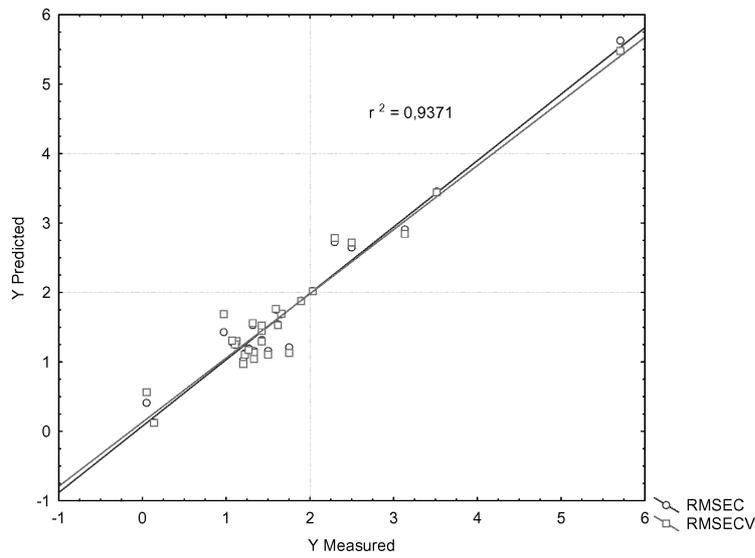


Figure 2 – PLS calibration and internal validation curves for Asphaltene weighted percentage, using the reference method (Y measured) and the data obtained by the chemometric model (Y predicted), using four latent variables

Another considered aspect was the metal content that is shown in Figure 3, which values are strongly correlated with API degrees and asphaltene contents.

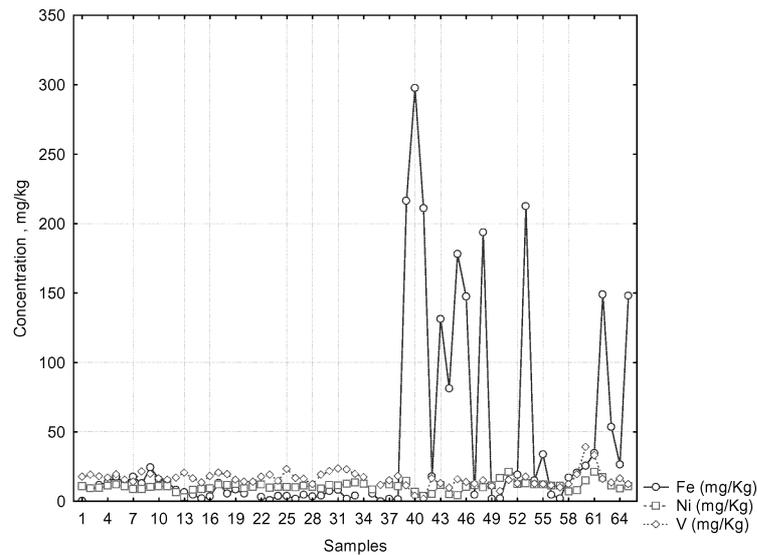


Figure 3. Iron, nickel and vanadium contents of crude oil samples showing higher iron levels for heavier samples.

4. Conclusion

This work shows a nice way to determine crude oil parameters with several advantages over the features of standard reference methods, as the speed, not use of reagents and reliability. The use of X-ray scattering as analytical signals to determine oil parameters is fundamental to open a new perspective in X-ray Spectrometry, showing better performance than reference methods. The models were obtained by applying chemometric tools, as PCA (*Principal Component Analysis*) and PLS (*Partial Least Square Regression*), with correlation coefficients above 0.9 between measured and previewed values. So, this work is pioneer, opening new possibilities for future simultaneous applications in petroleum and co-products characterizations.

5. References

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