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Sulfur Determination in Diesel using 2D Fluorescence Spectroscopy and Linear Models

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Abstract: Control of sulfur content in diesel streams demands for on-line measurement of this component, with low pure time delay and easy operation. In this way, 2D fluorescence Spectroscopy becomes a reasonable choice for soft-sensor development. This work reports a different strategy to overcome the aforementioned lack of selectivity or signal overlapping using the selection of individual fluorescence spectral components combined into multilinear models to predict sulfur content in diesel streams from Ultra Low Sulfur Diesel and Diesel S100. The results obtained using Pure Spectral Chemometrical Modeling and Ant Colony Optimization showed good results as a source of information to determine the sulfur content in diesel.

Keywords: Optical spectroscopy, Optimization problems, Qualitative analysis, Processes, Fuel control.

1. INTRODUCTION

Concerns about human and environment health have had a significant increase in last decades. All big cities are affected by seriously problems caused by soil, water and air pollution. The introduction of contaminants into the natural environment is highly correlated with the use of fossil fuels. This fact creates a necessity to produce fuels with less concentration of certain pollutant ion molecules (Goverment, 2005, Betha and Balasubramanian, 2013).

Oil is a highly complex mixture of hydrocarbons with small amounts of heteroatoms like sulfur, oxygen, nitrogen and organic metals. Among these, sulfur is the most abundant and is considered an undesirable compound by refineries. (Andrade *et al.*). Around the world, many countries had developed legislation to promote the Ultra-Low Sulfur Diesel (ULSD) production, as an attempt to improve the quality of fuels and minimize the air pollution, caused by fossil fuels combustion (De la Paz-Zavala *et al.*, 2013).

In Brazil, since December 2013, the resolution number 50 from National Agency of Oil, Gas and Biofuels (ANP) regulates the quality of diesel commercialized on national territory after January 1st 2014. This resolution sets that all metropolitan diesel must contain less than 10 ppm of sulfur (also known as Diesel S10), framing it as a ULSD. This regulation forces refineries to treat the products to adequate it to the sulfur limit content (Moreira *et al.*, 2014).

Conventional hydrodesulfurization (HDS) is a catalytic chemical process used in refineries for efficient elimination of sulfur compounds, particularly efficient for light compounds, such as thiophenes and benzothiophenes (Aburto *et al.*, 2014). Evolving, side by side, with the technology for desulfurization, is the capability to measure sulfur content in process streams.

Today, sulfur monitoring is developed according standard methods published by American Society for Testing and Materials (ASTM): ASTM D2622 and ASTM D5453. Those methods require sample preparation by specialized people, high-cost instruments, high sample volume, uses of reagents or solvents and incapability to implement it in on-line form (Sajjad *et al.*, 2014).

Therefore, refineries are demanding fast and efficient on-line sensors for sulfur content determination in diesel streams. These sensors are crucial from economic and technological point of view, since they can considerably improve the industrial unit performance (de las Obras-Loscertales *et al.*, 2014). A variety of spectroscopic techniques have been used over the last few decades for the analysis, characterization, and classification of crude oil, most because of their inherent sensitivity (Macho and Larrechi, 2002).

Spectroscopic techniques advantages include, for instance: high robustness, requirement of minimal sample preparation, relatively inexpensive equipment costs (for customized versions), non-invasiveness, fast time response, and high resolution (Whitford and Julien, 2007). Among optical spectroscopic techniques, vibrational infrared (IR), UV-vis, and fluorescence spectroscopies have shown the highest potential in that field. Optical sensors based on spectroscopy principles can be considered a suitable and promising option for developing an on-line sulfur content analyzer.

The Near Infrared Spectroscopy (NIR) is one of the most studied techniques for determination of diesel analites, including sulfur. As showed by Breitkreitz (2003), this technique can satisfactorily quantify total sulfur concentration in a range between 0.07 and 0.33% (w/w), with results as good as standard procedures. However, for sulfur amounts lower than 15 ppm (case of ULSD), this technique did not show good results, making it not a useful principle for S10 Diesel characterization (Bueno, 2011).

Among spectroscopy techniques, fluorescence spectroscopy appears as a promising alternative for sulfur quantification in diesel streams. This method shows good sensitivity and better limits of detection, up to three orders higher than the ones presented by absorption spectroscopies (Stasiuk *et al.*, 2000). Once many sulfur compounds on diesel emit fluorescence, it seems to be natural to apply the fluorescence principle to develop an optical sensor for diesel streams. However, the selectivity is often reduced because of extensive spectral overlap or the presence of fluorescence phenomena interferences (Aburto *et al.*, 2014).

Despite the apparent viability of the fluorescence spectroscopy application for sulfur determination in diesel, many technical issues must be solved before the construction of sensors using this technology (Zhu *et al.*, 2008).

In this paper, we report a different strategy to overcome the aforementioned lack of selectivity or signal overlapping using the selection of individual fluorescence spectral components combined into multilinear models to predict sulfur content in diesel streams. The analysis and selection of fluorescence data is made using the Pure Spectra Chemometric Modeling (PSCM) strategy. The PSCM is a type of Linear Discriminant Analysis (LDA), where the input variables are fluorescence pairs intensity, combined using multilinear models. Selection of fluorescence pairs (wavelength of Excitation/Emission) among all possible fluorescence spectral candidates is made by Ant Colony Optimization (ACO).

Aburto *et al.* (2014) shown good results for quantification of sulfur content using fluorescence spectroscopy with an enzymatic pretreatment for partial oxidation of sulfur compounds. According Aburto et al. (2014) oxidation of samples is mandatory for the sulfur characterization. Our contribution focus in applying supervised learning techniques directly to the 2D fluorescence spectrum data, dispensing any sample pretreatment. Our proposed approach can successfully characterize ULSD samples for sulfur content without any pretreatment reaction.

2. MATERIALS AND METHODS

Here, different samples corresponding to Diesel S10 (ULSD) and Diesel S100 (previously characterized according to the corresponding sulfur content) are analyzed using 2D fluorescence spectroscopy measurements. All the samples were provided and certified by a Brazilian Petroleum Refinery.

Two different diesel classes are tested to compare results of fluorescence spectroscopy characterization capability in diesels samples with considerable difference in sulfur content. Distinguished classes are also tested to evaluate the methodology robustness.

2.1 Diesel S10 samples - ULSD

Samples were certified for sulfur content according to ASTM D-7039. Eleven samples were used in this study, with sulfur content in the range between 5.7 ppm and 6.4 ppm, with sulfur concentration average of 5.8 ppm.

2.2 Diesel S100 samples

The total amount of samples from HDT treatment was 51. Each sample was characterized for total sulfur content by ASTM D-4294. The frequency of sampling was of one sample each three days, during a period of three months of samples collection.

The sample group presented sulfur amount range between 73.7 ppm and 138.6 ppm, with sulfur average concentration equal to 100.3 ppm. Once the average concentration of sulfur in this sample group was close to 100 ppm, this samples were called here as Diesel S100, despite this group presented some samples with more than 100 ppm of sulfur concentration.

2.3 2D Fluorescence Spectroscopy

The Fluorescence Spectra were measured by the equipment HORIBA Fluoromax-4®, equipped with a xenon lamp of 150W. The measurements were done in the range of excitation wavelengths between 260 nm and 600 nm, and emission wavelengths between 290 nm and 850 nm. Both excitation and emission wavelengths varied with increment of 10 nm.

Measurements of Diesel S10 samples were made using a quartz cuvette with optical path of 1 cm, while Diesel S100 samples were measured using remote optical fiber accessory. Before spectroscopic measurements, each sample temperature were equalized at 25°C in a thermostatic bath.

2.4 Chemometric Analysis

Methods classified as Supervised Techniques (ST) are applied on two groups of variables: independent, e.g., variables arising from analytical techniques; and dependent variables, e.g., sulfur content on samples. STs establish a relationship between independent and dependent variables (Anzanello *et al.*, 2011, J. Anzanello *et al.*, 2014).

Pure Spectral Chemometric Modeling (PSCM) is a chemometric methodology based on two main pillars: selection of pure spectral elements and model adjustment for state variable prediction, by finding a relationship between variables. The selection of model structure is crucial, not only for correct capture of spectral behavior in function of analyte variation in the medium, but also for viable fitting of model parameters.

In this work, we applied multilinear model structure to the description of sulfur concentration into diesels samples, using spectral fluorescence intensities as input data. The choice for linear models was based on the fact that, in principle, those kind of model can represent fluorescence sample behavior in a satisfactory way. Additionally, the estimation of models parameters can be easily made using Ordinary Least Squares (OLS), without significant time consumption, which is interesting, once the parameters are fitted thousands of times during algorithm running, presenting a significant impact on running time.

The quality of the model depends not only on which variables are used in the regression, but also on how many. A small subset of predictor variables is often preferable against using all available data, because it reduces cost and time spent in the measurements, tending to present a more simple physical interpretation, and in the case of multiple linear regression, reduces the uncertainty of prediction, since this uncertainty increases with the ratio between the number of explanatory variables and the number of samples used in calibration (Brown *et al.*, 2009).

The selection of spectral elements is crucial for the success of PSCM approach. Selection of spectral group aims to choose spectrum components that have a direct correlation with state variables. Once usual size of spectral data is around thousands of elements per spectra (depending on spectral resolution), the use of exhaustive search become impracticable. Ant Colony Optimization (ACO) comes to solve this practical problem using an optimization approach.

ACO is a stochastic optimization algorithm used for finding good paths through graphs (e.g. traveling salesman problem). The benefits obtained from this methodology are not only the stability of the model in terms of collinearity in multivariate spectra, but also the interpretability of the relationship between the model and the sample compositions, as initially presented by Allegrini and Olivieri (2011). A more detailed description about implementation and characteristics about PSCM and ACO (e.g. algorithm, objective function, input and output data format, etc) can be obtained at Ranzan *et al.* (2014).

2.5 Calibration and prediction samples segmentation

Diesel samples from each class were segmented into two groups: (*i*) calibration and (*ii*) prediction. Samples located into calibration data set are applied for chemometric models calibration while samples classified for prediction are applied for model test. In this way, samples used for model test do not participate either of the model calibration phase and neither in the selection of spectral components.

This segmentation was performed using Y-rank strategy. On this methodology, samples are sorted in ascending order of the interest variable. Based on the sorted data set, two samples are allocated for calibration group while one is inserted into prediction (or test) group. Proportion of two by one is maintained until the total segmentation of samples groups. More information about Y-Rank can be obtained in Wehrens (2011).

2.6 Statistics used in model analysis

Appropriate criteria for model evaluations are crucial to rank the models. This work applies the RMSE (Root-Mean-Square Error) and R^2 (Coefficient of determination) as metric for model quality, which are defined by:

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{N}\left(y_{p,i}-y_{m,i}\right)^2}{N}} \qquad (1)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{N}\left(y_{p,i}-y_{m,i}\right)^2}{\sum_{i=1}^{N}\left(y_{m,i}-\bar{y}_m\right)^2} \qquad (2)$$

Here the sub-index p refers to the vector of the predicted variable values, resulting from model evaluation, and m to the measured variable values, N is the number of measurements and y is the vector of interest variable.

The RMSE and R^2 when calculated using the calibration data set are represented by RMSEC and R^2c, respectively. To quantify the corresponding prediction metrics, the test data set is used. In this case, the adopted notation is RMSEP and R^2p, respectively.

3. RESULTS AND DISCUSSION

3.1 2D Fluorescence Spectroscopy measurements

Figure 1 shows average 2D fluorescence spectra from Diesel S10 and S100 samples. Those results are originated from normalized spectral data, using Standard Normal Variate (SNV). Figure 1 shows the corresponding contour plots of the 2D fluorescence spectra from each diesel class.

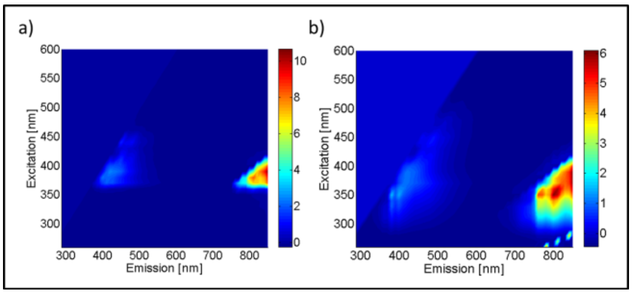

Figure 1. Contour plots of the 2D Fluorescence Spectroscopy of (a) Diesel S10 and (b) Diesel S100 corresponding to the average spectral data.

Both diesel classes have similar spectral data, with two pronounced regions: *Region 1* [Excitation 300nm – 450nm / Emission 400nm – 500nm]; *Region 2* [Excitation 300nm – 450nm / Emission 750nm – 850nm], being region 2 more evident, with higher fluorescence intensity, than region 1.

The main difference between both sample data in 2D fluorescence spectrum is related with the relative intensity of fluorescence peaks. Diesel S100 samples have shown smaller fluorescence intensity than Diesel S10 samples, indicating that the more aggressive process of hydrodesulfurization has withdrawn compounds responsible for fluorescence quenching, leading to the increase of fluorescence phenomena with the reduction of sulfur content (Aburto *et al.*, 2014).

Previous studies (Ranzan, 2014) showed that despite the quantitative difference shown between fluorescence data of diesel types, the information about fluorescence data peaks cannot be applied individually for sulfur content prediction.

This impossibility is due to the fact that fluorescence is highly sensitive to medium variations and environmental properties (e.g. temperature, pH, viscosity, etc.), forcing the combination between distinguished fluorescent spectral regions to make the prediction reliable.

3.2 *Chemometric Analysis*

The Chemometric analysis has two main purposes: (*i*) provide useful information about qualitative data and (*ii*) propose chemometric models for on-line sensors development.

3.2.1 Qualitative Analysis

The first objective, i.e., the analysis of fluorescence data, is developed using PSCM qualitative information vector. This technique is initially applied to each sample group and then, it is applied to both groups as if they are a single dataset.

This first analysis aims to provide a mapping of significant information region content into fluorescence spectral data. This information is collected during ACO running in the form of an evolutionary vector (it actualizes its contents based on the objective function values presented by the use of spectral elements to predict interested variable). Spectral regions that present high linear correlations with interest variable are highlighted. In this way, this qualitative information is directly associated with the signature of interest variable in the fluorescence matrix data and presents useful information to spectral analysis.

Figure 2 shows the qualitative signature based on the pheromone distribution calculated for diesel S10 and diesel S100 using ACO and plotted in the 2D fluorescence spectrum diagram of excitation/emission wavelengths in function of sulfur concentration. Since the information obtained by this analysis has only qualitative characteristics, the results are rescaled from zero to one. Another important characteristic is that the actualization of the weighting vector (i.e., pheromone vector) is inversely proportional to the objective function evaluations and with a decay factor of 0.5.

Visual comparison between qualitative information extracted from diesel S10 and Diesel S100 shows that diesel S10 has two prominent specific regions, in contrast with diesel S100 results, that showed several regions, distributed all over the spectrum, with linear correlation with sulfur content.

Figure 2 clearly shows the qualitative difference between fluorescence data from Ultra Low Sulfur Diesels (case of diesel S10 class) and sulfurs that pass by less hydrodesulfurization. Diesel S100 has more molecules and elements that emit fluorescence and/or promotes quenching of sample fluorescence. This feature makes fluorescence data from diesel S100 noisier and disperse when compared with fluorescence data from diesel S10.

Comparing Figure 1 (fluorescence spectra from each diesel class) with Figure 2, it is possible to see that PSCM methodology can identify spectral regions as significant for sulfur determination in regions where there is not any prominent fluorescence peak (particularly for diesel S100). This result is because PSCM methodology evaluates combinations of regions to search for the best group able to quantify the interest variable. During this search, many regions that present small fluorescence signal, but are more dependent of interest variable, are indicated as significant and highlighted from regions with more prominent peaks, but less correlated with interested variable.

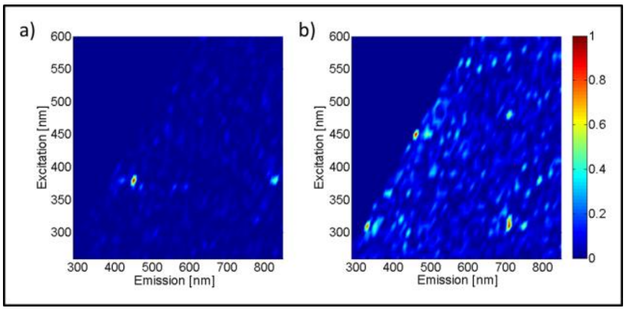

Figure 2. Qualitative information (dimensionless) obtained from PSCM analysis from (a) diesel S10 samples and from (b) diesel S100 samples.

3.2.2 Quantitative Analysis

After qualitative analysis of fluorescence data, PSCM was applied to the quantitative determination of sulfur. PSCM was applied individually for each diesel class, searching for spectral elements that, when combined linearly, could predict sulfur concentration.

The supervised methodology was applied searching for models from one to eight input variables. In other words, it means that PSCM searched for combinations between one and eight pairs of fluorescence. This search is based on calibration data set adjustment of models into sulfur prediction, evaluated using statistical parameters.

The best models from one to eight fluorescence pairs are tested using prediction group data set, and the results are presented on Tables 1 and 2, for diesel S10 and S100, respectively. Tables 1 and 2 also shows the performance metrics calculated using the calibration data set, i.e., RMSEC and R^2c.

Tables 3 and 4 present the fluorescence pairs selected for each model size, according PSCM for prediction of sulfur on class S10 and class S100. Tables 3 and 4 follow the same order of the models discussed in Tables 1 and 2.

Table 1. PSCM quantitative analysis of diesel S10.

Model size	RMSEC	R^2c	RMSEP	R^2p
1	0,23	0,62	0,33	0,07
2	0,15	0,85	0,18	0,54

3	0,09	0,94	0,20	0,77
4	0,09	0,94	0,16	0,69
5	0,06	0,97	0,26	0,50
6	0,04	0,99	0,20	0,71
7	0,05	0,98	0,21	0,32
8	0,04	0,99	0,32	0,77

Table 1 shows that models using fluorescence pairs can predict sulfur concentration in Diesel S10 with a maximal coefficient of determination of 0.77, for models with three or eight input variables. Those models, as seen on Table 2, selected similar fluorescence pairs, indicating that significant information contained on fluorescence data matrix from diesel S10 are concentrated in regions around fluorescence pairs included in the model with three pairs. These regions are the same highlighted by PSCM qualitative analysis in Figure 2 (a).

Table 2. PSCM quantitative analysis of diesel S100.

Model size	RMSEC	R^2c	RMSEP	R^2p
1	11,23	0,22	8,55	0,37
2	8,98	0,50	9,95	0,32
3	8,69	0,53	11,01	0,16
4	7,93	0,61	8,97	0,33
5	7,41	0,66	8,94	0,41
6	7,05	0,69	7,06	0,55
7	6,89	0,71	9,13	0,46
8	6,83	0,71	8,43	0,50

Table 3. Fluorescence spectral pairs selected by PSCM for prediction of sulfur into diesel S10 samples.

Model size	Fluorescence pairs
1	Ex390/ Em820
2	Ex460/ Ex450/ Em470 Em560
3	Ex370/ Ex350/ Ex390/ Em380 Em480 Em820
4	Ex470/ Ex390/ Ex440/ Ex410/ Em530 Em520 Em510 Em430
5	Ex290/ Ex410/ Ex440/ Ex490/ Ex410/ Em420 Em620 Em490 Em510 Em430
6	Ex280/ Ex450/ Ex370/ Ex520/ Ex350/ Ex410/ Em510 Em560 Em400 Em530 Em470 Em840
7	Ex360/ Ex560/ Ex350/ Ex400/ Ex480/ Ex550/ Ex470/ Em680 Em590 Em470 Em830 Em660 Em720 Em480
8	Ex550/ Ex410/ Ex400/ Ex370/ Ex530/ Ex370/ Ex520/ Ex380/ Em730 Em840 Em520 Em400 Em540 Em380 Em540 Em480

Regarding the characterization of sulfur content in diesel S100, despite increase of determination coefficient in the calibration step, with the increase of model size, results were not satisfactory. Prediction tests did not show good results either, with R^2p reaching a maximum of 0.55. This result indicates what was previously seen on Figure 2(b), were PSCM was not able to highlight significant spectral regions, and presented many dispersed regions with equivalent importance.

Table 4. Fluorescence spectral pairs selected by PSCM for prediction of sulfur into diesel S100 samples.

Model size	Fluorescence pairs
1	Ex450/ Em460
2	Ex410/ Ex450/ Em470 Em510
3	Ex570/ Ex450/ Ex410/ Em820 Em490 Em470
4	Ex390/ Ex300/ Ex420/ Ex450/ Em450 Em350 Em460 Em480
5	Ex450/ Ex330/ Ex410/ Ex410/ Ex320/ Em490 Em640 Em460 Em620 Em350
6	Ex330/ Ex440/ Ex430/ Ex450/ Ex270/ Ex510/ Em470 Em600 Em470 Em460 Em810 Em660
7	Ex320/ Ex410/ Ex340/ Ex450/ Ex370/ Ex280/ Ex310/ Em500 Em520 Em550 Em460 Em380 Em550 Em350
8	Ex350/ Ex430/ Ex490/ Ex450/ Ex380/ Ex470/ Ex410/ Ex410/ Em380 Em490 Em640 Em460 Em390 Em500 Em780 Em470

These results indicate that spectroscopic fluorescence data from diesel S10 possibly present less noisy inductor molecules, according sulfur determination, while diesel S100, mainly because of more sulfur content and other components, like polycyclic aromatic hydrocarbons, presented dispersed information, resulting in difficulties for characterization using fluorescence pairs directly.

A possible solution for the problem of dispersed information of diesel S100 spectral data is to use non-linear models to describe of sulfur content using fluorescence intensities. This modification can lead models with increasing prediction capability, reducing quenching effects on the models and producing equations that are more reliable.

4. CONCLUSION

Sulfur content determination in diesel samples became a problem to process optimization, once these measurements are usually time-consuming and require specialized people and equipment. Therefore, the development of a new on line sensor capable to quantify sulfur in diesel streams is a significant advance for oil refinery.

The 2D fluorescence Spectroscopy measurements of diesel S10 and S100 samples have shown good results as a source of information to determine the sulfur content in diesel. Although, more studies should be made to find a more representative model structure for sulfur content using fluorescence data as input variables. Linear models have produced satisfactory results for S10 samples, but for diesel S100 samples, the model and prediction qualities must be improved.

This paper has shown that it is possible to apply 2D fluorescence spectroscopy principle for developing an on-line sensor for determination of sulfur contamination in diesel. Despite the fact that the results presented by linear models aren't satisfactory for real world application, they confirm the capability on application of this spectroscopic methodology on diesel characterization. The results could be probably improved using non linear models, although the results of this are not ready.

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