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Determination of 2-ethylhexyl Nitrate in Diesel Oil Using a Single Excitation Emission Fluorescence Spectra (EEF) and Chemometrics Analysis

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Abstract

A highly sensitive spectrofluorimetric method has been developed for the determination of 2-ethylhexyl nitrate in diesel fuel. Usually, this compound is used as an additive in order to improve cetane number.

The analytical method consists in building the chemometric model as a first step. Then, it is possible to quantify the analyte with only recording a single excitation-emission fluorescence spectrum (EEF), whose data are introduced in the chemometric model above mentioned. Another important characteristic of this method is that the fuel sample was used without any pre-treatment for EEF.

This work provides an interest improvement to fluorescence techniques using the rapid and easily applicable EEF approach to analyze such complex matrices. Exploding EEF was the key to a successful determination, obtaining a detection limit of 0.00434% (v/v) and a limit of quantification of 0.01446% (v/v).

Introduction

In order to improve the fuel properties of diesel and obtaining lower exhaust emissions, numerous studies on alternative liquid and gas fuels have been performed. Furthermore, some investigations on various additives and cetane improvers [1] used to obtain better combustion characteristics have been conducted [2].

Several kind of chemicals such as alkyl nitrates, ether nitrates or nitroso compounds have been identified as effective for increasing the cetane number. The most commonly used for this purpose is the 2-ethylhexyl nitrate (EHN), that it is able to improve the combustion characteristics, shortening ignition delay and decreasing the burning point. The primary effect of the additive is to initiate early formation of a radical pool by providing an efficient mechanism for hydroxyl production. Specifically, unimolecular decomposition of EHN creates nitrogen dioxide (NO_2), which further reacts with available hydrogen atoms to produce hydroxyl radicals [3]. This effect is greatest at lower temperature and density conditions, corresponding to low-load and start-up conditions in a diesel engine, and becomes negligible at the highest temperature–density conditions examined.

This additive is a large-scale commodity, the worldwide production of which is estimated to be about 100,000 tons per year. It has long been considered as presenting no particular risk to human health. Although, the EHN is a basic product, it can be considered as a potential pollutant for soils and natural water. According the standard procedure of carbon dioxide (CO_2) Headspace Test [4], EHN was considered as being not readily biodegradable. The use of 2-ethylhexyl nitrate cetane improver increases the engine-out NOx for premixed low-temperature diesel combustion. It appears that decomposition of the nitrate cetane improver forms nitric oxide (NO) and NO2, adding an additional NOx formation mechanism, with approximately one-third of the nitrogen in the fuel additive contributing to additional NOx in the exhaust. The magnitude of the NOx formation causing an increase in engine-out NOx emissions is significant with respect to the low NOx emissions produced by premixed low-temperature diesel combustion [5]. Taking into account all these reasons above the EHN is consider as an atmospheric contaminant [6].

The ASTM D 4046 standard test method is used for determining the amount of alkyl nitrate added to diesel fuel to judge compliance with specifications covering any alkyl nitrate. This method is a spectrophotometric determination which includes a tedious liquid-liquid extraction with organic solvents and a subsequent derivatization. Alternative methologies were developed using chemiluminescence spectrometry [7] and chromatography [8]. But, in the routine daily work, the petrochemistry and automotive industry demand the development of new rapid and low cost for determining these additives.

The usefulness of spectrofluorimetric method has been widely applied as a quantitative tool in different samples. The fluorescence methods were being increasingly recognized because of their excellent sensitivity, selectivity, non- invasiveness, rapidity and low-cost equipment [9]. However the usage of spectrofluorimetry in real analyses is hampered by the complexity of real sample matrices, which may have a great variety of inherently fluorescent compounds, whose spectra appear overlapped [10]. Biodiesel and diesel show native fluorescence [11,12], and they are examples of very complex matrix, a mixture of thousands of individual compounds with carbon numbers between 9 and 23 (number of carbon atoms per hydrocarbon molecule). The diesel compounds are paraffinic, naphthenic and aromatic in different ratios. In addition biodiesel blend, incorporate esters, glycerides, pigments and antioxidants. Some fluorescent problems cannot be solve ignoring the excitation spectra, by using only the emission spectra could not provide enough information to obtain the

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analytical solutions of the problem [13]. Owing to a higher selectivity and simplicity, synchronous fluorescence spectroscopy (SFS) has been successfully explode in our recent works to discriminate biodiesel samples with respect to the base oil employed in their production [14] and quantified several parameters in diesel blends [15]. Another solution for multicomponent determination is the excitation emission matrix fluorescence spectroscopy (EEM) [16] and the non-linear angle synchronous spectrofluorimetry [17]. Other approach used in previous work to solve overlapping is single excitation and emission spectra [18].

The aim of this work is to develop a fluorimetric method for determining EHN in such complex matrices as diesel without any pre-treatment of sample. Also, by obtaining a single EEF spectrum of the raw diesel is possible to quantify the analyte.

Materials and Methods

Apparatus

Spectrofluorimeter Jasco FP6500, with a xenon discharge light source (150 W), was used to obtain all the spectra. Spectra were performed using a flux quartz cell of 18 µL.

ERASPEC uses a Fourier transform infrared (FTIR) spectrometer to directly measure the cetane improver EHN. This instrument comes preconfigured with a huge database of several hundred international calibration samples. This instrument lets the determination of various parameters with repeatability and reproducibility agrees with those required by the standard ASTM Methods [19].

Samples

A collection of twelve commercial diesel samples of different brands were acquired in Bahia Blanca. Six samples had grade 3 specifications and the other 6 grade 2. The collection was carried out in a period of 2 years. During this time occurs a change in regulations and the first 5 samples have 5% of biodiesel and the second ones 7%.

2-Ethylhexyl nitrate (CAS 27247-96-7), purity: >= 97%, was acquired in Sigma Aldrich.

A set of 30 spiked samples were prepared mixing diesel and EHN, including pure diesel oil samples, in order to obtain spiked samples with 0, 0.05, 0.1, 0.2, 0.3 and 0.5% EHN (v/v) in triplicate. The IUPAC establishes that at least 5 points in triplicate to validate a model [20]. This set was prepared using 5 commercial samples free of EHN.

In order to evaluate the applicability of the proposed method for the quantification of EHN in diesel fuel for routine purposes, the method was applied for the analysis of seven commercial diesel fuel samples, which had previously been measured using the standardized (FTIR) method (0.0024 %EHN (v/v) of repeatability).

Excitation and emission fluorescence spectra acquisition

The emission spectra were obtained with 3 nm in slits, a response of 0.5 seconds, scan speed of 1000 nm/min and 340 volts in PMT. The emission range was 350-500nm with an excitation wavelength of 346 nm. The excitation spectra were obtained with 400 volts in PMT and the studied range was 220-350nm, collecting data at 675nm. The Figure 1 shows the studied spectra in a 3D spectrum of a spiked diesel sample.

Chemometrics

Quantitative method in this study was based on the ratio between the signal intensity and the modification of the sample. Interference and
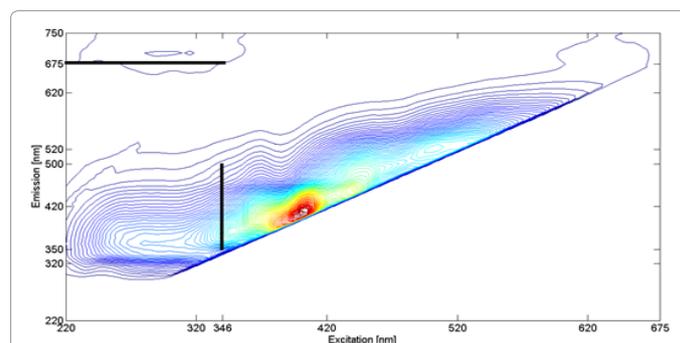

Figure 1: Selected Excitation and Emissionspectra in a 3D fluorescences pectrum of a diesel samples piked with 0.5% EHN.

overlapping of the spectral information might be overcome by using multicomponent analysis such as partial least squares (PLS) [21]. This method allowed an approach using the full spectral region rather than unique and isolated analytical bands. PLS performs data decomposition into spectral score and loading matrices prior to model building with the aid of these new variables, using spectral and concentration data. The algorithm was based on the ability to mathematically correlate spectral data to a property of interest while simultaneously accounting for all other significant spectral factors that interfered in the spectrum.

The full cross-validation leave-one-out procedure was applied, which consists of systematically removing one of the training samples in turn, and using only the remaining ones for the construction of the latent factors and regression models [22].

The predictive capability of calibration model was expressed by the determination coefficient (R-square), root mean square error of cross validation (RMSECV), and standard error of prediction (SEP).

The optimal number of principal components (PCs) was chosen in function of the first local minimum based on the RMSEC curve after cross validation in the calibration set. Predictive capability of model was evaluated by predicting the external prediction set with commercial formulation.

Results and Discussion

Conventional fluorescence may be preferred to determine one fluorophor concentration or when the mixture being analyzed contains only a limited number of compounds with fluorescence properties and a quenching effect are not to be expected. Ignoring the excitation spectra by using only the emission spectra could not be enough to obtain the solutions of the problem. So, besides the emission spectra, it seems essential to include also the analysis of excitation spectra possessing abundant information. The determination in diesel oil may contain many fluourophors. This task is further complicated by the fact that the fluorophors of interest have different characteristic excitation and emission ranges in the different samples. An inherent problem of many fluorimetric procedures is that real sample composition often includes absorption of undesirable exciting and/or emitted radiation by dissolved compounds (either fluorescent or not) or by the fluorophore itself [23]. This is termed the inner filter effect and leads to a variation not only in intensity but also in spectrum shape [24].

Modeling

The raw data Figure 2 was modeling by using PLS. The best choice for measuring the calibration merits is RMSECV that explains the

ruggedness of the model. The ability of a model to predict a new sample is expressed in terms of Root Mean Square of Prediction (RMSEP).

By observing Table 1 whit the results of EHN determination using only the excitation spectra (Ex), only the emission spectra (Em) and both together (EEF), we can demonstrate that the EEF solve efficiently the fluorescence problem. This approach achieve modeling the notably differences between the different samples.

The predict values in the CV step for the EEF model can be observed in Figure 3 compared with reference value.

The limit of quantification (LOQ) was defined as the lowest amount of an analyte in a sample that can be determined quantitatively with convenient precision and accuracy. The LOQ founded for our method is 0.01446% (v/v). The detection limit, lower limit of detection (LOD), is the lowest quantity of a substance that can be distinguished from the absence of that substance. The LOD founded for our method is 0.00434% (v/v). The resultant LOD and LOQ are better than those founded in the bibliography [8].
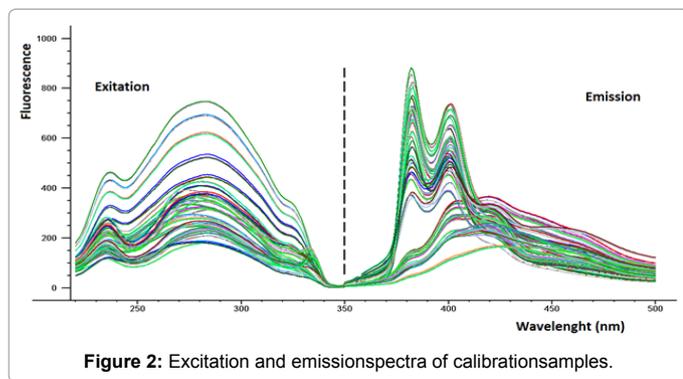

Figure 2: Excitation and emission spectra of calibration samples.

Model	Ex	Em	EEF
PLS-Latent var.	7	7	7
R-Square	0.9647	0.9817	0.9943
RMSECV	0.032	0.017	0.013
SEP	0.032	0.016	0.013
Bias	-0.000742	-0.000199	-0.000270
Offset	0.00662	0.00086	0.00126

Table 1: Compare different PLS models using only the excitation spectra, only the emission spectra and both together.
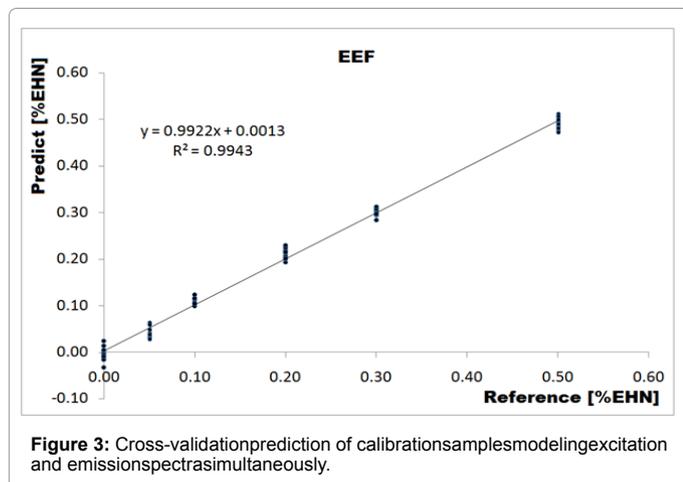

Figure 3: Cross-validation prediction of calibration samples modeling excitation and emission spectra simultaneously.
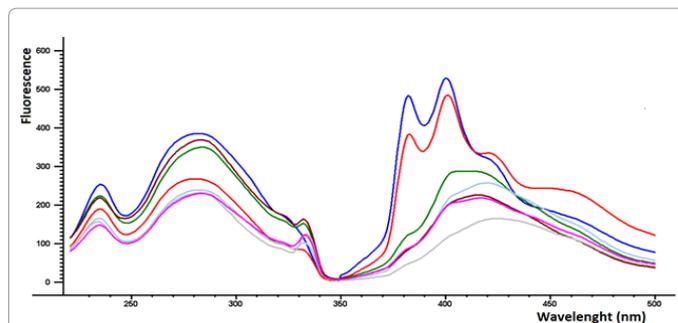

Figure 4: An EEF spectrum of the 7 commercial samples.

Sample	Real [%EHN]	Predicted [%EHN]	SD*
1	0.125	0.119	0.0132
2	0.441	0.450	0.0185
3	0.147	0.136	0.0060
4	0.235	0.240	0.0114
5	0.208	0.213	0.0170
6	0.470	0.465	0.0078
7	0.351	0.357	0.0259

*Analysis in triplicate (n=3).

Table 2: Results obtained by standardized and our proposed methods.

Commercial samples

The validated EEF model was applied to commercial diesel fuel samples (Figure 4). Table 2 shows the results obtained by the standardized method and newly developed method for 7 samples. Concentrations ranged from 0.047 to 0.470% v/v. Triplicate analyses were performed for each determination. The model predict with an RMSEP =0.018% EHN (v/v), R-square = 0.9846 SEP = 0.01856% EHN(v/v) and Bias = -0.002516.

As can be observed, for all analyzed samples, the obtained concentrations by proposed method were in close agreement with those obtained of reference method.

Conclusions

The present method is useful to be used in refineries and petrochemical industries where EHN has to be determinate.

As the developed method is simple and rapid can be proposed like an alternative to the tedious standard method EHN determination.

The analysis results are fast obtained because after the chemometric model was built, it only needs to record one excitation and one emission fluorescence spectrum of the unknown sample. The fuel sample is measured directly in the spectrofluorimeter, without any pre-treatment. The EEF data is processed by the chemometric model and the EHN concentration is obtained immediately.

Since this additive is an ambient pollutant, their control is very important, and the present approach can be use in gas stations too.

EEF approach provides an interesting improvement to fluorescence techniques being possible to quantify the analyte in complex matrix like diesel fuel, who presents inner filter effects.

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