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Short Communication

Single excitation–emission fluorescence spectrum (EEF) for determination of cetane improver in diesel fuel

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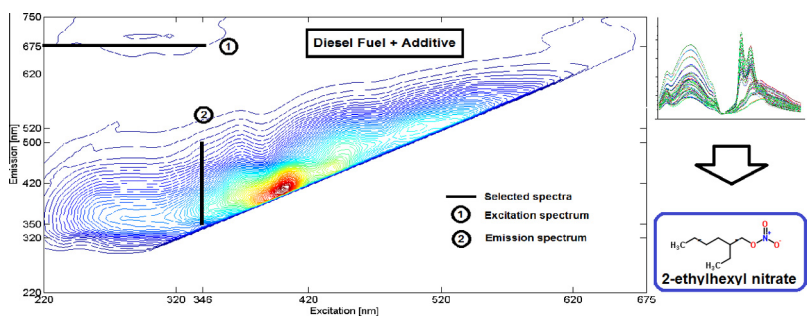
HIGHLIGHTS

- A highly sensitive spectrofluorimetric method was developed for a diesel fuel additive.
- Quantify by using a single excitation–emission fluorescence spectrum (EEF).
- This work provides an interest improvement to fluorescence techniques.

GRAPHICAL ABSTRACT



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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 kinds of chemicals such as alkyl nitrates, ether nitrates or nitrous 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 flash point (the lowest temperature at which it can vaporize to form an ignitable mixture in air). 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

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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 and density conditions examined.

This additive is a large-scale commodity, the worldwide production 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 NO_x for premixed low-temperature diesel combustion. It appears that decomposition of the nitrate cetane improver forms nitric oxide (NO) and NO_2, adding an additional NO_x formation mechanism, with approximately one-third of the nitrogen in the fuel additive contributing to additional NO_x in the exhaust. The magnitude of the NO_x formation causing an increase in engine-out NO_x emissions is significant with respect to the low NO_x emissions produced by premixed low-temperature diesel combustion [5]. These are the reasons why EHN is considered as an environmental pollutant [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 methodologies were developed using chemiluminescence and infrared spectrometry [7,8] and chromatography [9]. But, in the routine daily work, the petrochemistry and automotive industry demand the development of new rapid and low cost methods for the determination of these additives.

Spectrofluorimetric method has been widely applied as a potential tool for quantitative analysis in different samples. The fluorescence methods are being increasingly recognized because of their excellent sensitivity, selectivity, non-invasiveness, rapidity and low-cost equipment [10]. However, the analysis of real samples by spectrofluorimetry is hampered by the complexity of the matrices. Among the components of the samples may be a variety of intrinsically fluorescent compounds, whose spectra may appear overlapped [11]. Biodiesel and diesel show native fluorescence [12,13], and they are examples of very complex matrices, 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 analytical solutions of the problem [14]. 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 [15] and quantified several parameters in diesel blends [16]. Another solution for multicomponent determination is the excitation emission matrix fluorescence spectroscopy (EEM) [17] and the non-linear angle synchronous spectrofluorimetry [18]. Other approach used in previous work to solve overlapping is single excitation and emission spectra [19].

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

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 allows the determination of various parameters with repeatability and reproducibility in agreement with those required by the standard ASTM Methods [20].

Samples

Twelve commercial diesel samples of different brands from Bahía Blanca, Argentina were collected. Six samples had grade 3 specifications (46% v/v Benzene minimum, 10 ppm sulfur maximum) and the other 6 grade 2 (45% v/v Benzene minimum, 500 ppm sulfur maximum). The collection was carried out in a period of 2 years. During this time the regulation changed and the first 5 samples have 5% of biodiesel and the remainder 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. In order to validate the model IUPAC establishes that at least 5 points in triplicate should be performed [21]. 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 s, scan speed of 1000 nm/min and 340 volts in PMT. The following experimental conditions were chosen using a 3D fluorescence spectrum of pure EHN: the emission range was 350–500 nm with an excitation wavelength of 346 nm, the excitation spectra were obtained with 400 volts in PMT and the studied range was 220–350 nm, collecting data at 675 nm. Fig. 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 overlapping of the spectral information might be overcome by using multicomponent analysis such as partial least squares (PLS) [22]. 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 two spectra of a sample were collocated sequentially in each row, creating a matrix **X** with 90 rows (samples) and 281

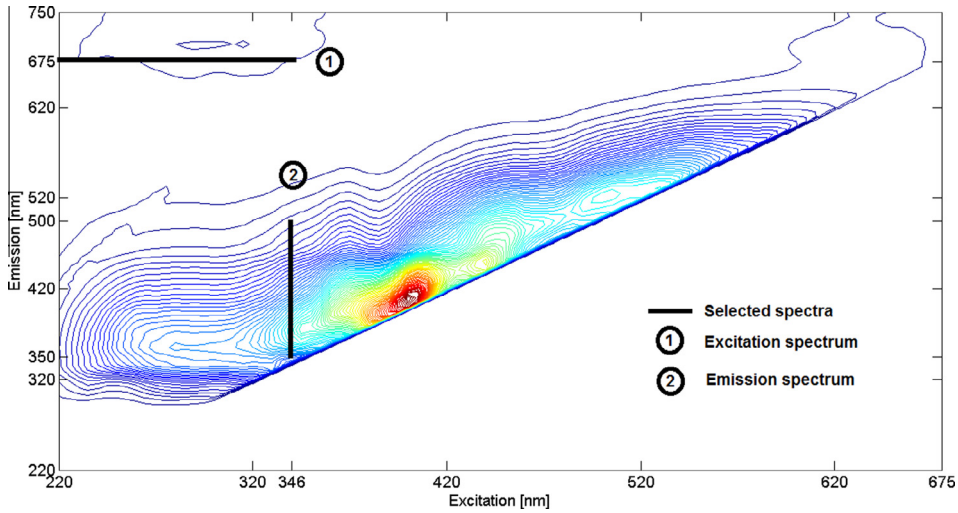

Fig. 1. Selected excitation and emission spectra in a 3D fluorescence spectrum of a diesel sample spiked with 0.5% EHN.

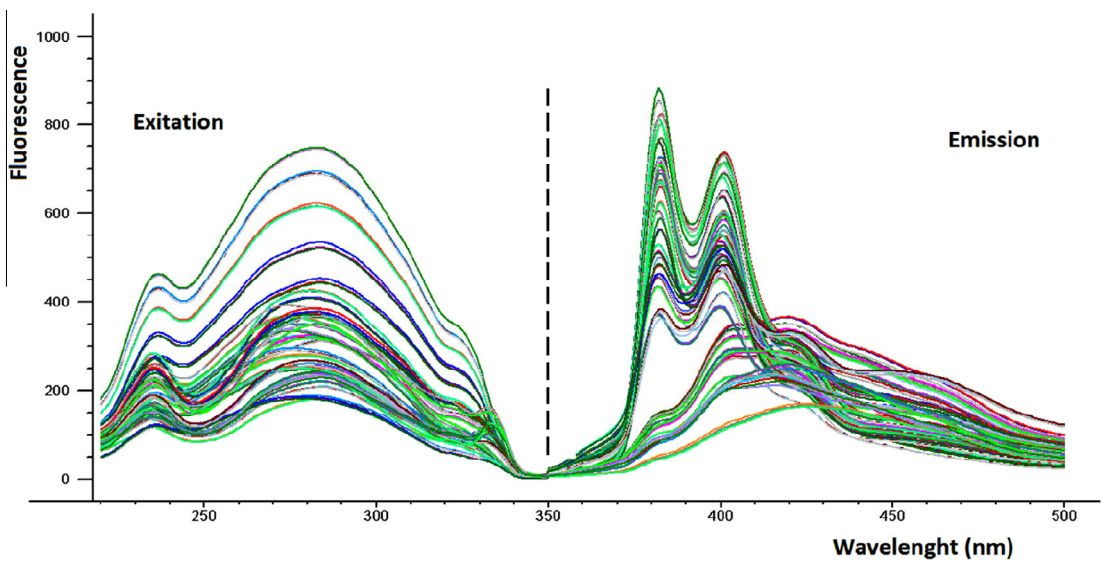

Fig. 2. Excitation and emission spectra of calibration samples.

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

	Ex	Em	EEF	%Difference Ex:EEF	%Difference Em:EEF
PLS-latent var.	7	7	7	–	–
R-square	0.9647	0.9817	0.9943	3.1	1.3
RMSECV	0.032	0.017	0.013	−59.3	−23.5
SEP	0.032	0.016	0.013	−59.3	−18.8
Bias	−0.000742	−0.000199	−0.000270	−63.6	35.7
Offset	0.00662	0.00086	0.00126	−81.0	46.5

columns (wavelengths) and a matrix **Y** with 90 rows and 1 column to construct the model. The idea of PLS is diminish the 281 variables to a few Latent Variables (LV) including enough information to explain new samples. PLS regression decomposes both **X** and **Y** as a product of a common set of factors and a set of specific loadings. So, the independent variables are decomposed as $\mathbf{X} = \mathbf{TP}^{\mathbf{T}}$ with $\mathbf{TT}^{\mathbf{T}} = \mathbf{I}$, with **I** being the identity matrix. **T** is called the score matrix, and **P** the loading matrix. Likewise, **Y** is estimated as $\hat{\mathbf{Y}} = \mathbf{TBC}^{\mathbf{T}}$ where **B** is a diagonal matrix with the "regression weights" as diagonal elements. The columns of **T** are the LV. The optimal number of LV was chosen in function of the first local minimum based on the RMSEC curve after cross validation in the calibration set. 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 [23].

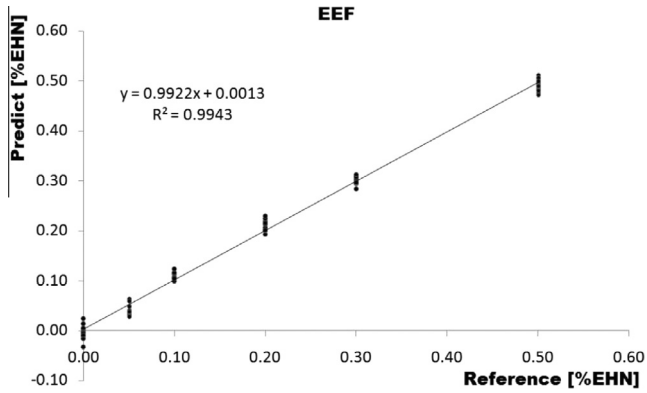

Fig. 3. Cross-validation prediction of calibration samples modeling excitation and emission spectra simultaneously.

Predictive capability of model was evaluated by predicting the external prediction set with commercial formulation.

Results and discussion

Conventional fluorescence may be preferred for the determination of one fluorophore concentration or when the mixture being analyzed contains only a limited number of compounds with fluorescence properties or when a quenching effect is not 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 fluorophores. This task is further complicated by the fact that the fluorophores 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 [24]. This is termed the inner filter effect and leads to a variation not only in intensity but also in spectrum shape [25].

Table 2
Results obtained by standardized and our proposed methods.

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 ($n = 3$).

Modeling

The raw data (Fig. 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 Fig. 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 of the proposed method is 0.00434% (v/v). The resultant LOD and LOQ are better than those found in the bibliography [9].

For the multivariate models, LOD and LOQ were calculated using the equation: LOD (or LOQ) = $k\sigma||b_k||$, where $k = 3.3$ for LOD, and $k = 10$ for LOQ, σ is the standard deviation of the net analytical signal (NAS), and $||b_k||$ is the Euclidean norm of the vector of regression coefficients estimated from the multivariate calibration model for analyte k. The idea of using NAS is extracting the part of the signal that is directly related to the concentration of the

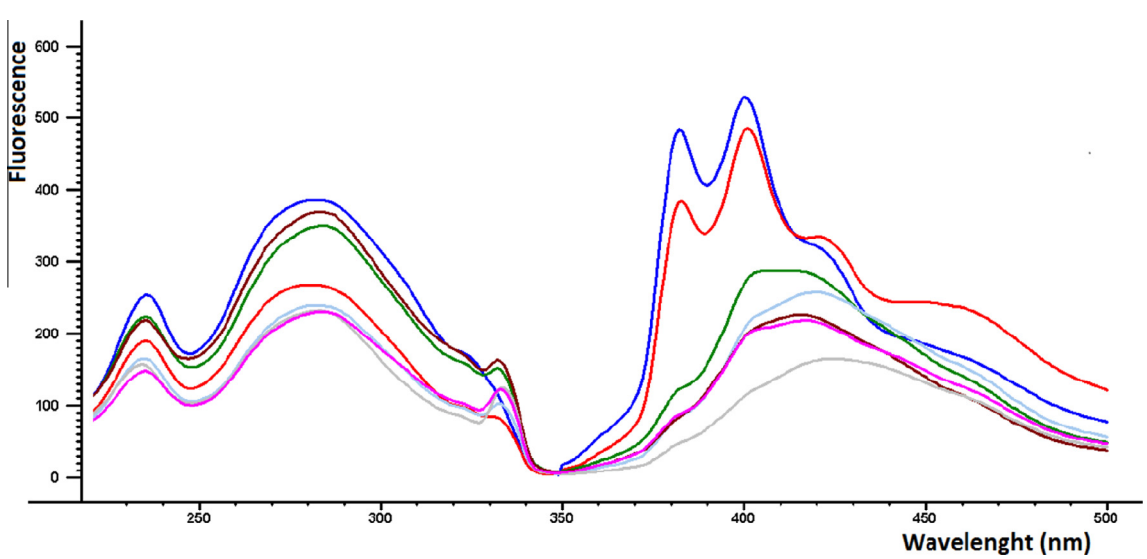

Fig. 4. An EEF spectrum of the 7 commercial samples.

analyte of interest. The NAS is obtained using an approach based on the PLS regression vector to calculate the NAS vector $r^* = b(b^Tb)^{-1}b^Tr$, where $r(j \times 1)$ is the EEF spectrum vector (j is the number of variables) and $b(j \times 1)$ is the regression vector of the PLS regression. In this work, were used the norms of 20 NAS vectors (r^*) corresponding to 20 spectra (r) of the 0% v/v EHN samples [26].

Commercial samples

The validated EEF model was applied to commercial diesel fuel samples, see Fig. 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. The procedure was performed in triplicate 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 in Table 2, the concentrations of EHN obtained by the proposed method for all analyzed samples are in close agreement with those obtained with the reference method.

Conclusions

The proposed method is simple and fast, being a good alternative to be used in refineries and petrochemical industries for the determination of EHN replacing the tedious standard EHN determination method.

Obtaining the results of the analysis is not time consuming because after the construction of the chemometric model, it is only necessary to record an emission and an excitation spectrum of each of the unknown samples. 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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