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Simultaneous determination of Solvent Yellow 124 and Solvent Red 19 in diesel oil using fluorescence spectroscopy and chemometrics ☆

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ABSTRACT

Differences in tax levels for diesel oil stimulate the illegal removal of characteristic diazo compounds purposely added to designate its possible usage. In order to reduce the losses in the national income, there is a strong need to develop a sensitive and cost-effective analytical procedure for the detection of this illegal action. In this study, we describe a novel analytical approach for a qualitative and quantitative determination of two diazo compounds (Solvent Yellow 124 and Solvent Red 19) that are usually added to diesel oil. The methodology proposed combines the use of excitation–emission matrix fluorescence spectroscopy as an analytical technique and partial least squares regression as a multiple modeling tool. With this new methodology, relatively low root mean square errors of prediction (for independent set of test samples) that are equal to 0.223 for Solvent Red 19 and 0.263 for Solvent Yellow 124, were obtained and the results were stable, which were indicated by an analysis performed after 48 and 96 h. The methodology is also nondestructive and allows for (i) simultaneous detection of diesel oil additives, (ii) determination of satisfactory limits of detection (0.048 and 0.042 mg L^{-1} for Solvent Red 19 and Solvent Yellow 124, respectively), and (iii) obtaining of considerably low relative standard deviations of 2.33% for Solvent Yellow 124 and of 3.23% for Solvent Red 19 in comparison with the existing norm level.

1. Introduction

Diesel oil is a commonly used fuel for transport, heating, and agricultural machinery drive purposes. Depending on its usage, the tax levels are different in many European and American countries. A low tax fuel (used for heating and agricultural machinery drive purposes) is spiked with additives which change its color from yellow to red. The type of additives varies from country to country, but everywhere a marker and a dye are added at the stage of oil production. In the European Union countries, Solvent Yellow 124 (SY124) is a common marker added to low tax fuels in concentration levels strictly defined in the range of 6.0 mg L^{-1}–9.0 mg L^{-1} [1]. Various dyes like Solvent Red 164 (SR164), Solvent Red 19 (SR19), and Solvent Red 26 (SR26) can be used to ensure the red color of the fuel, but their specific use and concentration levels are legally regulated in every country. In Poland, SR164 and SR19 dyes are added interchangeably in diesel oil and their concentration levels must be higher than 6.6 mg L^{-1} and 6.3 mg L^{-1}, respectively, while the concentration of Solvent Yellow 124 is regulated by the European Norm [2].

Several analytical procedures for the determination of the dye and marker in different types of oils have been described in other literature. In 2004, a validated procedure for determination of SY124 in gas oil and kerosene was introduced as the EU reference method [3]. The method is based on high performance liquid chromatography (HPLC) determination of SY124 spiked with different dyes. Another procedure for simultaneous quantitative determination of both SY124 and SR19 (a dye used in Poland and other European countries) in fuel has been developed [4]. However, it requires the separation of the reagents of interest with the HPLC technique before their qualitative or quantitative determination with UV-vis or diode array (DAD) detector. Recently, a method for detection of SR164 in vehicle exhaust has also been described in [5].

SY124 and diazo compounds SR19, SR164, and SR26, also known as Sudan dyes, have fluorescence properties since their molecules contain aromatic rings and coupled double bonds. Chen et al. have proposed [6] the use of conventional fluorescence spectroscopy for the determination of the Sudan IV dye in food samples. Traditionally, either the maximum intensity of the emission spectrum or the emission spectrum in a selected range of wavelengths is recorded at a single excitation wavelength

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characteristic for the analyzed fluorophor. This method of analysis may be preferred when the concentration of one fluorophor is to be determined or when the mixture being analyzed contains only a limited number of compounds with fluorescence properties and a quenching effect is not to be expected. In this context, the simultaneous determination of the dye and marker introduced in diesel oil, which may contain many other fluorophors, by the conventional fluorescence spectroscopy can be a difficult task. This task is further complicated by the fact that the fluorophors of interest have different characteristic excitation and emission ranges.

Excitation–emission fluorescence spectroscopy allows for the simultaneous collecting of excitation and emission spectra of samples. A sample is described by a two-dimensional signal that contains peaks from all excited fluorophors. All two-dimensional signals collected for a set of samples form a complex three-way data (third-order tensor) of dimensions: *samples* × *excitation wavelengths* × *emission wavelengths*. Such a type of data follows the trilinear or parallel factor analysis (PARAFAC) model. Construction of multivariate or multi-way calibration models [7–10] offers the possibility to simultaneously determining the dye and marker that were added to diesel oil when the samples contain many constituents that are not of interest. This is the so-called second-order advantage [10–12]. In general, the calibration models using the unfolded second-order data for a sample are to be preferred when the analyte-background interactions or changes in spectral properties of samples are examined [11].

The aim of this work is to develop a new analytical approach for the simultaneous determination of SY124 and SR19 in diesel oil without any sample preparation. For this purpose, the excitation–emission fluorescence spectroscopy is used as the analytical technique and the results of two calibration methods, e.g. partial least squares regression and N-way partial least squares regression, are compared [13] for the studied problem.

2. Materials and methods

2.1. Samples preparation

Diesel oil was purchased from a local gas station, while SY124 (98.0% purity) was obtained from Sigma-Aldrich. A stock solution was prepared by dissolving 5 mg of SY124 in 50 mL of diesel oil, while 5 mg of SR19 (obtained from IBPO Poland, 92.3% purity) was dissolved in 50 mL diesel oil in order to obtain a stock solution of SR19. The SR19 and SY124 stock solutions were mixed so that the concentration of each reagent in the mixture was varied in the range of 0–10 mg L^{-1}. A total of 20 mixture combinations were considered (see Fig. 1). Three samples were prepared (three laboratory replicates) for each mixture combination (for example 8 mg L^{-1} of SR19 and 4 mg L^{-1} of SY124, see Fig. 1), and for each of them the EEM fluorescence spectroscopy measurements were repeated three times (technical replicates). Thus, a total of 180 EEM fluorescence images were registered. The scheme of the experimental deign is shown in Fig. 1.

To determine the limits of detection and quantification, nine laboratory replicates containing SY124 at a concentration level of 2×10^{-3} mg L^{-1} and nine laboratory replicates containing SR19 at a level of 2×10^{-3} mg L^{-1} were additionally prepared. Repeatability was evaluated using a set of 18 samples at three concentration levels (4, 5, and 6 mg L^{-1}). Three solutions at each concentration level were prepared for SY124 (a total of 9 samples) and the same number of solutions at the same concentration levels were prepared for SR19 (9 samples). The measurements were performed immediately after sample preparation. In order to evaluate the stability of the measurement results over time, 18 samples (used for testing the repeatability) were analyzed after 48 and 96 h.

2.2. Fluorescence measurements

A Carry Eclipse Varian FL0811M000 spectrofluorometer with right angle geometry was used to perform the measurements. The emission spectra were registered in a 2 nm interval from 350 to 800 nm (226 wavelengths) at 46 excitation wavelengths selected in a 10 nm interval in the range of 250–700 nm. Detector sensitivity was set to 500 V and the excitation and emission slits were set to 5 nm. Raw spectral data were subjected to a further chemometric analysis and modeling.

2.3. Preprocessing of fluorescence signals

One of the most important preprocessing steps when working with fluorescence signals is the correction of Rayleigh scattering, which is chemically irrelevant. Different approaches for scattering correction have been described in the literature. The matrix elements corresponding to the spectral regions with the Rayleigh scattering can be (i) replaced with zeros [14,15], (ii) treated as missing values [16], or (iii) removed and the missing elements of the signal can be interpolated in different possible ways [17,18]. In this paper the scattering effect was removed and the signals were interpolated by the Delaunay triangulation [17].

2.4. Modeling of excitation–emission data

2.4.1. Partial least squares regression

Partial least squares regression, PLS, is a popular chemometric tool used to construct multivariate calibration models. The aim of the multiple PLS regression is to describe the relationship between a set of explanatory variables, **X** (a set of matricized EEM images as: *samples* × (*excitation wavelengths* × *emission wavelengths*)) and a response variable, **y** (a marker or a dye concentration) [13]. In other words, the original strongly correlated spectral signals are replaced by a small number of latent factors (new variables), **T**, for which the maximum covariance with the modeled property, **y**, is observed. The PLS-1 model can be described in the following way:

$$\mathbf{X}=\mathbf{T}\mathbf{P}^{\mathbf{T}}+\mathbf{E} \tag{1}$$

$$\mathbf{y}=\mathbf{T}\mathbf{q}+\mathbf{r} \tag{2}$$

where $\mathbf{X}(I\times JK)$ is the matricized form of the data, vector $\mathbf{q}(f\times 1)$ holds the regression coefficients for f PLS factors, $\mathbf{T}(I\times f)$, the elements of $\mathbf{P}(JK\times f)$ matrix the PLS loading values, matrix $\mathbf{E}(I\times JK)$ holds the differences between the observed and predicted **X** with f PLS factors and the residual vector $\mathbf{r}(I\times 1)$ contains the differences between the observed and predicted $\mathbf{y}(I\times 1)$ values.

2.4.2. N-way partial least squares

The N-way partial least squares, N-PLS, is a generalization of the classic PLS regression for higher order data arrays [19]. In the course of the model construction, three-way data array, $\underline{\mathbf{X}}$, of size $I\times J\times K$ (e.g. *samples* × *excitation wavelengths* × *emission wavelengths*), is decomposed into new variables (the so-called triads). The number of the new variables constituting the triads depends on the dimensionality of modeled data.

Prior to modeling, the three-way array is metricized into a data matrix. For the data matrix, $\mathbf{X}^{I\times JK}$, of size $I\times JK$, where I is the number of samples, J is the number excitation wavelengths, and K is the number of emission wavelengths, the decomposition can be presented as follows:

$$\mathbf{X}=\mathbf{H}(\mathbf{W}^{J}\,|\otimes|\,\mathbf{W}^{K})^{T}+\mathbf{E} \tag{3}$$

where $\mathbf{X}(I\times JK)$ is the matricized form of the data, $\mathbf{H}(I\times f)$ is the score matrix, $\mathbf{W}^{J}$ and $\mathbf{W}^{K}$ are the respective loading matrices for

Reagent	Concentration[mg · L^{-1}]																			
SY124	0	0	0	0	2	2	2	4	4	5	5	5	7	7	7	9	9	10	10	10
SR19	0	2	5	10	0	2	7	3	8	0	5	10	0	2	7	3	8	0	5	10

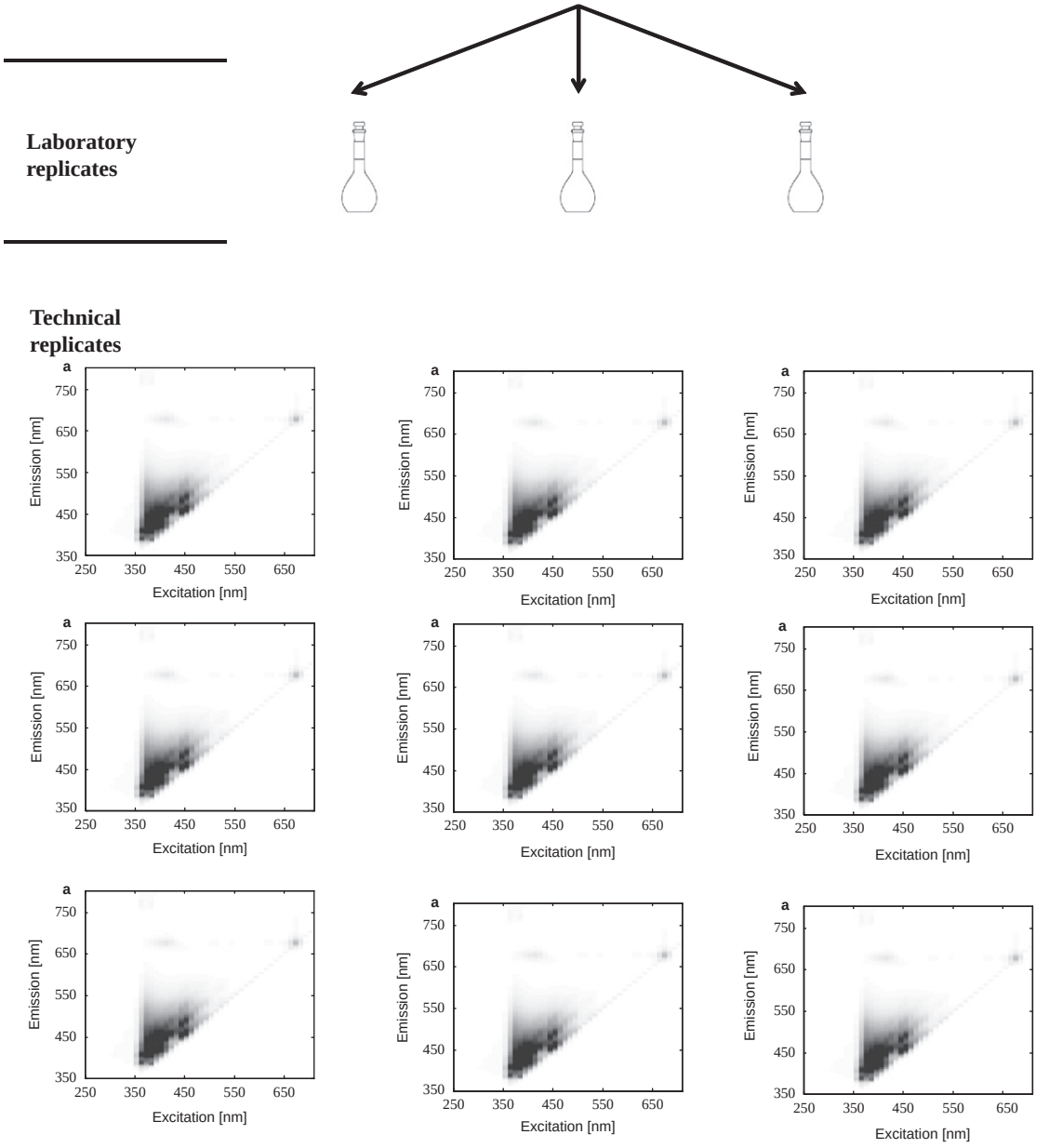

Fig. 1. Design of the experiment with respect to concentrations of a marker compound (Solvent Yellow 124, SY124) and a dye compound (Solvent Red 19, SR19).

the excitation mode and the emission mode, $\mathbf{E}(\mathrm{I} \times \mathrm{JK})$ is the error matrix. The symbol $|\otimes|$ denotes the Khatri Rao product [20].

The construction of triads is optimized in order to maximize the covariance between **H** and **y**. Calibration models are constructed using the new variables. A more detailed description of the N-PLS method can be found in [19].

2.5. The complexity of regression models

The number of new variables (factors) used for the model's construction is called the complexity of the model, *f*. To determine the optimal complexity a cross-validation procedure is usually used [21]. At each step of the validation procedure either a sample or a subset of *p* samples (a validation set) is removed from the data and PLS models with increasing complexity are built for the remaining samples (a model set). Then, a prediction is performed for the removed samples based on the model set. The procedure is repeated for the next subset of *p* objects removed from the data, while all possible subsets are not considered when validating the models with an increasing complexity. The root mean square error of cross-validation, RMSECV, is calculated as a measure of the model's performance using the following equation:

$$\mathrm{RMSECV}(f) = \sqrt{\frac{1}{m}\sum_{i=1}^{m}(y_{-1} - \hat{y}_{-i(f)})^2} \tag{4}$$

where y_{-i} is the *i*-th experimental value of the response variable removed during the cross-validation procedure, $\hat{y}_{-i(f)}$ is the *i*-th

predicted value of the removed response variable using the PLS model with f latent factors and m is the number of objects in the model set.

The optimal PLS model is the one characterized by the lowest or acceptable RMSCV. The choice of p in the leave-p-out cross-validation scheme depends on the user and data dimensionality. The Monte Carlo cross-validation procedure is a cross-validation scheme where the validation set of samples is selected randomly from the model set [22]. In our study, during the cross-validation procedure all of the technical replicates were included in the same validation set of samples (a cancelation group). Once a calibration model of a definite complexity is constructed, its fit is scored by the root mean square error (RMSE):

$$\mathrm{RMSE} = \sqrt{\frac{1}{m}\sum_{i=1}^{m}(y_i - \hat{y}_i)^2} \quad (5)$$

where y_i is the i-th experimental response value, $\hat{y}_i$is the i-th predicted response value using the model of definite factors and m is the number of samples in the model set.

The prediction properties of the constructed model are evaluated on the basis of an independent test set (dataset that was not used for the model's construction) and expressed as root mean square error of prediction (RMSEP):

$$\mathrm{RMSEP} = \sqrt{\frac{1}{m_t}\sum_{i=1}^{m_t}(y_i^t - \hat{y}_i^t)^2} \quad (6)$$

where y_i^t and $\hat{y}_i^t$ are the i-th experimental and i-th predicted response value for the i-th independent test sample using the calibration model of a definite complexity and m_t is the number of independent test samples.

2.6. Software

All calculations were performed within the MATLAB environment. PLS models were constructed using the freely available TOMCAT toolbox [23]. The algorithm for scattering correction described in [17] was used. The N-way Toolbox (version 3.1) [24] was adopted to construct N-PLS models.

3. Results and discussion

The raw spectra collected were characterized by a relatively high signal-to-noise ratio and therefore, neither a noise correction nor baseline elimination was performed.

The characteristic Rayleigh scattering was observed for the samples examined, e.g. samples of a clean diesel oil without additives, an oil with the SY124 marker, an oil with SR19 dye and an oil spiked with both the SY124 marker and the SR19 dye. Fig. 2a displays the scattering effect as a diagonal line of peaks starting at the wavelength of 350 nm. As was mentioned earlier, the Rayleigh scattering is a chemically irrelevant component and should be removed prior to the models' construction (the first step of the raw data preprocessing). The correction procedure used in this article consists of detecting the maxima of the Rayleigh scattering peaks followed by counting the number of sampling points with the scattering effect and replacing the values of the sampling points with a scattering effect with values interpolated using the Delaunay triangulation [25]. For our dataset, it was found that seven sampling points on the left side and seven sampling points on the right side of the detected maxima were sufficient to handle the scattering effect in all EEM fluorescence images. A contour map of the EEM fluorescence image obtained from a pure diesel oil sample after removing the Rayleigh scattering is presented in Fig. 2b. It should be emphasized that only meaningful spectra were considered, e.g. the spectra for each sample were recorded so that the lower emission wavelength level was at least equal to the lower excitation wavelength level.

3.1. Construction of PLS models for SR19 and SY124

Prior to the construction of the multiple PLS models, the EEM data containing 180 excitation–emission spectra were unfolded in the form of *spectra* × (*emission wavelengths* × *excitation wavelengths*). Then, model and test sets were selected. The PLS model calibrating Solvent Yellow 124 was built using 117 spectra (model set) describing samples with analyte concentration at levels of 0, 5, 7, and 10 mg L^{-1}. The remaining 63 spectra (i.e. samples with SY124 concentrations equal to 2, 4, and 9 mg L^{-1}) formed the test set. To construct model for calibration of Solvent Red 19 spectra were divided into a model set containing 108 spectra (EEMs of samples with concentrations of SR19 equal to 0, 3, 5, 7, and 10 mg L^{-1}, respectively) and a test set formed by 72 spectra (containing 2, 5, and 8×10^{-3} mg L^{-1} of SR19).

Two individual PLS-1 models were constructed to predict the concentration of SY124 or SR19, respectively. The Monte Carlo cross-validation scheme with a validation set of 20 samples ($p=20$) was adopted to evaluate the optimal complexity of the models. At each cross-validation step, 20 samples out of 500 were randomly selected for the validation set.

Firstly, the PLS-1 model for the prediction of the concentration of SR19 was constructed. The model with eight latent variables, presented in Fig. 3a, was considered as the optimal. Its RMSCV was equal to 0.174. The fit and the prediction properties, expressed as RMSE and RMSEP, were found to be 0.153 and 0.223, respectively. As indicated in Fig. 3a, the model has similar variances for the predictions of the model and test set samples regardless of their concentration levels.

The optimal PLS model obtained for SY124 also contained eight latent variables. RMSE and RMSEP were equal to 0.229 and 0.263, respectively. Compared to the PLS model constructed for SR19, a larger scatter of the values predicted for the model and test set samples was observed. The variances of concentrations predicted for the model and test set samples are comparable at different concentration levels (see Fig. 3b).

3.2. Construction of N-PLS models for SR19 and SY124

A possible improvement of the calibration models can be expected when using N-PLS because of the well-defined three-linear structure of the excitation–emission data. Therefore, the N-PLS models were built for the same model and test set samples (see Section 3.1) as those used to construct the conventional PLS-1 models on the metricized data, but the data sets were arranged as *spectra* × *excitation wavelengths* × *emission wavelengths*. Orthogonality constraint was not considered for any of the modes. Two N-PLS models, each of which had 10 latent variables, were used for the prediction of the concentrations for SR19 and SY124, respectively.

As indicated in Table 1 and the graphical representation in Fig. 3d, the N-PLS model and the classic PLS model constructed for SY124 have virtually the same performance (compare the values for fit and prediction shown in Table 1). On the other hand, when modeling SR19, PLS outperforms the N- PLS model (see Table 1 and Fig. 3b and d) and requires a smaller number of latent variables compared to the N-PLS model.

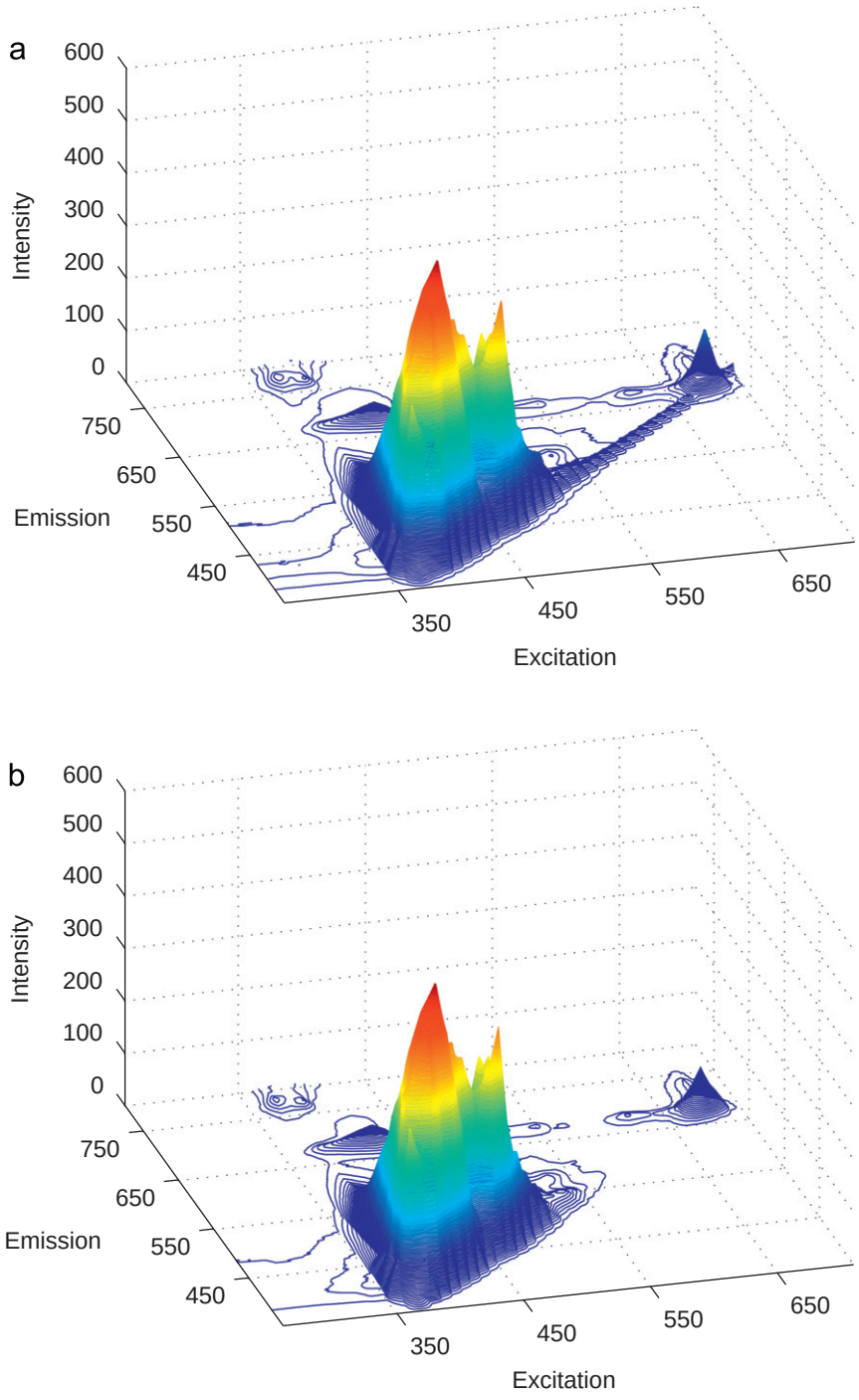

Fig. 2. Landscapes of excitation–emission matrices for pure diesel oil: (a) with the Rayleigh scattering effect and (b) without the Rayleigh scattering effect.

3.3. *Figures of merit of PLS models*

Considering a good performance of classic PLS models, figures of merit were calculated as described in [26,27]. The sensitivity was calculated as the inverse of Euclidean norm of vector containing regression coefficients, and was equal to 13.67 and 11.49 for models describing concentration of SR19 and SY124, respectively. Selectivity of PLS models was equal to 0.015 for SR19 and 0.036 for SY124.

Next, the ratio between instrumental noise and sensitivity was calculated for both calibration models. On the basis of the ratios, limits of detection (LODs) were calculated as the ratio times 3.3 for both analytes (a dye and a marker).

The LOD value of 0.048 mg L^{-1} and 0.042 mg L^{-1} was obtained for dye and for marker, respectively. The limits of quantification (LOQ) were calculated as 10 times the ratio values for both analytes. The LOQ values were equal 0.144 and 0.126 mg L^{-1} for SR19 and SY124, respectively.

3.4. *Analytical validation*

Next, the repeatability of the proposed analytical approach was tested. Predicted mean concentration values, relative standard deviations (RSD), and the uncertainty for the three concentration levels that were obtained by conventional PLS are shown in Table 2.

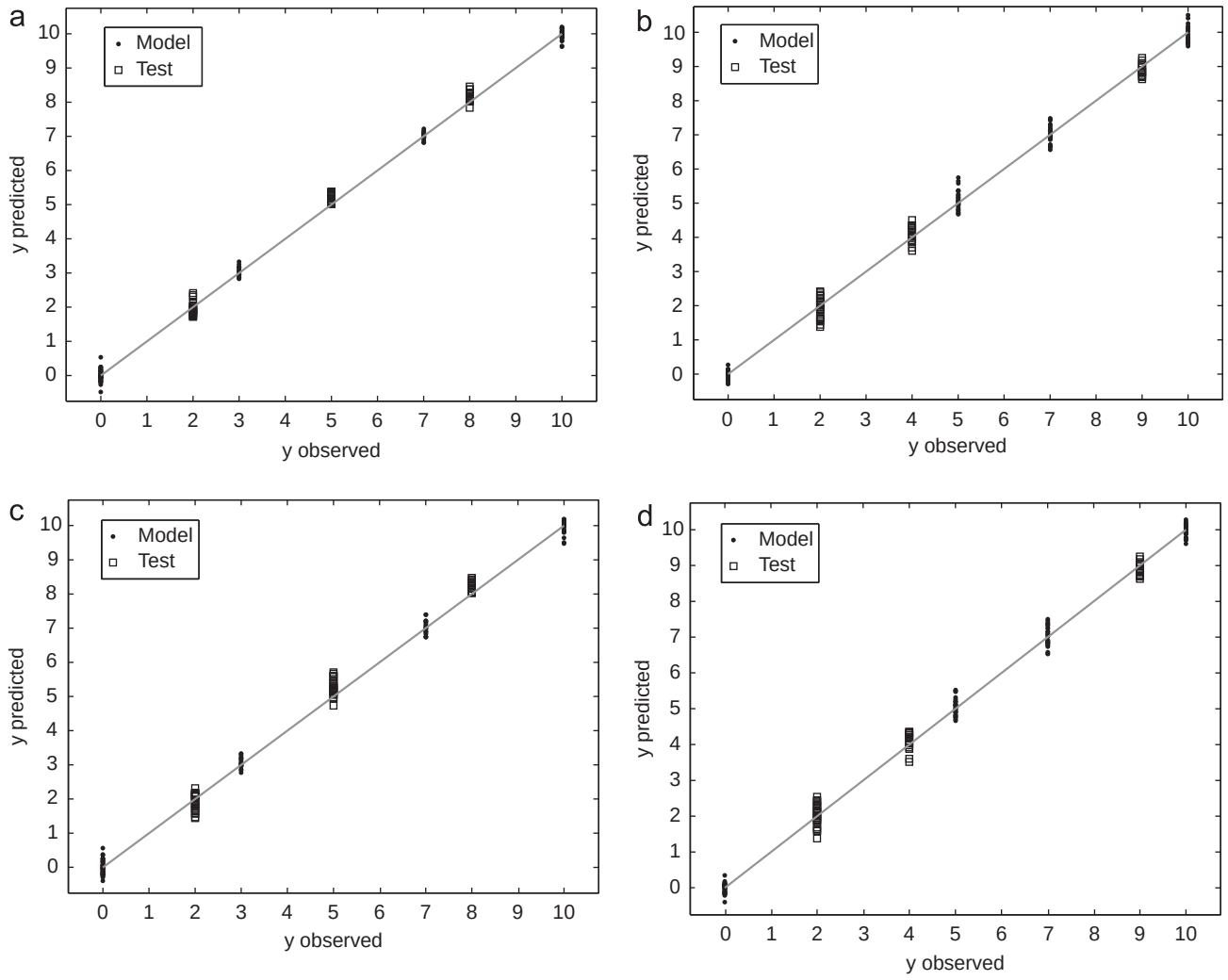

Fig. 3. Calibration models are presented as **y** predicted vs. **y** observed for model (•) and test set samples (□). The PLS models of complexity eight for: (a) dye (Solvent Red 19) and (b) marker (Solvent Yellow 124). The N-PLS models of complexity ten for: (c) dye (Solvent Red 19) and (d) marker (Solvent Yellow 124).

Table 1
Fit and prediction properties of calibration models constructed for SR19 and SY124. PLS models were constructed with eight factors, for N-PLS models construction 10 factors were used.

Additive	PLS		N-PLS	
	RMSE	RMSEP	RMSE	RMSEP
SR19	0.153	0.223	0.193	0.305
SY124	0.229	0.263	0.212	0.260

Table 2
Repeatability of proposed method obtained from three concentration levels. Mean values were calculated for three laboratory replicates, uncertainty calculated for 95% confidence interval. PLS models were constructed with 8 factors.

Concentration [mg L^{-1}]	PLS					
	SY124			SR19		
	Mean [mg L^{-1}]	RSD [%]	± [mg L^{-1}]	Mean [mg L^{-1}]	RSD [%]	± [mg L^{-1}]
4	3.559	3.14	0.341	4.049	1.33	0.164
5	4.394	3.25	0.435	5.129	1.24	0.194
6	6.027	3.31	0.607	6.282	4.42	0.846

From the RSD values presented in Table 2, one can conclude that the validated approach for SR19 performs better than the one for SY124. In the literature [3], the analytical validation of the HPLC method for Solvent Yellow determination is presented. RSD (calculated at the level of 6 mg mL^{-1}) and LOD are equal 0.68% and 0.02 mg mL^{-1}, respectively. The corresponding values for presented method are 3.14% and 0.048 mg L^{-1} for RSD (at the same concentration level) and LOD, respectively. The HPLC method for the dye determination presented in [4] is not validated thus comparison of the results cannot be compared.

The stability of the results obtained from PLS method was tested statistically using the measurements performed immediately after preparation (set as a conditional level of 0 h) and after 48 and 96 h. The results of the analysis in three 48 h intervals are presented in Table 3.

Two statistical hypotheses were checked for the dye and marker concentrations predicted by the conventional PLS method using F-test. The first hypothesis is that there is no difference in the variances of the predicted values obtained from PLS for samples analyzed at a conditional time of 0 h and after 48 h. For oil samples spiked with a dye the F-value was equal to 1.107, while a F-value of 0.899 was calculated for the oil samples mixed with a marker. The p-values calculated for the two-sided F-test

Table 3
Robustness of proposed method calculated for three concentration levels tested after 0 h , 48 h, and 96 h. Mean values were calculated for three laboratory replicates, uncertainty calculated for 95% confidence interval. PLS models were constructed with eight factors.

Concentration [mg· L^{-1}]	Time [h]	PLS SY124			SR19		
		Mean [mg L^{-1}]	RSD [%]	± [mg L^{-1}]	Mean [mg L^{-1}]	RSD [%]	± [mg L^{-1}]
4.000	cond. 0	3.559					0.164
	48	3.233	3.65	0.360	3.941	1.92	0.350
	96	3.410	2.33	0.242	3.917	1.65	0.197
5.000	cond. 0	4.394	3.25	0.435	5.129	1.24	0.194
	48	4.727	3.27	0.471	5.076	3.29	0.663
	96	4.518	4.37	0.505	5.017	3.69	0.564
6.000	cond. 0	6.027	3.31	0.607	6.282	4.42	0.846
	48	5.647	2.26	0.388	6.100	4.21	0.967
	96	5.787	4.82	0.849	5.996	3.52	0.644

are 0.9492 and 1.053, respectively. The null hypothesis is rejected when the p-values are smaller than a definite significant level value, α, of 0.01 or 0.05. For the studied case, the null hypothesis of no significant differences in the two variances calculated for the PLS predicted values can be accepted for both types of samples at a level of significance of 0.05. The second null hypothesis is that there is no difference in the variances of the predicted values obtained from PLS for the samples analyzed at a conditional time of 0 h and after 96 h. The values of the estimated F ratios were 1.154 (p-value of 0.9284) for the samples with the dye and 0.899 (p-value of 1.053) for the samples mixed with the marker. Again the null hypothesis can be accepted at a significant level of 0.05.

Assuming a significant level of 0.05 it can be concluded that the proposed analytical approach is stable over time (there are no significant differences in models' performance) and constructed calibration models allow for the determination of analytes in samples after 48 and 96 h with comparable and acceptable error levels.

4. Conclusions

In this paper, a novel approach combining an excitation–emission matrix fluorescence spectroscopy as an analytical technique and partial least squares regression as a multiple modeling tool was developed to quantitatively and qualitatively determine Solvent Red 19 and Solvent Yellow 124 in diesel oil. It is a nondestructive procedure which does not require expensive reagents and laborious sample preparation prior to analysis. The results obtained from the validation procedure give evidence that the approach is stable over time. These attractive features make the proposed methodology a potential screening technique that can be used directly at the place where samples are collected and thus to support the actions of the customs office and related agencies. Two calibration methods were evaluated and compared, namely PLS and N-PLS. Calibration models constructed to predict concentration of SY124 in samples have comparable fit and prediction properties. Compared to PLS, the N-PLS model describing content of SR19 was characterized with higher RMSE and RMSEP values. In our application, the PLS model is preferred due to its conceptual simplicity. In terms of validation parameters (RSD and LOD), the HPLC method for SY124 determination performs better than the proposed approach. On the other hand, simplicity and low cost of fluorescence spectroscopy encourage its use.

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