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Energy Fuels, **Just Accepted Manuscript** • DOI: 10.1021/acs.energyfuels.7b00870 • Publication Date (Web): 21 Jun 2017

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NIRS coupled with multivariate methods for the characterization of ethanol adulteration in Premium 91 gasoline

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Abstract

Ethanol, due to its high octane rating of 108, is often added as adulterant to premium 91 gasoline fuels to boost up their octane ratings to 96 or more but it does not provide the same power to engine as that of super-premium 96 gasoline fuels. In this study, a sensitive near infrared spectroscopy (NIRS) coupled with chemometrics was proposed for analysis of ethanol content in Premium 91 gasoline fuels. Standard samples of Premium 91 octane gasoline were collected from Oman's national refining and Petrochemicals Company commonly known as ORPIC. The Premium 91 samples were then intentionally spiked with ethanol at various levels. The near-infrared spectroscopy was employed in the absorption mode to obtain the spectra of all samples scanning from 700 to 2500 nm. Then, partial least-squares (PLS) regression, partial least-squares discriminant analysis (PLS-DA) and principal component analysis (PCA), and were applied to model and interpret the near-infrared spectra. A PLS-DA model was developed to discriminate between the pristine gasoline samples and those intentionally mixed with ethanol, with excellent results ($R^2 = 98\%$ and $RMSE = 0.049$) by random cross validation. A PLS regression model was established to determine the ethanol content in Premium 91 gasoline samples, with values of $R^2 = 99\%$ and $RMSECV = 1.88$ and $R^2 = 99\%$ and $RMSEP = 1.58$ for cross-validation and test-set validation results, respectively. This newly developed method, is simple, rapid, and can quantify less than 2 % of ethanol adulteration in premium 91 gasolines.

Keywords

Near-infrared; gasoline; ethanol; Multivariate methods.

1. Introduction

Fossil fuel plays a major role in today's world economy as it is the main energy source of most of the vehicles currently in use¹. Nowadays, fossil fuel reserves are being depleted due to over exploitation and high demand in many developing countries as a result of the improving living standards². The increasing demand and the heavy taxation imposed by many governments worldwide, due to environmental concerns, has skyrocketed the prices of petrol derivatives. As a consequence of this situation, blending of gasoline and other fuels has become a common practice in many places where the prices of adulterants is much lower as compared to those of pure fuels^{1,2}. However, excessive adulteration of gasoline and diesel fuels for financial gains has led to serious environmental and health problems³. Adulterants are selected based on economic benefits, ease of blending, availability and physicochemical similarities to the fuel⁴. Kerosene, industrial solvents such as paint thinner and recycled lubricants are common adulterants in fuels due to the lower taxes imposed on these adulterants as compared to the taxation on gasoline^{5,6,7,8}.

Ethanol has also been added to the list of adulterants found in fuels because of its physicochemical properties. Ethanol, which is a renewable fuel, is economically viable and ecologically safe and it is a recommended additive for fuel as it increases the combustion efficiency of gasoline and reduces air pollution. However, a high ethanol percentage in gasoline may result in corrosion of the metallic components of the fuel system, variation in the fuel vapor pressure and in the amount of air needed for efficient combustion, which ultimately leads to low engine power or even engine knock^{9,10}.

The need for the estimation of the ethanol adulteration in gasoline, before reaching the petrol stations, is more important than ever. Several analytical methods are currently available for the detection and quantification of ethanol in gasoline. These methods include the measurement of density, rate of evaporation, viscosity and ash content, and also the use of spectroscopic or chromatographic techniques^{11, 12, 13, 14}.

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5 In the past two decades near infrared spectroscopic methods combined with multivariate analysis
6 have gained special attention thanks to their ease of use, reliability and reproducibility of results
7 and cost effectiveness^{15, 16}. At industrial level, NIR spectroscopic methods have been used for
8 extraction and quantification of a wide range of products, such as crude extracts or pure
9 compounds that may have direct or indirect absorbance. NIR spectra are retrieved quickly and
10 are used to determine the quality of gasoline based on the octane rating, alcohol percentage, and
11 also the percentages of the other components of the gasoline fuel^{17, 18}. The NIR spectrum is
12 usually employed for qualitative analysis of samples, but quantitative analysis of physico-
13 chemical properties with NIR is also possible by using multivariate regression techniques¹⁹. NIR
14 spectroscopy has shown far better results in the detection of adulteration in gasoline samples
15 when compared to other analytical methods^{20, 21, 22}. NIR spectroscopy combined with
16 multivariate models^{23,24} has been shown to be an appropriate method for the determination of
17 super-premium 95 octane gasoline adulteration with premium 91 gasoline¹⁹.
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30 Herein, a simple, rapid and reliable method, combining NIR spectroscopy and multivariate
31 methods, is proposed for detection and quantification of ethanol adulteration in premium 91
32 gasoline.
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38 **2. Experimental**

39 *2.1. Preliminary characterization of fuel samples*

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42 This research work is related to Near Infrared (NIR) spectroscopic methods to determine
43 chemical, chemical-based and physical properties of hydrocarbon fuels, which were obtained
44 from the petrochemical industry of the Sultanate of Oman. Fuel physiochemical properties such
45 as aromatic hydrocarbons content, total sulfur content, density, and many others were already
46 established for the characterization of fuel samples²⁵⁻³². The newly developed NIR spectroscopic
47 methods was used for checking the quality as well as the quantity of adulterant of petroleum
48 products obtained from different oil refineries and from different geographical regions of Oman.
49 These newly developed NIR spectroscopic methods combined with multivariate methods will
50 complement the standard ASTM methods thanks to their versatility, efficiency, rapidity.
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2.1.1. Preparation of Adulterated Samples

Standard samples of Premium 91 octane rating gasoline were collected from the Oman's national refinery and petrochemicals company (ORPIC). Premium 91 octane rating samples were spiked with ethanol at the following percentage levels: 0 %, 1 %, 3 %, 5 %, 7 %, 10 %, 15 %, 20 %, 25 %, 30 %, 35 %, 40 %, 45 %, 50 %, 55 %, 60 %, 65 %, 70 %, and 75 %. Analysis of each sample was performed by triplicate for reliability reason. A total of 60 samples used were 60 for this study. All the samples were grouped into two sets, a training set which constitutes 70 % of the total samples for the purpose of establishing the PLS regression model, and a validation set which constitutes 30 % of the samples for evaluating the prediction performance of the model.

2.2. NIR Spectroscopic analysis

A Frontier NIR spectrophotometer (BSEN60825-1:2007) by Perkin Elmer was used to measure the absorption of all the samples from 4000 cm^{-1} to 10000 cm^{-1} , at resolution of 2 cm^{-1} and employing CaF_2 sealed cell with a path length a 0.2 mm.

2.3. Statistical analysis

For statistical analysis, The Unscrambler version 9.0 software and Microsoft Excel 2010 software were used. Multivariate models like PLS, PLSDA and PCA were established for both the pristine and the ethanol spiked gasoline 91 samples. PCA analysis is a dimensionality reduction multivariate exploratory method. PCA is helpful in revealing trends in the samples and in identifying outliers in the data set¹⁹.

In order to remove the noise from information two types of spectral pretreatment like 1st derivative with S-Golay of 2nd polynomial order and 11 smoothing points and SNV were applied to the collected NIR spectra. Leave-one-out cross validation procedure was used the internal validation of the PLSDA model. But for the PLSR model both the internal and external cross validations were performed¹⁹. Random cross validation was employed for the internal cross validation of PLSR. External cross validation was applied by using the test set. RMSCEV and RMSEP were used as measures to check the predictive ability of the PLS regression model both for internal and external validations. In case of optimal PLSR model the measured RMSECV as well as RMSEP values should be minimum with less number of factors and with the highest number of R^2 .

3. Discussion & Results

3.1. Characterization of fuel oil

For determination of physiochemical properties of gasoline samples from spectral data base, classification methods, mainly PCA, PLS-DA, and prediction methods, mainly PLSR, were used for data analysis. The spectral regions of NIR data base most related to the physiochemical properties of the fuel oil sample were identified. Multivariate exploratory method, PCA was applied for the visual analysis of the spectral data. At last, the PLSR was used to quantify the value of ethanol adulterant in premium 91 gasoline samples from spectral NIR data.

3.1.1. NIR spectra

The NIR spectra for both the adulterated and un-adulterated gasoline samples is shown in Figure 1. The absorptions peaks in NIR spectra are due to combinations and overtones molecular vibrations absorptions of C-H hydrocarbons.

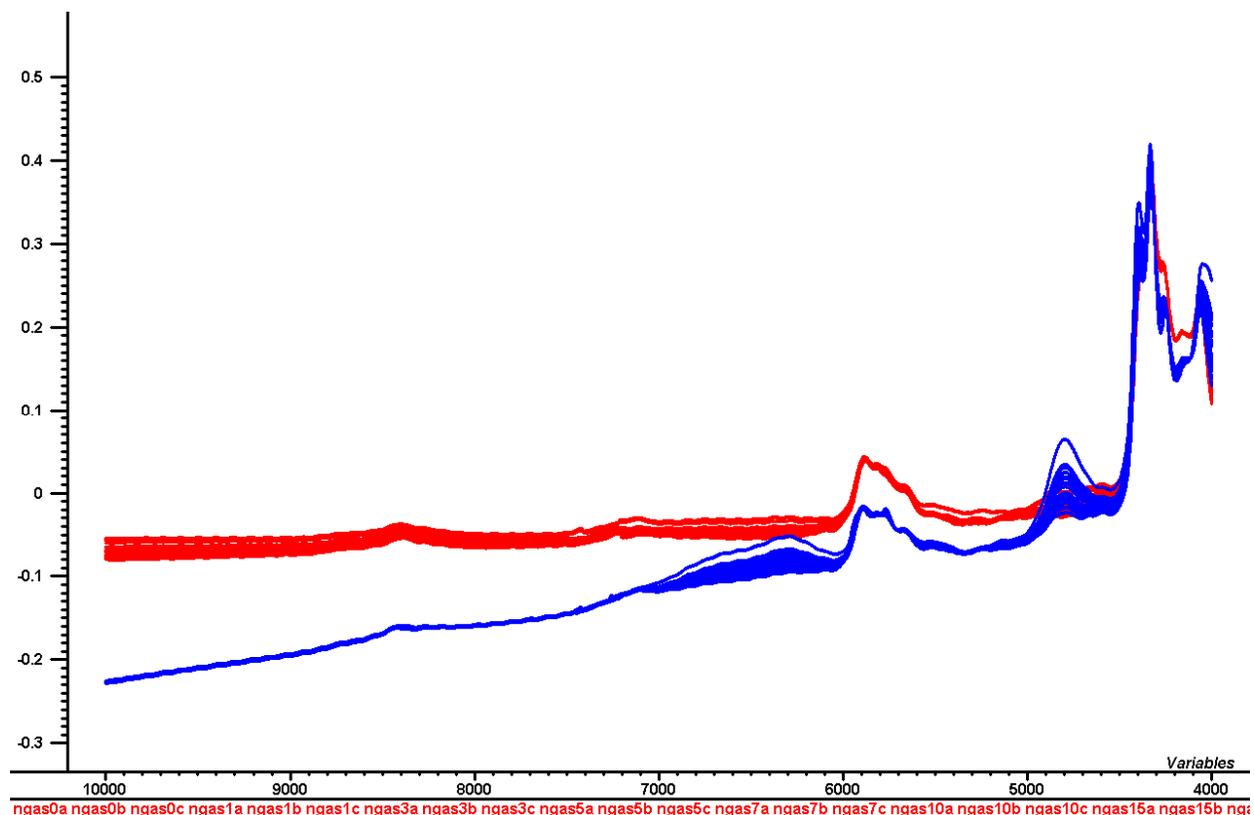


Figure 1. Raw (not pre-processed) NIR spectra of all premium 91 gasoline samples, both pure and adulterated with ethanol

The NIR spectra of the both adulterated and un-adulterated gasoline samples is shown in Figure 1. The absorption peaks in regions from 3500 to 3700 cm^{-1} are due to OH combinations, while the peaks at regions from 7100 to 7700 cm^{-1} are due to absorption of 1st overtone of ethanol OH group. While the peaks at 8403.36 is due to 2nd overtone of C-H from methyl group, at 8264.46 is due C-H from methylen group and at 8726 is due to C-H from aromatics from gasoline samples²⁵. In order to eliminate the scattering effect of the gasoline samples and to remove noise from the information two types of preprocessing like SNV and 1st derivative were applied on the spectral data, as shown in Table 1.

Table 1. Selection of Pre-processing

Type of spectra	Pre-processing	PLS regression		PLS-DA		PLS prediction		# of factors
		RMSECV	R ²	RMSEC	R ²	RMSEP	R ²	
Full Spectra (4000 to 10000 cm^{-1})	Without pre-processing	1.82	0.996	0.013	0.99	1.60	0.997	2
Spectra (4000 to 7500 cm^{-1})	Without pre-processing	1.82	0.996	0.318	0.75	1.63	0.997	2
Full Spectra (4000 to 10000 cm^{-1})	SNV	2.96	0.989	0.164	0.88	24.22*	-1.84*	2
Spectra (4000 to 7500 cm^{-1})	SNV	2.94	0.989	0.165	0.88	28.71*	-0.44*	2
Full Spectra (4000 to 10000 cm^{-1})	1 st deriv. with 13 smoothing points	1.885	0.995	0.0769	0.97	1.585	0.997	1
Spectra (4000 to 6500 cm^{-1})	1 st deriv. with 13 smoothing points	1.89	0.995	0.012	0.99	1.586	0.997	1

As it can be seen from Table 1, that the use of 2nd polynomial order of the 1st derivative functions with S-Golay of 13 smoothing points on the spectral data has improved the accuracy of the PLSR models in term of the parameters like RMSECV, R² as well as RMSEP. In case of optimal PLSR

models the measured RMSECV as well as RMSEP values should be minimum with the highest number of R^2 and with less number of factors. The preprocessed spectra is given in Figure 2.

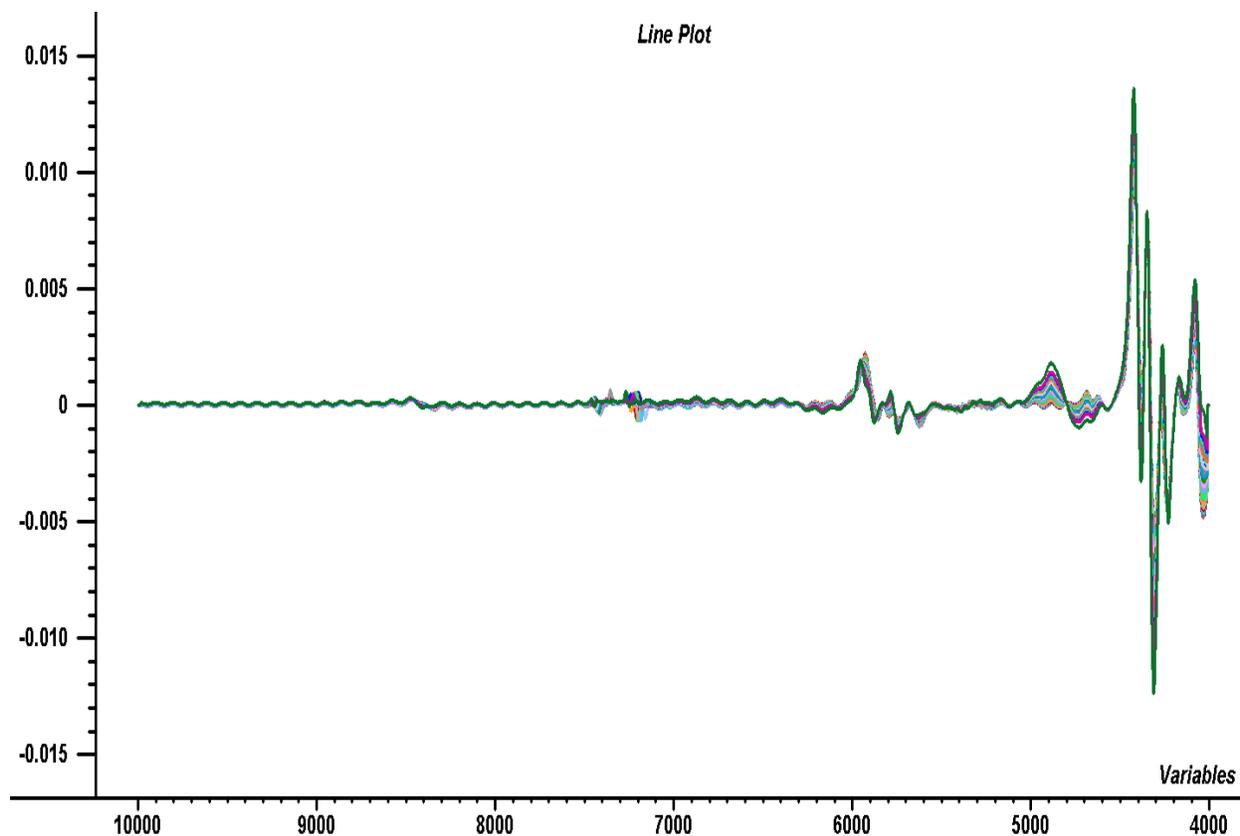


Figure 2. Preprocessed NIR spectra with 1st derivative functions with S-Golay smoothing (13 points with polynomial of order 2)

For a better visualization of the effect of variation between the pure premium 91 octane rating gasoline samples than those adulterated with ethanol the exploratory data analysis method, principal components analysis was used as shown in Figure 3.

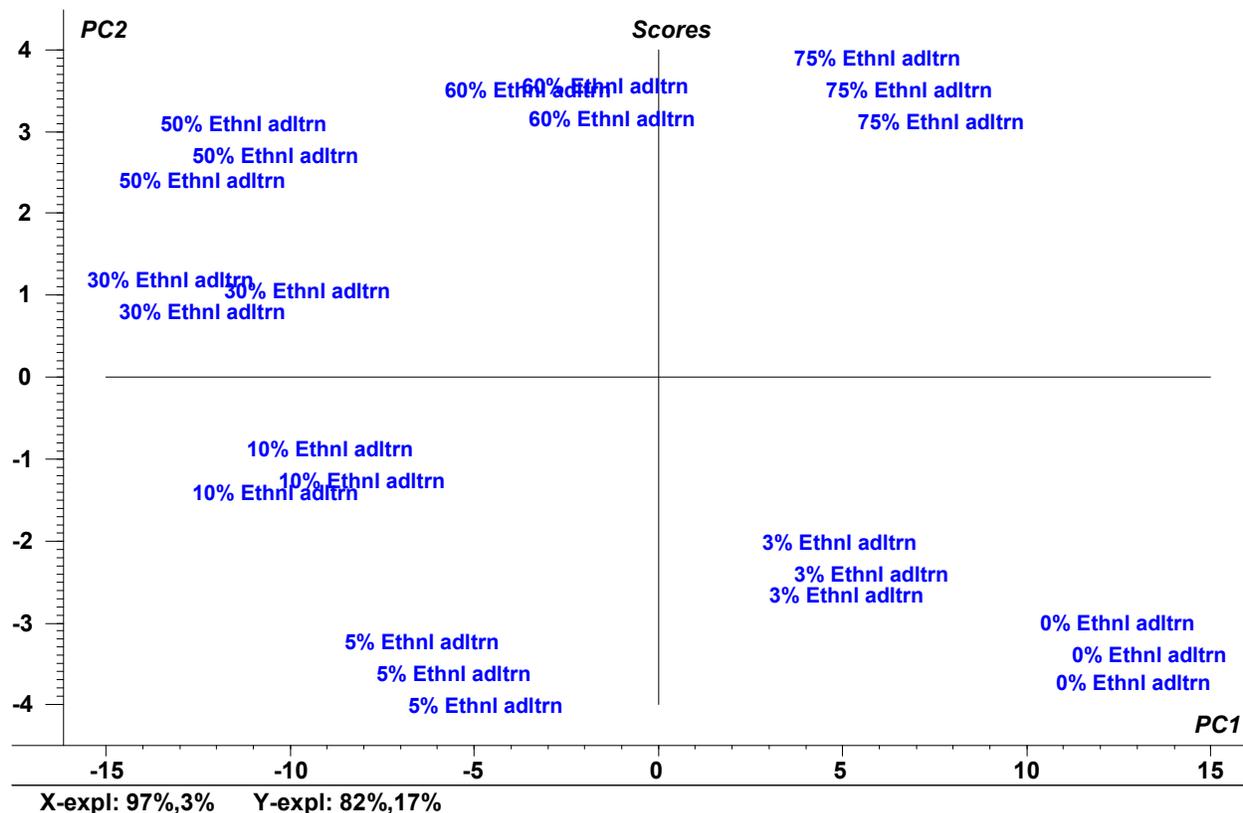
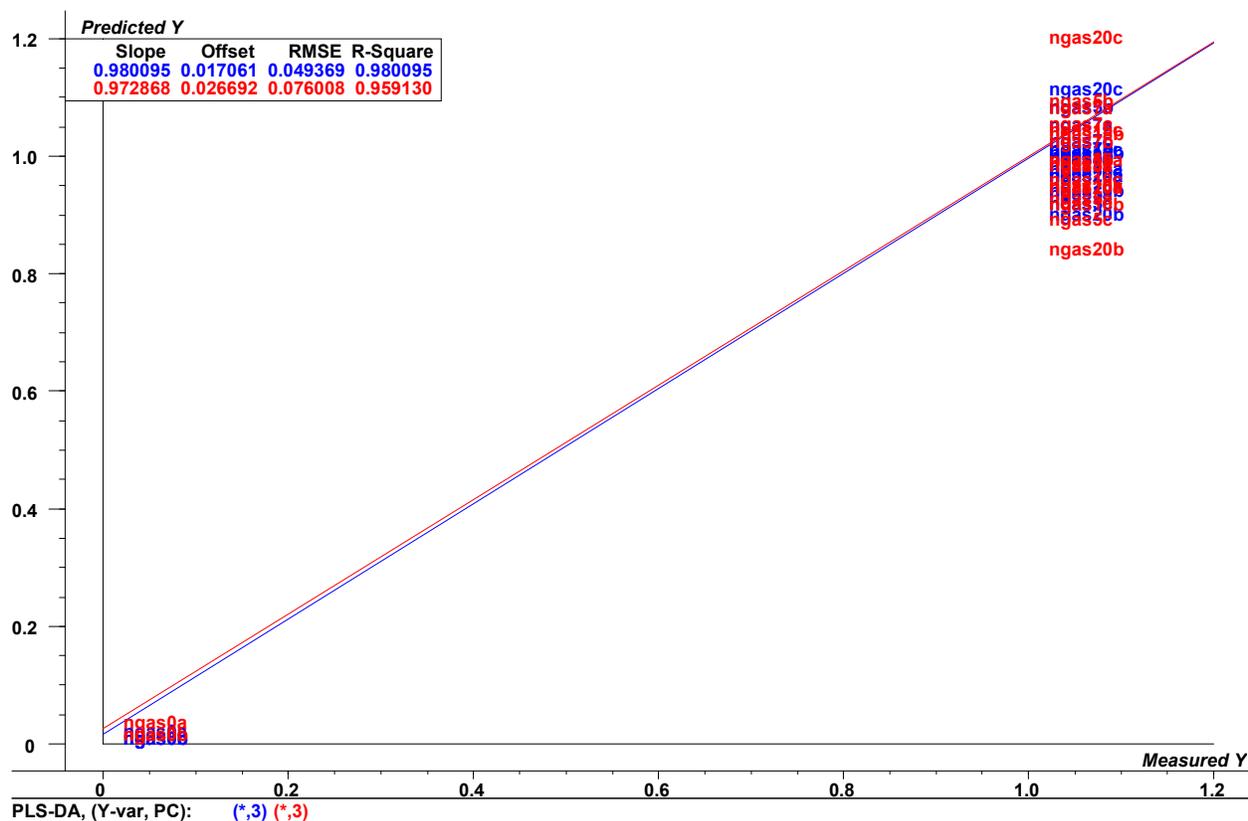


Figure 3. PCA score plot of pure premium 91 against various levels of ethanol adulterant in premium 91 samples.

The PCA score plot in Figure 3 shows a complete map of the classification of pure premium 91 gasoline samples against various levels of ethanol adulterant in premium 91. They are spaced in different parts of the score plot of the PCA model. It is based on the differences in their respective NIR spectra due to ethanol adulterant. It shows with changing the percentage of ethanol in premium 91 has prominent effect on premium 91 gasoline samples.

Similarly, as a discrimination tool to check the presence of the ethanol adulterant in premium 91 octane rating gasolines PLS-DA model was made by using spectral data of the pure gasoline premium 91 (0 % ethanol) and those spiked with various levels of ethanol, as given in Figure 4.



31 Figure 4. PLS-DA model for pure premium 91 gasoline against ethanol adulterated samples

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33 Figure 4 shows that pure Premium 91 samples are completely discriminated from those
34 adulterated with ethanol due to the change in spectral data because of the presence of ethanol.
35 The PLS-DA model is an excellent tool for detection of the adulteration.
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38 3.2 PLS regression Model

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40 In order to propose and develop a quantification tool for the ethanol adulterant in premium 91
41 samples a PLSR model was built at the following percentage levels: 0 %, 1 %, 3 %, 5 %, 7 %, 10
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47 It is shown in Figure 5.

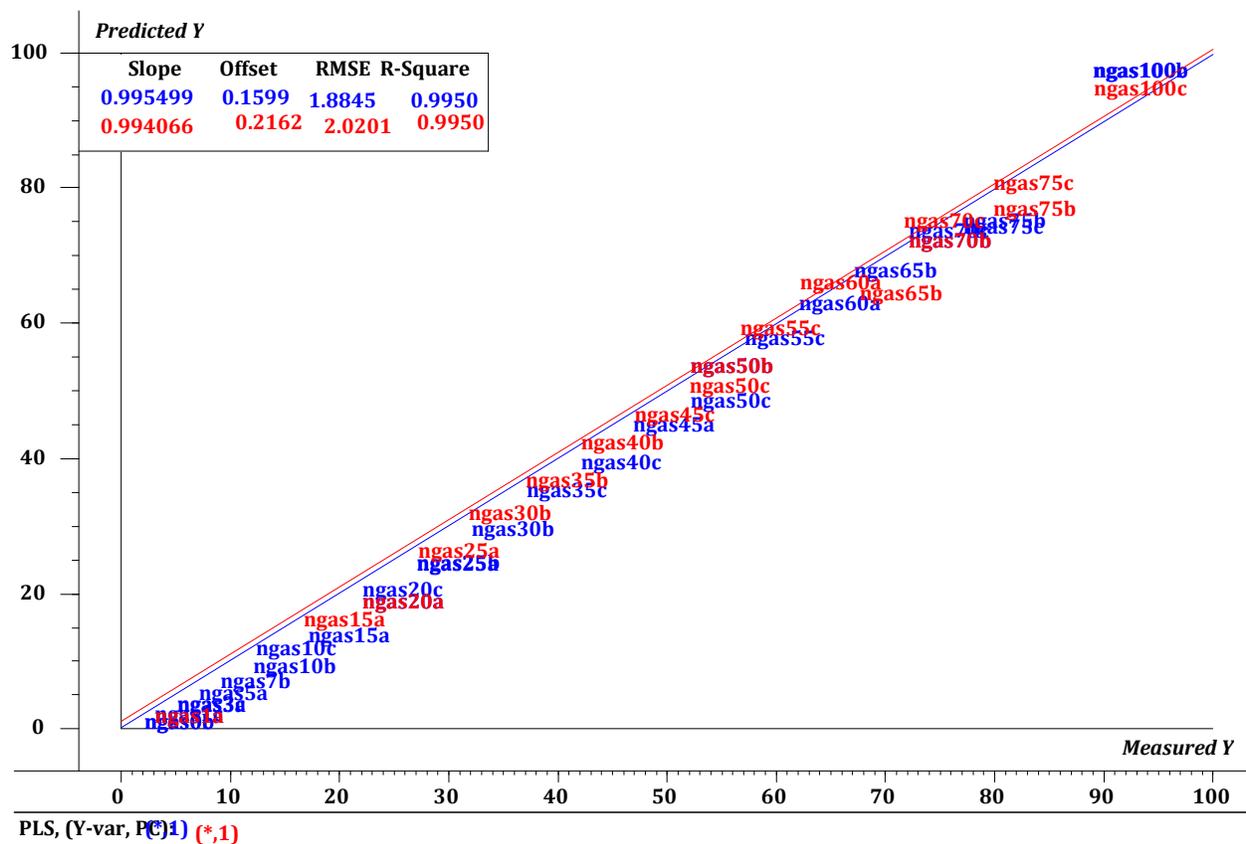
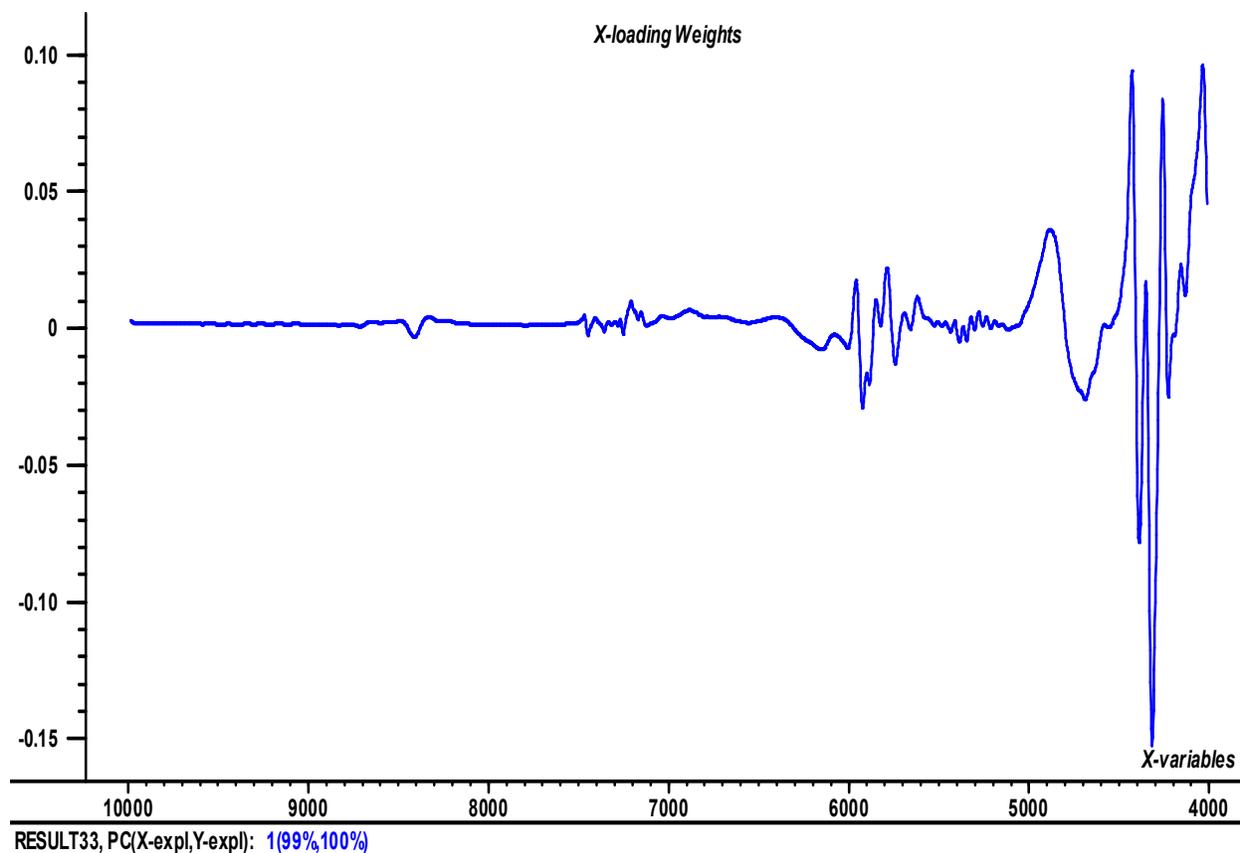


Figure 5. PLS regression model for 91 gasoline samples (pure and adulterated with ethanol)

Figure 5 shows that the RMSECV and R^2 values for the proposed PLS model with 1 factor are 1.885 % and 99%, respectively. The RMSECV value is a measure to check the performance of the internal predictive ability of the PLSR models. RMSECV is given as shown in the Eq. 1:

$$RMSECV = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n}} \quad \text{---(1)}$$

Smaller value of the RMSECV indicates the better performance for the prediction ability of the PLSR model.



32 Figure 6. Factor loading plot of the PLS model for factor 1

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34 Figure 6 shows the loading vector for factor 1. It tells us how much of the variation in a variable
35 is explained by the factor. In this case, factor1 contains 99 % variation.

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37 In fact, the loading plot tells us what variables (wave numbers) are important to predict the
38 property (% ethanol).

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41 The optimized PLSR model was then applied to the test set (described in the experimental
42 section) to check its prediction ability. The results are shown in Figure 7.

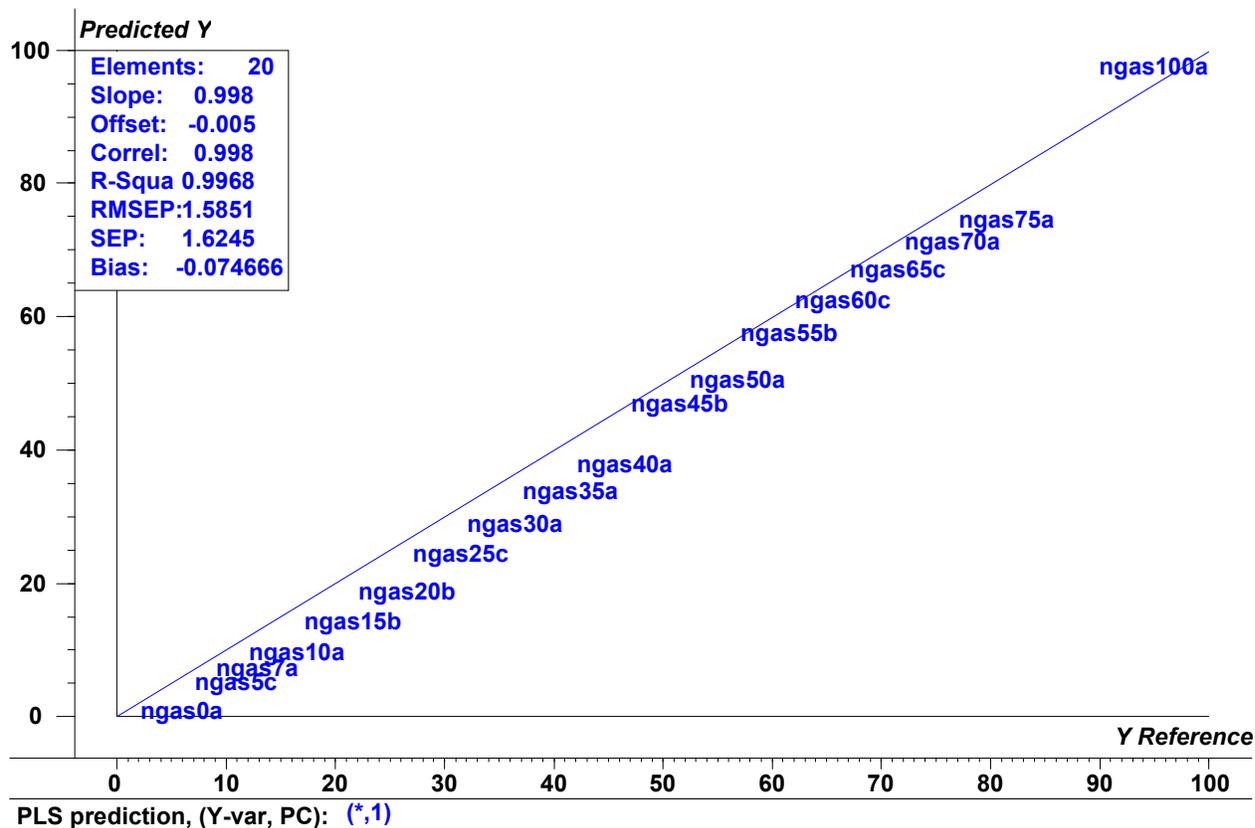


Figure 7. Prediction plot for the 30 % test samples as an external validation set

It can be seen the PLS model in Figure 7 has a good prediction ability, with an RMSEP value of 1.58%. The RMSEP is calculated as shown in Eq. 2:

$$RMSEP = \sqrt{\frac{\sum_{i=1}^{n_t} (y_{t,i} - \hat{y}_{t,i})^2}{n_t}} \quad \text{-----(2)}$$

The RMSEP value is an external measure to check the predictive ability of the PLSR model. Smaller value of RMSEP gives the better performance of the PLSR model when it was applied to the unknown test set of the samples that was not included in building the PLSR model.

4. Conclusions

The proposed NIR spectroscopy, together with multivariate methods, was found a good tool for estimation of ethanol adulteration in premium 91 octane rating gasoline samples with results of

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3 RMSECV, RMSEP and R^2 . In this methodology both PCA and discriminant analysis i.e. PLS-
4 DA were used to distinguish between pure gasoline samples from those intentionally adulterated
5 with ethanol. The R^2 value of the PLS-DA model was found 98 % along with 0.049 % value of
6 the RMSE using random cross validation. The proposed multivariate regression method i.e.
7 PLSR model was developed to estimate the amount of ethanol in Premium 91 gasolines and the
8 values of R^2 found was 99 %, along with value of RMSECV obtained was 1.88 %. This newly
9 developed method, is simple, rapid, and can quantify less than 2 % of ethanol adulteration in
10 premium 91 gasolines.
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List of abbreviation

- Near Infrared spectroscopy (NIR)
- Principle component analysis (PCA)
- Partial least discriminant analysis (PLS-DA)

- Partial least regression analysis (PLS)
- Root mean square error (RMSE)
- Root mean square error of cross validation (RMSECV)
- Root mean square error of prediction (RMSEP)
- Multiplicative Scatter Correction (MSC)