



Identifying the illegal removal from diesel oil of certain chemical markers that designate excise duty

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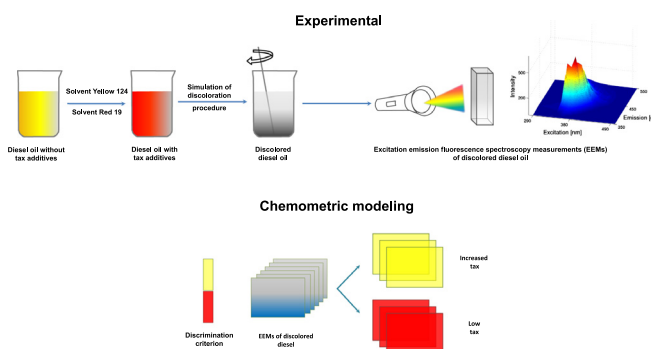
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HIGHLIGHTS

- Procedure of rebated tax diesel oil discoloration was performed in a laboratory.
- Fluorescence properties of discolored rebated tax diesel oil were studied.
- On the basis of 3D fluorescence signals discrimination models were constructed.
- A tool for discolored diesel oil discrimination is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

The fluorescent fingerprints of diesel oil samples were investigated in order to develop a fast and cost-effective method to facilitate the discrimination of rebated tax diesel fuel from oil that is illegally processed by the sorption process. In the experiment oil samples were spiked with a fiscal marker (Solvent Yellow 124) and a dye (Solvent Red 19) and then these were removed using a simulated sorption process. The excitation–emission fluorescence fingerprints were recorded for each sample. Discriminant models were constructed on the basis of fluorescence spectra to distinguish oil samples with respect to four possible discrimination schemes (corresponding to the concentrations of chemical additives). Using discriminant partial least squares models, in all of the discrimination cases that were considered, 100% of the samples from the model set were discriminated correctly. Prediction results for the test set samples were encouraging and varied between 77% and 100% of correctly discriminated samples.

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1. Introduction

Diesel oil is a complex mixture of different chemical compounds. The major components of diesel are saturated and aromatic hydrocarbon compounds (usually containing from 8 to 21 carbon atoms per molecule with a boiling point between 290 and 330 °C) [1]. Their amounts in commercially available diesel oil vary within a wide range. Different additives are also used to modify and improve the properties of a fuel and this considerably in-

creases the chemical variability of samples. Among the additives used, there are some that increase the cetane number, depressants, corrosion inhibitors, antioxidants, biocides, anti-foaming additives, dyes, markers, bio components (e.g. fame acid methyl esters – FAME), etc. Chemical additives are incorporated into the oil in various concentrations and thus diesel oil properties are deliberately modified. Consequently, oil can be characterized according to different criteria, for example, quality, which can be described by the cetane number, density, viscosity or sulfur content of the fuel [2]. The proposed use of diesel oil can be regarded as yet another classification criterion. It is commonly used for vehicle transport, heating, driving agricultural machinery and shipping goods. Diesel

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oil designated for purposes other than regular transport is spiked with chemical additives that change its physical properties (e.g. changing the color from yellow to red). This is done to prevent the illegal use and distribution of rebated excise tax diesel oil from being introduced on the market in order to reduce the costs of heating, agricultural production and marine transportation. Thus, another criterion for diesel oil characteristics is also available, i.e. tax rate criterion. Two excise tax components have been introduced in all countries that use such regulations. However, their type and concentrations are strictly defined by local laws. The first excise tax component is a marker. The same marker is used in all member states of the European Union – Solvent Yellow 124 (SY124). The second excise tax component is a dye that changes the color of diesel oil. Oil that is designed to be used for heating and agricultural machinery purposes usually contains a red dye and oil for marine transport is usually spiked with a blue dye. In Poland, two red dyes are used interchangeably: Solvent Red 19 (SR19) and Solvent Red 164 (SR164). Solvent Blue 35 (SB35) is the only blue dye used in Poland [3]. Diesel oil that is meant for vehicle transport has no tax components.

In order to distinguish diesel oil that has a rebated or full rate of duty, discrimination can be performed based on the chemical content of samples. It is a relatively easy task when samples of diesel oil are marked properly. Some typical methods that are used to describe the chemical content of samples, like UV–Vis spectrophotometry, have the potential to reveal differences between spiked and unspiked samples (i.e. samples are characterized by different colors and absorption properties). A problem occurs when the samples being examined are not genuine. In such a case, excise tax additives are removed from diesel oil and a ‘cleaned’ variant is sold at a higher price. Some efforts have been undertaken in order to detect the illegal process of the sorption of excise tax components. In 2007, Zadora and in 2011 Grabowski et al. investigated the chemical composition of sediment samples that were suspected to be the remains of the sorption process [4,5]. However, to the best of our knowledge, no procedure to distinguish illegally processed diesel oil samples from those with a full rate of duty or for the detection of residuals that remain after the sorption process has been described in the literature. The goal of our study was to develop a simple and cost-effective method to facilitate the discrimination of diesel oil after the removal of tax additives.

Because of the fluorescence properties of the diazo compounds that are introduced into diesel oil (i.e. marker and dyes), fluorescence spectroscopy is considered to be a sensitive analytical technique with the potential to detect the residue of tax compounds or changes in the chemical composition that are due to the discoloration process. In the literature, fluorescence spectroscopy has been acknowledged as a valuable method to characterize the quality of fuel [6–10].

Bearing in mind the different spectral characteristics of markers and dyes (i.e. different characteristic excitation and emission ranges) and possible analyte-background interactions (i.e. fluorescent molecules that are present in the matrix can contribute to analytical signal that is registered), the excitation–emission (EEM) fluorescence spectroscopy was the fingerprinting technique that was used to provide the comprehensive chemical information for complex mixtures in our study. Using the EEM spectroscopy, a sample is excited with a number of excitation wavelengths and the emission spectra for every excitation wavelength are registered. Thus, during a single measurement one can simultaneously observe the fluorescence of fluorophores that have different spectral properties. The complexity of the data that is obtained with EEM fluorescence spectroscopy is great and often chemical information that explains the phenomenon that is being studied requires chemometric data mining. Therefore, in order to extract the relevant

chemical information advanced chemometric methods are necessary [11–13].

In this study a set of oil samples with and without SY124 and SR19 was characterized by its EEM fingerprints. Then, these were preprocessed and a chemometric analysis was performed. Principal component analysis (PCA) [14] was carried out first in order to explore the structure of the data. Next, a partial least squares discriminant model (PLS-DA) [15] was built to explain any differences in the chemical composition of the oil samples with respect to the concentrations of SY124 and SR19 in order to detect any levels below the concentration limits that are acceptable under Polish law.

2. Materials and methods

2.1. Experimental

2.1.1. Preparation of samples

Diesel oil, which was purchased at a local gas station, was spiked with SY124 (obtained from Sigma–Aldrich, 98.0% purity) and dyed with SR19 (obtained from IBPO, 92.3% purity). The concentrations of the additives in the oil samples were kept within the range of between 0 and 10 mg L^{−1}. Then, the marker and dye were removed from the samples using the sorption process simulated in a laboratory environment. For each sample, the same discoloration procedure was performed. 10 mL of a freshly prepared sample was introduced into a vessel with 1.50 g of a sorption agent and mixed. After 10 min the sample was filtered using a paper filter. Then, the EEMs of the filtered and discolored samples were collected. In total, 20 different concentration levels of a marker and dye were tested. Three laboratory replicates for a particular concentration level were prepared (independent samples were prepared individually). For each laboratory replicate three EEMs were registered (the so-called technical replicates), which led to 180 EEMs.

2.1.2. Fluorescence measurements of diesel oil samples

All diesel oil samples were measured spectrofluorometrically in a 10 × 10 mm quartz cuvette using a Carry Eclipse Varian FL0811M000 spectrofluorometer with the right-angled geometry. The emission spectra from 350 nm to 800 nm were measured in 2 nm intervals (226 wavelengths) at 46 excitation wavelengths from 250 nm to 700 nm (10 nm interval) with the detector sensitivity of the detector set to 500 V.

2.2. Chemometric analysis of EEMs data

2.2.1. Data exploration – principal component analysis

Data exploration is one of the first steps in data analysis. It helps to uncover any similarities among samples and/or variables. The most popular method used for that purpose is principal component analysis (PCA) [14,16,17]. During PCA new features, called principal components (PCs), are constructed. They aim to maximize the description of the total data variance. When data variables are strongly correlated, a small number of PCs sufficiently summarize the data structure and data dimensionality is greatly reduced. An efficient data compression leads to a few PCs that can be used to visualize the data structure using the so-called score and loading plots. A score plot is a projection of samples onto a new coordinate system that is defined by selected pairs of PCs that explain a large portion of the data variability. Projection(s) often reveal a clustering tendency in the data (if any exists). Furthermore, coding samples on a score plot according to additional information, e.g. the concentration of the chemicals of interests, groups of samples,

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