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Determination of the Solvent Blue 35 dye in diesel fuel by solid phase extraction and high-performance liquid chromatography with ultraviolet detection

Tatjana Tomić[a,*], Sandra Babić[b], Martina Biošić[b], Nada Uzorinac Nasipak[a], Ana-Marija Čižmek[b]

[a] INA-Industrija Nafte d.d., Corporate Processes Function, Research and Development Sector, Central Testing Laboratory, Lovinčićeva bb, Zagreb, Croatia
[b] Department of Analytical Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev Trg 19, Zagreb, Croatia

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ABSTRACT

The method for the determination of blue dye Solvent Blue 35 (SB 35) in diesel fuel by high performance liquid chromatography (HPLC) coupled with UV-VIS detection was developed. The dye is separated from the hydrocarbon sample matrix and determined as a single component at 650 nm wavelength. Solid phase extraction (SPE) on the silica based solid phase sorbent was used as a pre-treatment method. Among investigated elution solvent mixtures, the mixture composed of chloroform and heptane in the volume ration of 1:0.75 (*v/v*) provided the best SB 35 recovery. During method validation two calibration models were tested: external calibration and matrix-matched calibration. For both models correlation coefficients were higher than 0.99 and slopes were compared using the Student's *t*-test. Precision was evaluated as repeatability and intermediate precision with relative standard deviations less than 7%. Low limit of quantification of 0.1 mg L^{-1} were obtained. Optimized procedure using 250 mg of sorbens provided recoveries ranged from 76.9% to 99.4% over a linear range (0.1–10 mg L^{-1}). The developed method has been applied to the analysis of blue diesel samples from the market and suspicious samples. The content of SB 35 dye in a commercial blue diesel samples was found to be around 0.5 mg L^{-1} while presence of SB 35 dye in suspicious sample was confirmed.

1. Introduction

Diesel oil is a commonly used fuel for different purpose such as vehicle transport, heating, and driving agricultural machinery. Some fuels as gas oils (diesel, light oil, fuel oil, etc.) used in agriculture, fishing, and households are often exempt from certain tax obligations [1–3]. Their prices are usually significantly lower than the prices of commercial motor fuels sold for passenger vehicles. Their composition, considering the hydrocarbon content, is equal to composition of commercial diesel fuel. They are primarily a medium distillate distilling between 180 °C and 380 °C. In order to improve fuel properties different additives are added. Some of them increase cetane number or may work as corrosion inhibitor, biocides, antioxidants or anti-foaming additives [4]. Additionally, in diesel fuels intended for purpose different from regular transport, markers and dyes are added to prevent the improper and punishable use of products with lower taxes.

The system of fuel marking varies in different countries and global regions. In the EU countries fiscal Euromarker, Solvent Yellow 124 (SY 124) (Fig. 1) is established by European Commission decision 2001/574/EC.

However, EU member states use their own systems to distinguish gas oils by using national dyes [5]. Thus, for example, in France marine diesel is dyed blue with Solvent Blue 35 (Fig. 2), in Italy all gas oils are dyed green with Solvent Green 33, in Germany all gas oils are dyed red with Solvent Red 19. In Croatia SB 35 is used to dye the diesel fuel that has applications in agriculture, fisheries, aquaculture, and marine culture [6]. Adding blue dye SB 35 in diesel fuel, color is significantly changed from light yellow to green/blue. SB 35 is commercially available under the various names: Sudan Blue II, Oil Blue 35, Blue 2N, Blue B and Oil Blue B.

While the content of SY 124 in the fuel is regulated by European Commission decisions 2001/574/EC and 2003/900/EC and it should be from 6 mg L^{-1} to 9 mg L^{-1}, the content of blue dye in the fuel is not strictly regulated. In some countries the concentration of SB 35 is regulated by national lows (5 mg L^{-1} in Denmark, Irish Republic, Portugal and Sweden; 10 mg L^{-1} in France; > 6 mg L^{-1} in Poland), while in others only visible inspection is supposed (Croatia, Austria, Belgium, Greece) [5,7]. In the commercially available mixtures of blue dye SB 35 and marker SY 124, SB 35 is usually present as one component of blue dye mixture, not as single compound. The accurate

* Corresponding author. INA-Industrija nafte d.d., Corporate Processes Function, Research and Development Sector, Central Testing Laboratory, Lovinčićeva 4, Zagreb, Croatia.
E-mail address: tatjana.tomic@ina.hr (T. Tomić).

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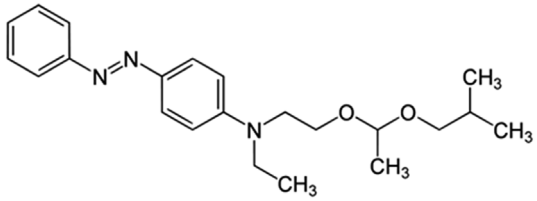

Fig. 1. Structural formula of N-ethyl-N-[2-[1-(2-methylpropoxy)ethoxy]ethyl]-4-phenyldiazenylaniline (SY 124).

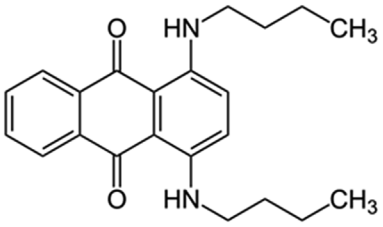

Fig. 2. Structural formula of 1,4-bis(butylamino)anthraquinone (SB 35).

content of SB 35 in such mixtures is not exactly known, but the most commonly is expressed as approximate mass percentage of total content of all blue dye components in the mixture [5]. Therefore, the possible improvement of current legislation should be in the direction of regulating the exact content of blue dye in the fuel samples due to the requirements for confirmation of the improper use of lower taxes fuels. In addition, it is necessary to develop analytical procedures that will enable determination of the dye content in the sample quickly and reliably.

Use of different analytical techniques and detection systems in dyes determination were described in literature. Spectrophotometric determination of the red dyes content in domestic fuel oils is set as the standard [8]. Trindade with co-workers in a series of papers has shown the successful application of electrochemical methods for dye determination in different fuel samples [9–11]. Also, HPLC methods were used for the determination and quantification of some dyes in fuel samples [12–14]. Sample preparation methods for chromatographic analysis of dyes in fuel samples were also described in literature. They are based on solid phase extraction with or without additional clean-up step [11,15]. Combination of excitation–emission matrix fluorescence spectroscopy as an analytical technique and partial least squares regression as a multiple modeling tool was proposed for simultaneous determination of Solvent Yellow 124 and Solvent Red 19 dyes in diesel oil [16]. Recently, Orzel et al. [17]. developed the fluorescent fingerprints method for diesel oil samples to facilitate the discrimination of rebated tax diesel fuel from oil that is illegally processed by the sorption process. A simple micro-analytical spot test for detection of Solvent Red 164 in vehicle exhaust has also been described in literature [18].

To the best of our knowledge, the HPLC method for the determination of blue dye SB 35 in diesel fuel samples were not described in the literature as well as determination of SB 35 and fiscal euromarker SY 124 under same chromatographic conditions.

With these points in mind, the main purpose of this study was to develop reliable and sensitive analytical method for SB 35 determination in diesel fuels under same chromatographic conditions with SY 124. The idea was to use EU reference HPLC method for SY 124 determination [19] after sample preparation using solid phase extraction. SPE procedure of blue diesel fuel was optimized regarding optimal elution solvent and mass of sorbent. The extracts were analyzed using HPLC with variable wavelength ultraviolet detector (UV). Optimized SPE-HPLC-UV method was validated in terms of linearity, detection and quantification limits, precision, and accuracy. Developed method has been applied to analysis of two types of diesel fuel samples. One of them was regular blue diesel samples from market and the second one was suspicious diesel samples obtained from regulatory body to confirm or reject illegal use.

2. Experimental

2.1. Chemicals and standards

Solvent Blue 35 standard (1,4-bis(butylamino)anthraquinone) (CAS number: 17354-14-2, Color Index (C.I.) number: 61554, purity > 98%) was purchased from Sigma Aldrich (St. Louis, MO, USA). A stock solution of the SB 35 standard was prepared by dissolving accurate quantity of the powdered standard in mobile phase comprising of toluene:ethyl acetate = 98:2 (*v/v*). The mass concentration of SB 35 in stock standard solution was 50 mg L^{-1}. Working standard solutions of SB 35 were prepared from stock solution by serial dilution with mobile phase. Commercial mixture Dayguard Blue MS25YCRO containing Euromarker SY 124 (15 - 18%) and liquid equivalent dye SB 35 (10–11%) was obtained from John Hogg Technical Solutions Ltd, (Manchester, UK). Liquid equivalent dye SB 35 contains SB 35 as one of the components in six-component dye mixture.

All chemicals used for the preparation of the mobile phase for liquid chromatography analysis, solid phase extraction and for the preparation of standard solutions were the HPLC grade. Ultrapure water was prepared by a Millipore Simplicity UV system (Millipore Corporation, Billerica, MA, USA).

2.2. Diesel fuel samples

For the development and optimization of sample preparation method and validation of SPE-HPLC-UV method spiked diesel fuel (DS) samples were used. Spiked DS sample (10 mg L^{-1}) was prepared by dissolving 5 mg of powdered SB 35 standard in 500 mL of DS. Working solutions of spiked DS were prepared from this spiked DS sample by serial dilution in the concentration range from 0.01 mg L^{-1} to 10 mg L^{-1}. DS was collected at gas station in Zagreb (Croatia).

For the confirmation of developed SPE-HPLC-UV method applicability, two types of diesel fuel samples were analyzed. The first type of diesel fuel samples was regular blue diesel sample (BDS) collected at gas station (Zagreb, Croatia) while the second type was suspicious diesel sample (SDS) obtained from regulatory body to confirm or reject illegal use.

2.3. Sample preparation

The SPE procedure was developed and optimized using 1 mL of DS spiked with SB 35 in concentration of 1 mg L^{-1}. The dye was extracted using SPE cartridge containing silica gel sorbent at apparatus designed for SPE (Supelco, Bellefonte, USA). The SPE column has been prepared using 3 mL polypropylene SPE empty reservoir (Agilent Technologies, Santa Clara, CA, USA) filled with appropriate mass of powdered silica gel. Frits were placed below and above the silica gel particle sorbent bed. Prior to the sample extraction, SPE sorbent was preconditioned with two column volumes of hexane. The fuel sample was applied to the SPE column, column was washed with 3 mL of hexane and then it was dried under vacuum for 5–10 min. The loaded SPE column was eluted with 5 × 2 mL of elution solvent. Extract was evaporated to dryness by rotary evaporation at 40 °C and reconstituted in 1 mL of mobile phase (toluene:ethyl acetate = 98:2 (*v/v*)). Unspiked fuel sample was also extracted in all experiments by the same procedure in order to enable detection of any possible contribution of the matrix components to analyte signal from the spiked sample. The extraction efficiency of SPE was determined by HPLC-UV. All experiments were done in triplicate.

In the preliminary experiments, two SPE sorbents were investigated: silica gel 60 GF_{254} (Merck, Darmstadt, Germany) and ready to use StrataX SPE column supplied by Phenomenex (Torrance, CA, USA).