Tatjana Tomić, Nada Uzorinac Nasipak

ISSN 0350-350X
GOMABN 54, 2, 101-107
Original scientific paper

DEVELOPMENT OF A METHOD FOR THE DETERMINATION OF THE BLUE DYE IN GAS OILS BY HYPHENATED NP-HPLC/DAD SYSTEM

Abstract
In the EU countries a system is in place for marking and coloring fuel to distinguish different fuel tax class. Fiscal marker present in fuel does not change the color of fuel and it is determined by the reference method for the determination of the European Union euromarker (Solvent Yellow 124) in gas oil (method of high performance liquid chromatography, HPLC with detection by UV / DAD) [1]. By adding the blue dye to a fuel it changes color significantly and it is possible to immediately distinguish the colored from uncolored fuels. In the laboratory the content of SY 124 marker is analyzed in extra light fuel oil (LUEL) and diesel blue (EU DG PL) by HPLC method. Analyses are performed on an Agilent liquid chromatography system 1100, and a column packed with silica gel is used for separation. For the mobile phase, a mixture of toluene and ethyl acetate is used in the system. The paper describes the development of a method for the determination of the blue dye in gas oil samples simultaneously with the determination of the marker, as well as problems and challenges of quantification.

Key words: blue dye, HPLC, fuel

1. Introduction

Pursuant to the Croatian Excise Tax Act, taxable products are fuels used as motor fuel or for heating and electricity. Tax rates depend on the use of the product and environmental considerations [2]. The blue diesel gas oil that is used in agriculture, fisheries and aquaculture is subject to the zero excise duty rate, being classified under fuels with a reduced tax rate. In order to distinguish fuels of different tax classes but similar or identical hydrocarbon composition and physical-chemical properties, blue diesel is colored by appropriate dye and marked with an indicator (fiscal marker). While euromarker is uniform at the EU level (Solvent Yellow 124, hereinafter SY 124), EU member states use their own systems to distinguish gas oils by using national dyes. In EU countries, blue dye Solvent Blue 35 (SB 35), Figure 1, is widely used. This dye is commercially available under the following names: Sudan Blue II, Oil Blue 35, Blue 2N, Blue B and Oil Blue B.

According to the Ordinance on the Application of the Excise Tax Act applying to gas oil colored with blue dye for the use in agriculture, fisheries, aquaculture and aquaculture, the blue dye CI Solvent Blue 35 is used for marking blue diesel in Croatia [3].

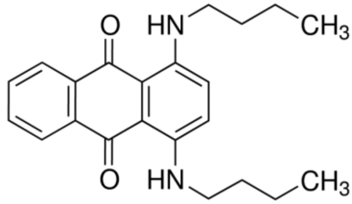

Figure 1: 1,4-bis(butylamino)anthracene-9,10-dione (IUPAC nomenclature)

The aim of this study was to develop a liquid chromatographic method (HPLC) for the simultaneous determination of SB 35 and euromarker SY 124 in samples of blue diesel with detection by UV / DAD detector which has the capacity of detection at several wavelengths at the same time. By high performance liquid chromatography (HPLC) individual components of complex mixtures are separated, identified and quantitated at a solid carrier (chromatography column) with a mobile phase by which the components travel through the column to the detector. The stationary phase selectively retains components of the mixture and leads to their separation.

2. Experimental

2.1 HPLC method

HPLC tests were carried out at liquid chromatography system Agilent 1100 (Agilent company), a modular instrument consisting of a high pressure pump, an automatic injector, a separation column filled with silica gel (Lichrosorb SI 60, 5 mm, 25x0.4 cm), an UV / DAD detector and a computer unit with a data collection and processing program. For the mobile phase a mixture of toluene / ethyl acetate, 98:2 (%, v / v) (manufactured by Claro Prom Ltd.), a chromatographic grade was used. The measurement wavelength for determinations was 650 nm, defined by the maximum of absorbance of the tested compound. Measurements were also performed at 450 nm, the wavelength at which the presence of SY 124 was monitored. Operating conditions are presented in Table 1.

Table 1: Operating conditions

mobile phase composition	98 vol.% toluene 2 vol.% ethyl acetate
flow rate	0.5 mL/min
stationary phase composition	silica gel
run time	20 min
measurement wave length	650 nm
column temperature	30 ^{o}C

2.2 Samples preparation

Before the analysis, a sample of gas oil is filtered through a filter of pore size 0.45 microns to remove any possible solid impurities. The sample is then injected into the column and the response at two wavelengths: 650 nm (SB 35) and 450 nm (SY 124) are simultaneously monitored. After stabilization of the instrument and the achievement of operating conditions, a chromatogram of the SB 35 standard is taken to determine the retention time of SB 35 at the stated operating conditions. It was found that the SB 35 retention time is 8.4 minutes (Figure 2).

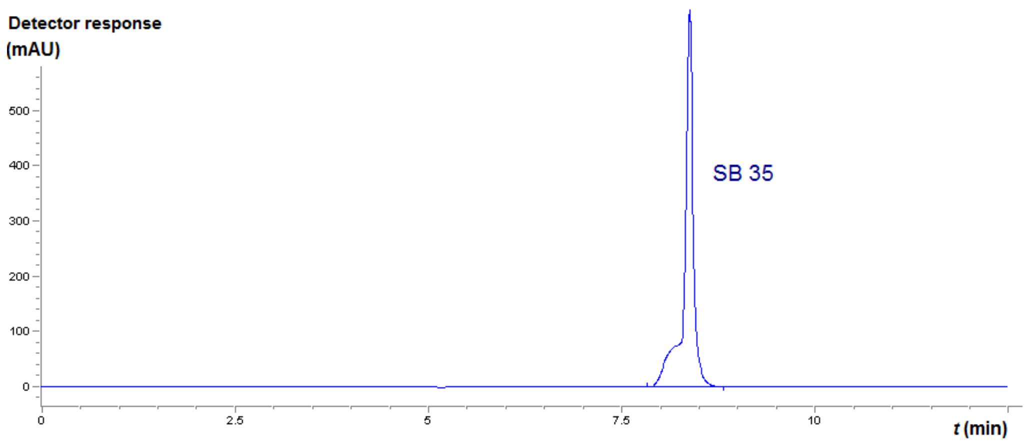

Figure 2: Chromatogram of SB 35 standard

2.3 Calibration

Calibration was performed by the external standard method. The primary standard solution (*c* (SB 35) = 50 mg/L) was prepared by dissolving the SB 35 standard (purity > 98 %) (Sigma-Aldrich) in xylene. The primary standard solution was diluted into four calibration levels (Table 2).

Table 2: Calibration levels

Calibration level	*c* (SB 35) / mg/L
1	5
2	10
3	25
4	50

By examining EU legislation it was found that the dye content in fuels varies from country to country from 5 mg/L to 25 mg/L; a wide range of concentrations was therefore taken for calibration. A calibration curve equation was determined, $y = 107.85 \times x - 43.56$ with the coefficient of determination $r^2 = 0.9997$ (Figure 3).

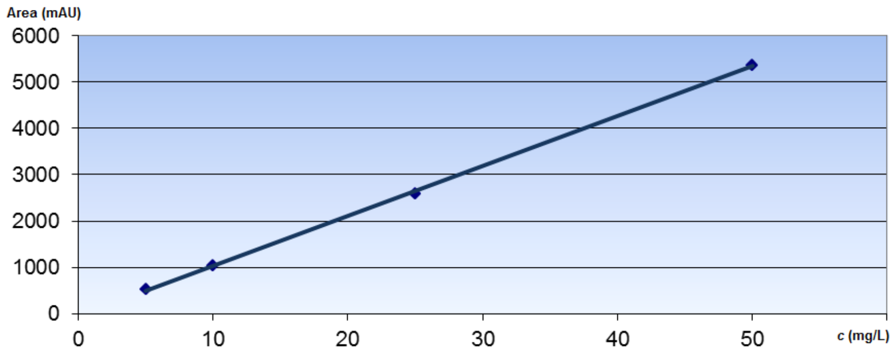

Figure 3: Calibration curve

3. Results and Discussion

As the goal of this study was to develop a chromatographic method that would allow a simultaneous determination of the SY 124 euromarker and the SB 35 blue dye, chromatograms of a prepared mixture of standards were recorded (Figure 4). The blue dye has a maximum of absorption at 650 nm, while SY 124 has a maximum of absorption at 450 nm. By comparing chromatograms from Figure 4, which were recorded at different wavelengths, it is evident that it is possible to simultaneously monitor the presence of the dye and the euromarker.

By comparing chromatograms of the commercial mixture which contains the SB 35 blue dye and SY 124, the possiblity to simultaneously determine these components thanks to their absorption maxima being at different wavelengths have been confirmed (Figure 5).

The possibility of determining the commercial mixture of the blue dye and the euromarker added to diesel fuel was examined. The chromatograms were recorded at 650 nm (Figure 6). The chromatogram of the fuel with the addition of the commercial mixture has the maximum absorption at the same retention times as the commercial mixture; however, in the chromatogram of diesel fuel, peaks are present at the start of the chromatogram corresponding to the fuel content.

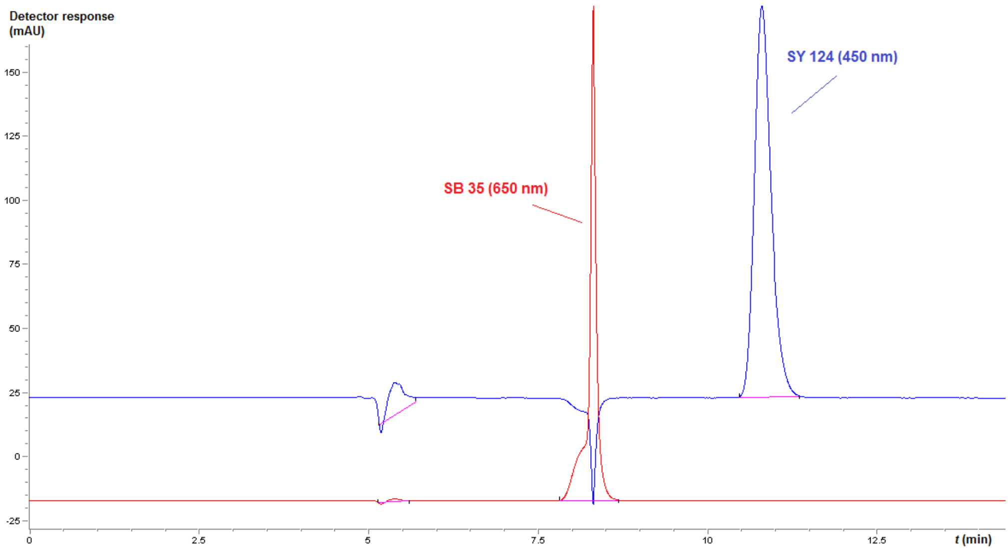

Figure 4: The chromatogram of a mixture of standards SB 35 and SY 124 recorded at standards absorption maxima

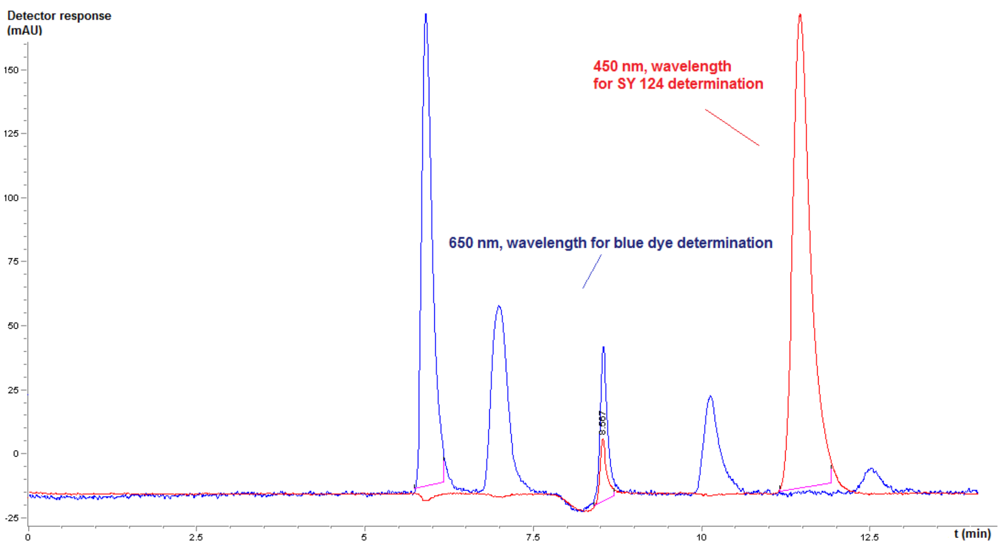

Figure 5: Comparison of chromatograms of the commercial mixture of SB 35 and SY 124 recorded at different wavelengths (650 nm for the determination of the blue dye and 450 nm for the determination of SY 124)

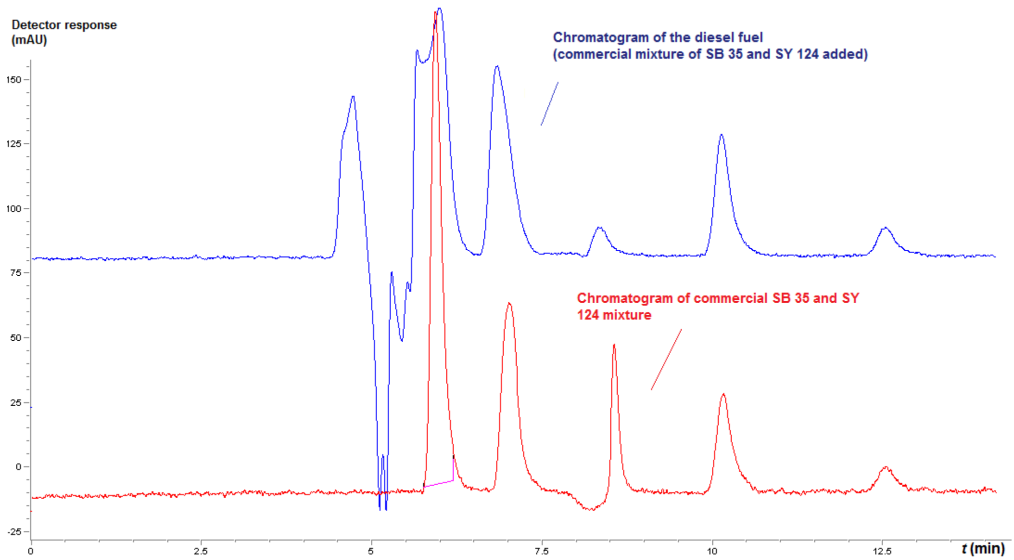

Figure 6: Comparison of chromatograms of diesel fuel with the addition of the commercial mixture of SB 35 and SY 124 and the chromatogram of the commercial mixture (650 nm)

By analyzing the chromatogram of the commercial mixture containing the SB 35 blue dye and SY 124, it has been established that at the wavelength of the blue dye detection (650 nm) more chromatographic peaks appear on the chromatogram, indicating that the dye is not a single component but a multi-component mixture. Manufacturers call such dyes SB 35 type dyes; they are often a mixture of several components and are used as a substitute for a pure dye. Spectral characteristics of such replacements are almost identical to those of a pure SB 35 dye, allowing the selection of equal absorption maxima of wavelengths and a qualitative determination of a dye in the final product into which the dye is mixed.

The problem occurs when it is necessary to determine the exact content of the pure SB 35 dye in a fuel sample because this leads to a measurement error and an incorrect interpretation, which can make it difficult to correctly determine the fuel tax class. Results of dye determination in fuel will vary depending on whether a pure SB 35 or a SB 35 type dye is used for coloring. Figure 7 shows a comparison of the spectra of SB 35 of pure components and SB 35 type dyes, showing a significant difference in absorbance [4].

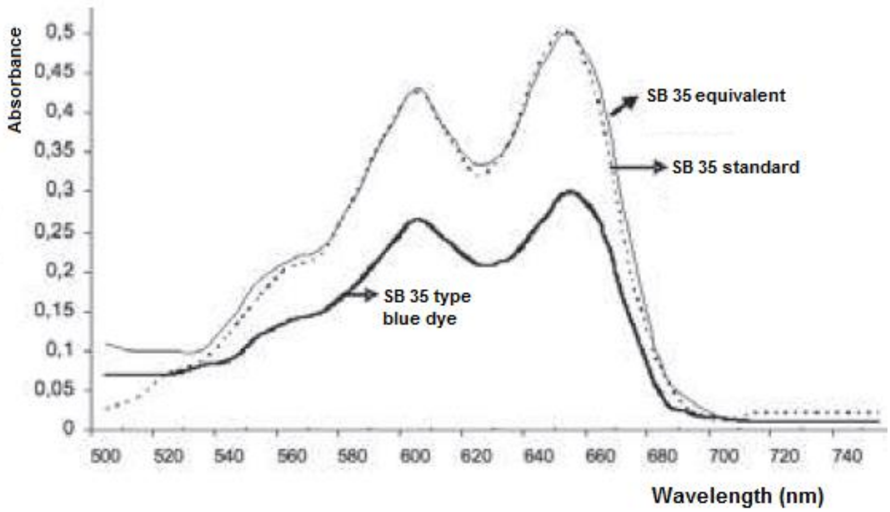

Figure 7: Comparison of the SB 35 type blue dye, SB 35 equivalent and the SB 35 standard spectra

4. Conclusion

From the obtained results it can be concluded that it is possible to simultaneously determine the SB 35 blue dye and the SY 124 euromarker in gas oil samples by liquid chromatography method with UV/DAD detection, which has the capacity of monitoring multiple wavelengths simultaneously as the components have different wavelength maxima. The problem is that in commercial SB 35 type dyes and SY 124 the dye is not a pure component but a mixture; it is therefore not possible to quantitatively determine the content of the SB 35 dye with sufficient accuracy. Unless the use of SB 35 blue color for fuel marking is regulated on the EU level, it will be impossible to determine the exact dye content in fuel by HPLC without an additional and complex preparation of samples.

Literature

1. Community Reference Method for the determination of SY 124 (Euromarker) in gas oil.
2. Zakon o trošarinama, NN 22/13.
3. Pravilnik o primjeni zakona o trošarinama što se odnosi na plinsko ulje obojano plavom bojom za namjene u poljoprivredi, ribolovu, ribogojstvu i akvakulturi, NN 156/13.
4. Czarnocka J., Zborowska U., Kesik A., Chemik, 65, 3, 200-203, 2011.

Authors

Tatjana Tomić, Nada Uzorinac Nasipak; E-mail: tatjana.tomic@ina.hr
INA Industrija nafte d.d., Centralni ispitni laboratorij, Lovinčićeva 4, Zagreb, Hrvatska

Received: 2.12.2014.

Accepted: 2.1.2015