TECHNICAL NOTE

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HPLC Analysis of Solvent Yellow 124—The Marker in Diesel Oil

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ABSTRACT: A method for the analysis of Solvent Yellow 124, a new marker added in diesel oil and sold in Sweden is presented. The method we describe involves analysis by HPLC on a normal phase column.

The diesel samples were injected directly onto the column. No enrichment of the marker prior to analysis was necessary and quantitative analyzing was possible at concentrations above 0.05 mg/L. The quantitative analysis was improved by the use of an internal standard (Pigment Yellow 3). The use of toxic solvents in the mobile phase was avoided.

KEYWORDS: forensic science, criminalistics, high-performance liquid chromatography, diesel oil, marker, solvent yellow 124

Since October 1, 1993, Swedish law (1) imposes tax on diesel oil for motor vehicles. Gas oil exempt from this tax is marked to facilitate detection of its misuse and to distinguish between the different gas oils available. Private cars, buses and lorries are not allowed to use the marked oil.

Solvent Yellow 124 (chemical structure shown in Fig. 1) is used as the marker. Solvent Yellow 124 is a yellow dye also used as a marker in some other European countries and in Sweden a concentration of 5–6 mg/L is prescribed. Furthermore, a derivative of 1.4-diaminoantraquinone (Fig. 2), is added in an amount that gives the oil "a clear green color."

To control and detect the misuse of marked oil, the police take spot checks on the fuel in diesel-powered motor vehicles at the roadside and elsewhere. A high fine is stipulated for those motorists who are found using marked oil in their vehicles. For practical reasons there is no zero limit imposed for traces of marker in the oil. A fine will probably be imposed when the amount of marker is higher than 0.25 mg/L.

There has been a number of articles on methodology for the detection of dyes (both markers and colorants) in the literature. Mass spectral characterization of petroleum dyes and tracers was reported (2). Solvent red 24 was determined quantitatively in hydrocarbon oils by derivative spectroscopy (3). Reversed HPLC methods were used for detection and determination of azo-dyes in edible oils (4) and of the marker and dye in heavy fuel oils (5). Quantitative determination of Sudan red dyestuff in fuel oil and its mixtures with diesel fuels was achieved by normal phase HPLC, where the samples were applied directly, without any pretreatment (6).

Three methods exist for analyzing Solvent Yellow 124.

1. The Irish State Laboratory in Dublin perform HPLC analyses of Solvent Yellow 124. A straight phase system is used which has the advantage that filtering of the oil is the only preparation needed. The drawbacks are that no internal standard is used and that the mobile phase contains toluene.[2]
2. BASF in Ludwigshafen, Germany has developed a method based on reversed phase HPLC.[3] The marker is quantitatively extracted from the oil by solid phase extraction prior to HPLC analysis. The advantage of this method is the possibility to concentrate the marker in a single step. The drawback is that the extra preparation step is time consuming and may also influence the precision of the method.
3. Dowling Marker Systems in Carlow, Ireland employ a spectrophotometric method.[4] The oil is treated with 6M hydrochloric acid which causes the Solvent Yellow 124 to hydrolyze and enter the acid phase. The color of the hydrolyzed marker is red and the concentration can be measured at 519 nm. This method is fast and easy to perform. The main drawback is that dirty oils might interfere to give too high values. This is unacceptable considering that the result of analysis determine the amount of fine imposed.

The purpose of this study was to develop a method for analysis of Solvent Yellow 124 in diesel oil without interference from color or dirt/impurities. The method should be rapid, accurate, and sensitive enough to detect the marker in concentrations down to 0.25 mg/L. HPLC analysis on a straight phase column and diode array detection proved suitable for this type of analysis. Quantitative determination was improved by use of an internal standard and toluene was not necessary in the mobile phase.

Experimental

Materials

HPLC-grade hexane, ethyl acetate and acetonitrile were purchased from Scandinaviska GeneTec AB and were used for the mobile phase and for washing the HPLC system without further purification. Swedish diesel oil class II was used for preparation of calibration standards.

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[2]Private communication, Irish state laboratory, Ireland.
[3]Private communication, BASF Ludwigshafen, Germany.
[4]Private communication, Dowling Marker System, Ireland.

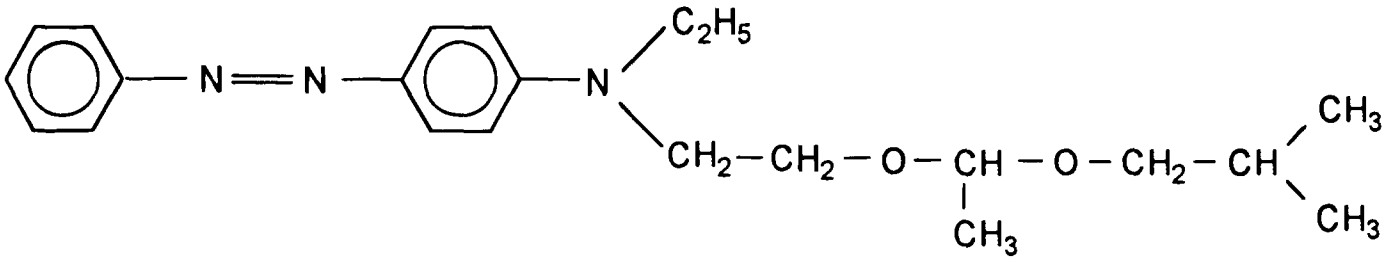

FIG. 1—*Chemical structure of Solvent Yellow 124.*

The markers employed were Solvent Yellow 124 from BASF, hydrolyzed Solvent Yellow 124 from Dowling Marker System, Solvent Blue 35 from BASF and Automate Blue 8 HF from Morton International.

Pigment Yellow 3 (Fig. 3) obtained from Casco Nobel Inks, AB G-man, Trelleborg was used as internal standard. Owing to limited solubility of Pigment Yellow 3 in diesel oil, a saturated solution was prepared. This solution contained about 15 mg Pigment Yellow 3 in per liter of diesel oil. The solution was filtered through a Millipore membrane filter FHUP 04700 (pore size 0.5 μm) before use.

Methods

Instrumentation

The chromatographic system consisted of a Hewlett Packard series II 1090 Liquid Chromatograph connected to the HP's HPLC^{3D} ChemStation. The instrument was equipped with autoinjector, autosampler and diode array detector from Hewlett Packard. HPLC separations were performed using a 20 cm 5 μm Nucleosil Si 50 (pore size 50 Å, surface area 450 m^2/g, i.d. 4.6 mm) stainless steel normal phase column (Scandinaviska GeneTec AB).

Conditions

A sample of diesel oil (9 mL) was mixed with 1 mL internal standard solution and filtered through a Millipore filter SLHV 025 NB (pore size 0.5 μm). A part of the filtrate was transferred into a vial fitted to the autosampler.

The samples were injected in 50 μL aliquots onto the HPLC column. The flow rate was 1.2 mL/min at room temperature.

The HPLC separations were carried out using the following gradient program (isocratic method did not eluate all the colored compounds present or added to diesel oil):

Time (min)	Hexane (%)	Ethyl acetate (%)
0	93	7
10	93	7
15	70	30
20	93	7

After completion of this gradient program, the column was re-equilibrated by maintaining the initial composition for 7 minutes.

The diode array detector was programmed to record chromatograms at 410 ± 10 nm (the wavelength was suitable for detection of Solvent Yellow 124 and the internal standard) and at 590 ± 10 nm for measuring the blue color. Full spectra were acquired on all significant peaks from 250 nm to 600 nm. Composition of the samples and the mobile phase prevented obtaining spectra at shorter wavelengths.

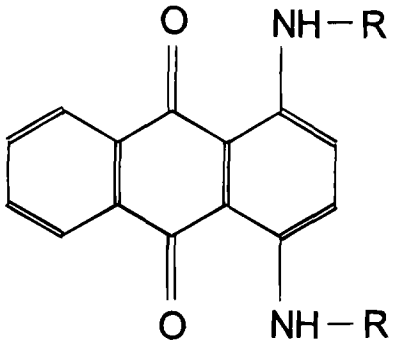

FIG. 2—*Chemical structure of blue additives in diesel oil.*

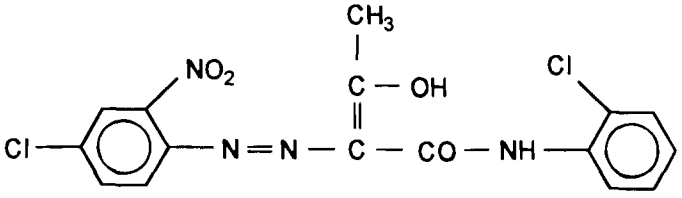

FIG. 3—*Chemical structure of Pigment Yellow 3.*

Results and Discussion

The chromatograms obtained by the method described here showed good separation between the marker and the internal standard. Figure 4 shows the separation achieved for a sample of diesel oil containing 1.0 mg/L marker and a saturated solution of internal standard. The chromatogram was recorded at 410 nm. The peak detected at 5.78 min corresponds to the marker and the peak detected at 6.93 min represents the internal standard. The presence of other yellowish compounds and the blue additives did not interfere. The blue additive was separated into several peaks and detected at 590 nm. The use of a diode array detector makes it possible to obtain spectra of the chromatographic peaks detected. Figures 5 and 6 show spectra of the marker and of the internal standard, respectively.

The sensitivity of detection is sufficient for the purpose of this analysis. It means that the analysis can be performed in a single step and enrichment of the marker or internal standard is not necessary. Figure 7 shows the chromatograms recorded at 410 nm for the lowest concentration of the marker investigated in this study—0.05 mg/L. Spectra obtained for the marker peak are still useful for identification purposes.

The aim of this method was to make a quantitative analysis of Solvent Yellow 124 in diesel oil, and therefore the calibration

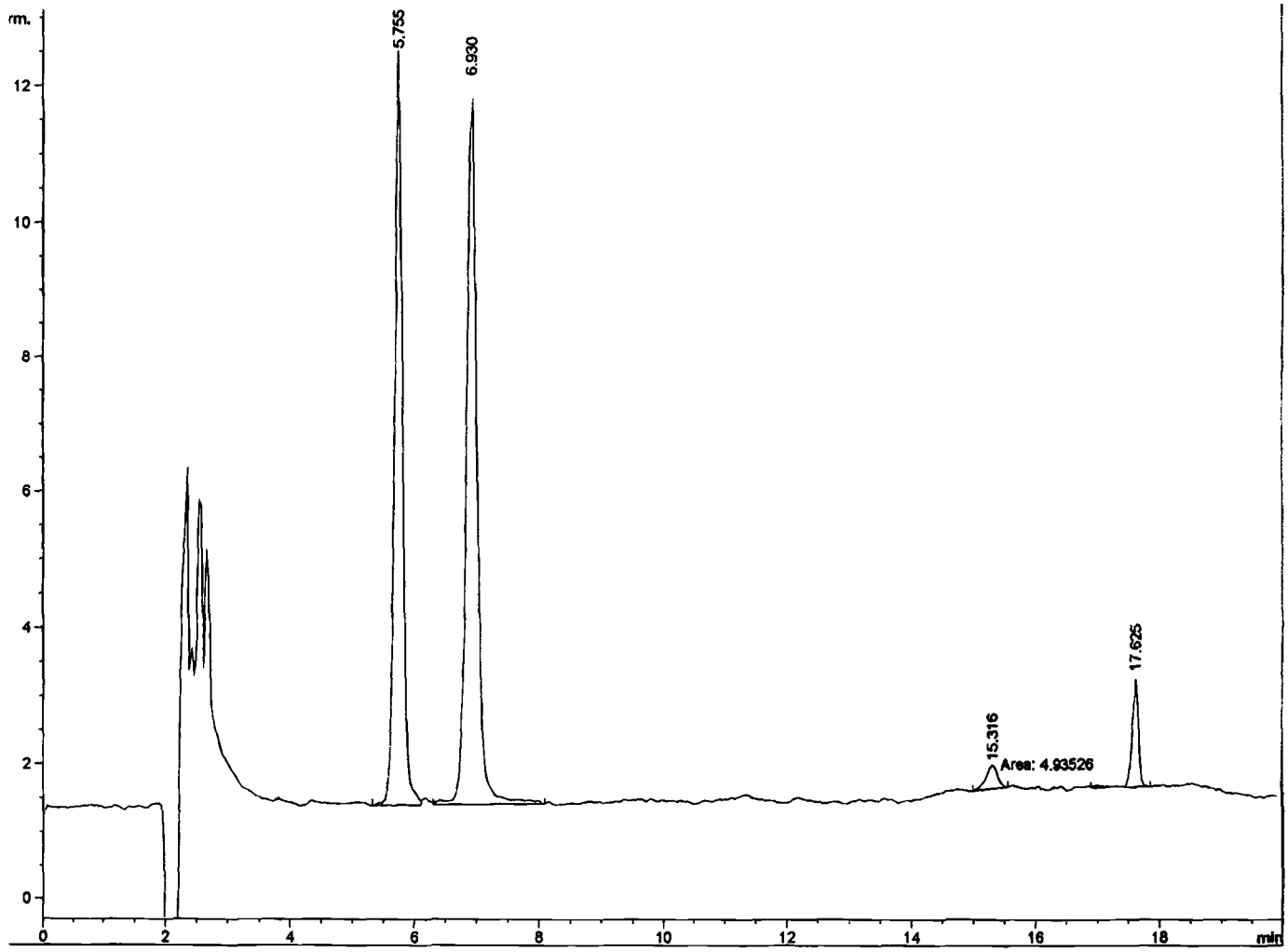

FIG. 4—*HPLC chromatogram detected at 410 nm for sample of diesel oil containing 1.0 mg/L marker (Solvent Yellow 124, RT = 5.8 min) and a saturated solution of internal standard (Pigment Yellow 3, RT = 6.9 min). The spectra of the observed peaks are shown in Figs. 5 and 6.*

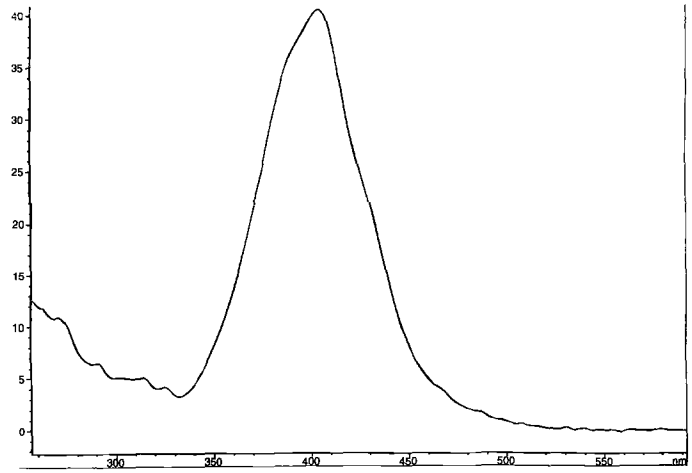

FIG. 5—*UV/VIS spectrum of the peak with retention time 5.8 min (Solvent Yellow 124) in Fig. 4.*

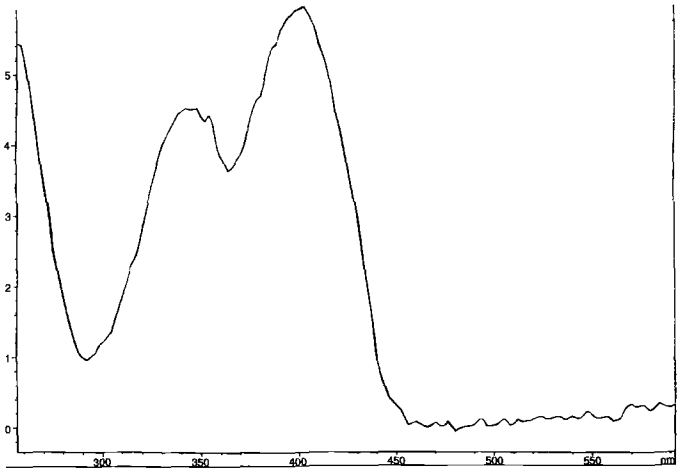

FIG. 6—*UV/VIS spectrum of the peak with retention time 6.9 min (Pigment Yellow 3) in Fig. 4.*

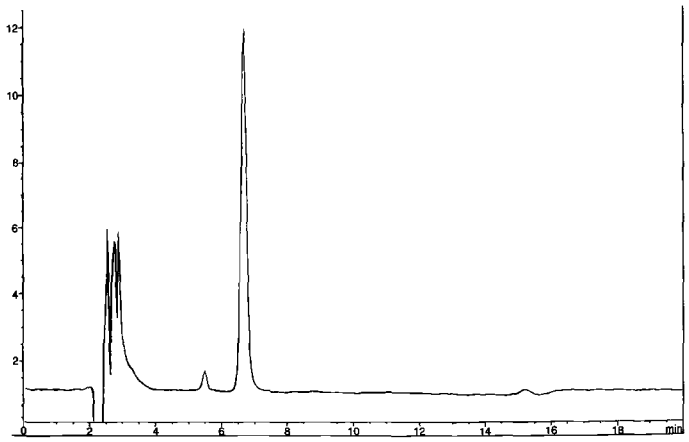

FIG. 7—*HPLC chromatogram monitored at 410 nm for sample of diesel oil containing 0.05 mg/L Solvent Yellow 124, the lowest concentration of the marker investigated in this study.*

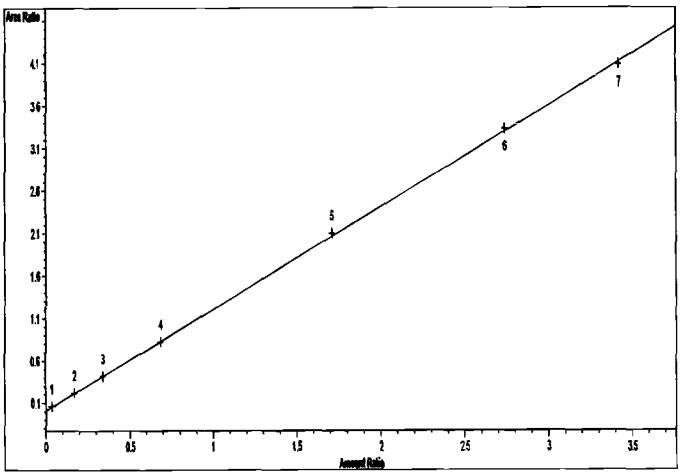

FIG. 8—*The calibration curve obtained for the analysis of Solvent Yellow 124 in diesel oil. Within the concentration range employed, the calibration curve is a straight line with correlation coefficient 0.99.*

curve was constructed and the standard deviation calculated. Calculations of concentration were made by internal standard method using Chemstation.

Seven samples of diesel oil were prepared with the concentration of Solvent Yellow 124 varying from 0.05 mg/L to 5 mg/L. The internal standard was added as described. The resulting calibration curve was a straight line with correlation coefficient 0.99 (Fig. 8).

The reproducibility of the method was evaluated by the following procedure. Six stock solutions of Solvent Yellow 124 in diesel oil were prepared at a concentration of about 515 mg/L. Solvent Blue 35 was added (approximately 350 mg/L) to two of these solutions. From each of these six solutions, five samples were made by mixing 10 μL stock solution, 1 mL internal standard and diesel oil to give a final volume of 10 mL. The 30 samples were analyzed during a period of 1 week with 5 samples/day being analyzed. In a second study, the repeatability of the method was tested when one of the samples was analyzed 12 times.

The relative standard deviation was calculated to be 2.4% in the first study (reproducibility) and 1.0% in the second study (repeatability). These results are acceptable considering possible sources of experimental error in the analysis, for example, dilutions and the chromatography.

Quantitative results from the method were controlled by the spectroscopic method from Dowling Marker Systems, calibrated with hydrolyzed Solvent Yellow 124. The composition of the standard samples analyzed by these two methods agreed satisfactory.

In conclusion, the method described in this paper is simple to operate, needs a minimum of preparation and is possible to automate. No toxic chemicals are needed, which is an advantage for the environment and the laboratory staff. The contact with diesel oil and the marker is limited and the use of toxic solvents is avoided.

References

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