



ELSEVIER

Journal of Chromatography A, 723 (1996) 395-398

JOURNAL OF
CHROMATOGRAPHY A

Short communication

Liquid chromatographic method for analysing the colour marker Solvent Yellow 124, N-ethyl-N-[2-(1-isobutoxyethoxy)ethyl](4-phenylazophenyl)amine, in diesel fuels

Staffan Henricsson, Roger Westerholm*

Department of Analytical Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

First received 14 July 1995; revised manuscript received 3 August 1995; accepted 3 August 1995

Abstract

This paper describes a liquid chromatographic method for analysing the colour marker Solvent Yellow 124 in diesel fuels. The method is robust and can easily be adapted by a routine laboratory; the throughput of samples can be as high as 180 samples per day, with a minimum of sample pretreatment. The coefficient of variation is 5.2% for a diesel fuel containing 5 mg/l of the coloured marker dye. An application of this method for analysing uncombusted residues from diesel engines and oil-fired boilers is also described.

Keywords: Diesel fuel; Solvent Yellow 124; N-Ethyl-N-[2-(1-isobutoxyethoxy)ethyl](4-phenylazophenyl)amine

1. Introduction

In December 1993, in response to reports of health problems associated with green oil colorant mixture, the Swedish Government decided to evaluate the marker system for certain oil products. The marker system enables fiscal authorities to trace the use of tax-reduced fuels, i.e. fuels to be used in agricultural and forestry machinery and in oil-fired boilers. To obtain the green colour of the diesel fuel a mixture of a yellow and a blue dye component is added. The yellow compound is added as a marker and the blue mixture added to give the desired colour. The

yellow dye consists of one well defined compound, Fig. 1, whereas the blue dye consists of a mixture of six isomers (alkylamino anthraquinones). The amount added to the fuel is 5 mg/l for the yellow dye. The corresponding amount of the blue mixture is also 5 mg/l. This means that the concentration of each blue component is six times lower, i.e. approximately 0.9 mg/l for each isomer. As a part of this study we have developed an analytical method for the analysis of

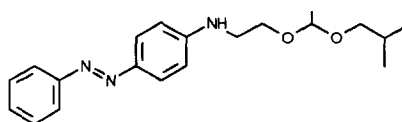


Fig. 1. Structure of Solvent Yellow 124.

* Corresponding author.

the marker dye, Solvent Yellow 124, in the green colorant added to diesel fuels.

Although photometric assays have been used for other markers [1], no method has been previously published for Solvent Yellow 124. The aim of the present paper is to describe a simple and robust method for the analysis and quantitation of traces of the marker in fuel samples. Applications are shown for both the analysis of the azo dye in diesel fuel and the analysis of the compound in the exhausts from a diesel engine and an oil-fired domestic boiler.

2. Experimental

2.1. Standards

Solvent Yellow 124 (BASF AG, Ludwigshafen, Germany) was dissolved in *n*-hexane to give a concentration of 1 mg/l as a stock solution. Working standards, in *n*-hexane or in a diesel fuel, were prepared from the stock to give concentrations ranging from 20 ng/ml to 10 µg/ml.

2.2. Samples and reagents

Fuel samples

Fuel samples were diluted 6 to 10 times with *n*-hexane. An aliquot of 10–20 µl was then analysed by HPLC.

Emission samples

Emission samples from both a diesel engine and an oil-fired domestic boiler were collected according to standard procedures [2], and prepared in analogy to a method described elsewhere [3]. Briefly, the crude sample is fractionated into three parts according to polarity on a deactivated silica column, using *n*-hexane (two fractions) and 25% dichloromethane in *n*-hexane. The dyes elute in the latter fraction. The blue and yellow dyes do not separate on the silica column. This third fraction was then subjected to chromatographic analysis. An aliquot, corresponding to approximately 2 m³ undiluted exhaust [4] or 10 m driving distance [5], respec-

tively, was injected and analysed for the presence of Solvent Yellow 124.

2.3. Liquid chromatography

The chromatographic analysis was performed on a liquid chromatograph Model HP1090A, equipped with an automatic injector and a diode-array detector (Hewlett-Packard, Waldbronn, Germany), all instrumentation being controlled by an analytical workstation Model HP79994A (Hewlett-Packard, Palo Alto, CA, USA). The separations were carried out on a YMC C₈-AQ column (YMC Co., Kyoto, Japan) packed with 5-µm particles, with a length of 25 cm, and an internal diameter of 4.6 mm. The mobile phase used was acetonitrile–25 mM ammonium acetate buffer (pH 4.8) (72:28, v/v) containing 5 mM dimethyloctylamine. The pH was measured in the buffer, not in the final mobile phase. The acetonitrile (chromatographic purity) came from Merck (Darmstadt, Germany), and all other chemicals from Fluka (Buchs, Switzerland). The eluate was monitored in the visual part of the spectrum and quantitations made at 420 nm. Chromatography was performed at room temperature using a mobile-phase flow-rate of 2.0 ml/min. With this chromatographic system the Solvent Yellow azo dye had a retention time of approximately 7.4 min.

3. Results and discussion

3.1. Repeatability

The repeatability was tested by injecting 10 µl of a solution of 14.5 ng azo dye in *n*-hexane eight consecutive times, using a 500-µl syringe. The relative standard deviation obtained was better than 5.2%. However, switching to a 50-µl syringe reduced the relative standard deviation to 1.2%.

3.2. Detection limit and sensitivity

The analytical system was tested for linearity in the range 0.5–100 ng and found to be linear with a coefficient of correlation $r = 0.996$. The

limit of detection was in the range 60–80 pg, and the limit of quantitation approximately 0.2 ng. Normal coloured fuel samples would contain approximately 20 ng yellow dye per injection, when diluted as described above.

3.3. Chromatography

Dimethyloctylamine was added to the mobile phase as a competing base to reduce or to diminish tailing of the azo dye. Upon the addition of the base the peak asymmetry factor was reduced from 1.36 to 1.04. Triethylamine did not give the desired reduction of peak tailing. Other organic modifiers, e.g. methanol and ethanol, were tested but gave a more pronounced tailing than acetonitrile. The ammonium acetate buffer was selected such that the mobile phase potentially could be used in a liquid chromatography–mass spectrometry system (LC–MS). The mobile phase, with a total volume of 1 l, was recirculated for 2 weeks, continuously, without any loss of performance. No adverse effects were observed on injection of more than 130 samples with respect to baseline drifting, pressure increase, and column performance.

3.4. Applications

The described method has successfully been applied to two different tasks, i.e. the quantitation of the marker dye in diesel fuels and the study of the presence/absence of the dye in exhausts from a diesel engine and an oil-fired domestic boiler. The method is easy to use for the fuel samples, which only require dilution prior to injection onto the chromatographic system. Fig. 2 shows a chromatogram from one fuel sample and one blank, i.e. a fuel sample without any marker added. Another sample can be injected immediately after elution of the azo compound, which means that the total analysis time is approximately 8 min. With the robustness of the analytical system this means that the throughput can be as high as 180 samples per day, making the method ideal for the routine forensic laboratory. The method has been used to analyse diesel fuels, but is also suitable for the

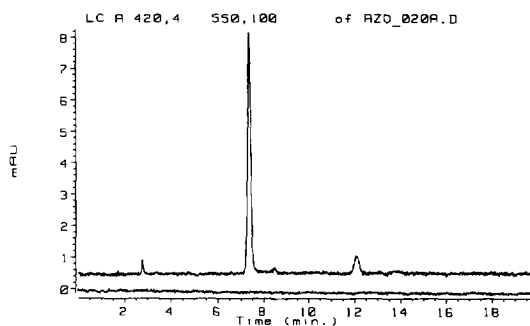


Fig. 2. Standard, 14.5 ng azo dye, prepared from a diesel fuel. Inserted is a blank, i.e. fuel without marker dye.

analysis of gasoline fuels. The results of the latter study indicate that the amounts of uncombusted dye in the engine and boiler exhausts were below the limit of quantitation, i.e. the emissions of the marker dye were lower than 0.01% for the diesel engine, and lower than 0.0001% for the boiler [3]. Fig. 3 shows a chromatogram from the particulate phase collected from a diesel engine, driven on coloured fuel, showing no residual dye.

4. Conclusions

The described method is an easily adapted technique for analysing the amount of Solvent Yellow 124 in different fuels with good accuracy and repeatability. Recirculation of the mobile phase makes this method also very economically viable. This robust and high-throughput method is well suited for the routine forensic laboratory to detect violations against tax regulations. Absolute confirmation of the presence of the marker

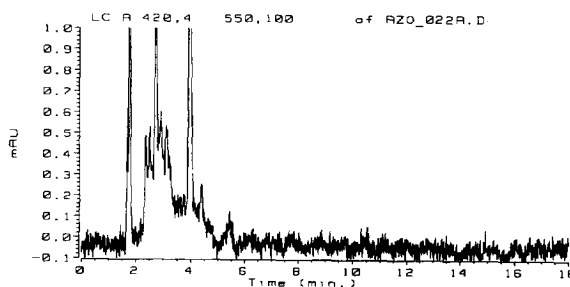


Fig. 3. Particulate phase of an emission from a diesel engine.

dye should also be easily made by running LC-MS without the competing base.

Acknowledgements

We are grateful to Mrs. Liselott Nielsen-Sundberg at the Swedish National Forensic Laboratory, Linköping, Sweden for the kind gift of Solvent Yellow 124, and to Carol Soontjens for reviewing the manuscript. This work was financed by the Swedish Department of Finance.

References

[1] G. Sweeney, H. Schmidt, A. Zimin, A. Caputo and M. Anderson, SAE Technical paper 942009, Warrendale, 1994.

- [2] R. Westerholm, J. Almén, H. Li, K.-E. Egeäck and K. Grägg, *Environ. Sci. Technol.*, 25 (1991) 332.
- [3] T. Alsberg, U. Stenberg, R. Westerholm, M. Strandell, U. Rannug, A. Sundvall, L. Rommert, V. Bernson, B. Pettersson, R. Toftgård, B. Franzén, M. Jansson, J.-A. Gustafsson, K.-E. Egeäck and G. Tejle, *Environ. Sci. Technol.*, 19 (1985) 43.
- [4] S. Henricsson, A. Christensen and R. Westerholm, *Statens Offentliga Utredningar*, 1995:3, Annex 7, Swedish Government, Archive Unit, S-103 33 Stockholm, Sweden.
- [5] K. Grägg, R. Westerholm and U. Rannug, *Statens Offentliga Utredningar*, 1995:3, Annex 8, Swedish Government, Archive Unit, S-103 33 Stockholm, Sweden.