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Note

Direct determination of 2,4-dimethyl-6-*tert.*-butylphenol in aviation turbine fuel by high-performance liquid chromatography

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2,4-Dimethyl-6-*tert.*-butylphenol (2,4M6B) is one of several hindered phenolic antioxidants which are approved for use in aviation turbine fuel (AVTUR). This phenol may be used in its commercially pure form or as the major component in antioxidants composed of mixed hindered phenols. British military specifications make the use of antioxidant mandatory in the case of hydrogen treated jet fuels. A maximum level of 24.0 mg/l is permitted with a minimum of 8.6 mg/l when the additive is mandatory. A quantitative method for the determination of 2,4M6B is therefore required for the quality assurance of fuels received from the refinery, or examination after long storage and also for experimental work on the depletion of antioxidant content.

Killer and Amos¹ have described a thin-layer chromatographic method for the detection of 2,4M6B in gasolines after a prior separation of alumina. This was later extended to the quantitative detection of 2,4M6B in aviation turbine fuels². A high-performance liquid chromatography (HPLC) method³ was used to determine 2,4M6B at the 20-mg/l level in naphtha. The use of an alumina separation followed by HPLC on a column of Porasil 60 with *n*-heptane as solvent and ultraviolet (UV) detection at 275 nm was shown to give improved repeatability⁴.

This Department has used an alumina separation followed by HPLC using a Durapak-OPN (Waters Assoc., Milford, Mass., U.S.A.) column with isooctane as solvent and UV detection at 280 nm (ref. 5) for the determination of 2,4M6B in AVTUR. The method was repeatable to within ± 1 mg/l over the 5-30-mg/l range with a limit of detection of 0.5 mg/l, and satisfied the requirements of this laboratory and has been widely used. A direct method, avoiding prior concentration on alumina, has obvious advantages and the development of such a method is described below.

EXPERIMENTAL

Apparatus

The equipment used was of modular construction consisting of a constant flow solvent delivery system (Waters Assoc. Model 6000A) with a septum injector (Perkin-Elmer, Norwalk, Conn., U.S.A.; Part No. 087-0315) using fluorosilicone rubber septa and a 50 cm \times 0.26 cm stainless steel column packed with Cyano-Sil-X, alkyl nitrile-modified silica (Perkin-Elmer). The solvent was 0.03% isopropanol in iso-

octane with a flow-rate of 1.4 ml/min. Detection was by a variable wavelength UV monitor (Cecil Instruments, Model CE212) set to 280 nm with a sensitivity of 0.02 absorbance units full scale (a.u.f.s.). Sample size was 80 μ l of neat aviation fuel, and the peak height of the 2,4M6B peak was compared with that obtained from 80- μ l injections of 10- and 20-mg/l solutions of 2,4M6B in isooctane.

RESULTS AND DISCUSSION

Initial HPLC studies to develop a quantitative method for 2,4M6B were carried out using Durapak OPN/Porasil C and 25% water-saturated isooctane as solvent. With this system a direct determination on the fuel was not possible as the main fuel peak completely masked the 2,4M6B peak. In order to remove the 2,4M6B from the bulk of the fuel, a batchwise separation was carried out using alumina. The 2,4M6B and other polar materials were removed from the alumina into ethanol and finally back extracted and concentrated into isooctane for analysis. It was found necessary to modify the isooctane by making it 25% water-saturated in order to maintain repeatable retention times. A typical chromatogram of unextracted and extracted fuel is shown in Fig. 1.

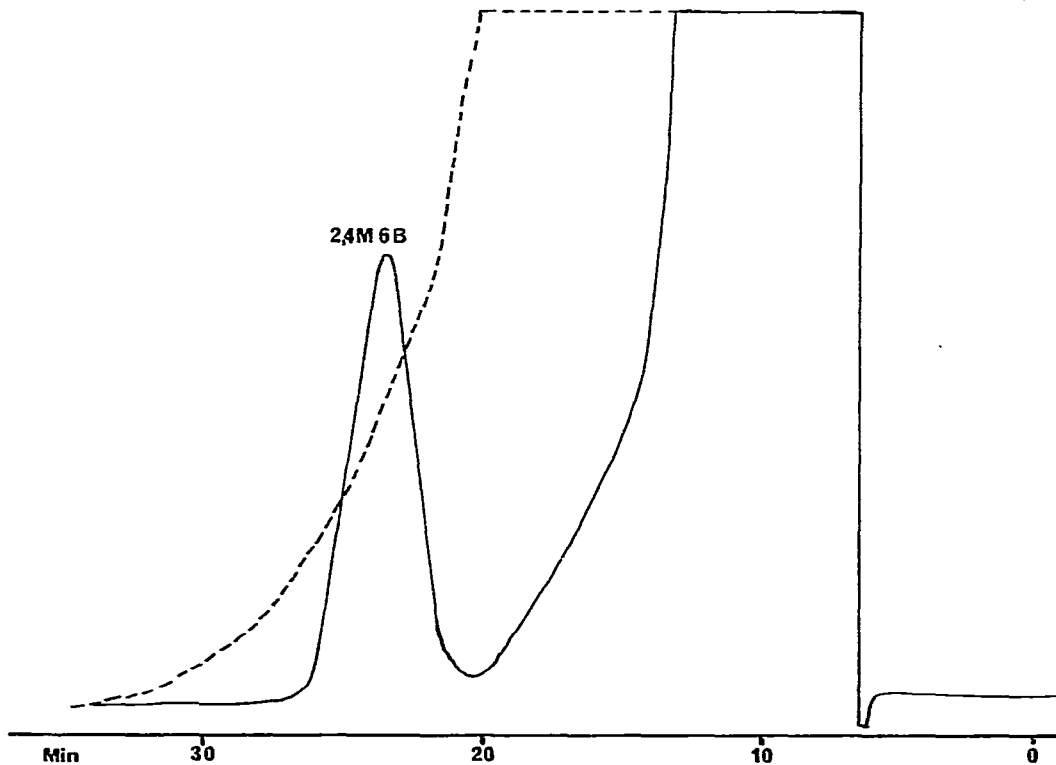


Fig. 1. Chromatograms of unextracted (---) and extracted fuel (—). Conditions: column, 1 m \times 2.3 mm I.D. Durapak OPN-Porasil C; solvent, 25% water-saturated isooctane; flow-rate, 0.5 ml/min; detector, UV at 280 nm.

Using microparticulate Cyano-Sil-X column packing material and 0.03% isopropanol in isooctane as the solvent, the chromatograms shown in Fig. 2 were obtained. The fuel was injected directly and no-pre-treatment was necessary. Past experience has shown that the reference AVTUR used is the most difficult for the determination of 2,4M6B. The main fuel peak is not fully resolved from the 2,4M6B peak, but resolution is good enough for quantitative analysis. The total time for this sample to eluate was 40 min at a flow-rate of 1.4 ml/min. Other samples of AVTUR were found to be free of late eluting peaks and an analysis time of 12 min was usual with complete resolution of the fuel and antioxidant peaks.

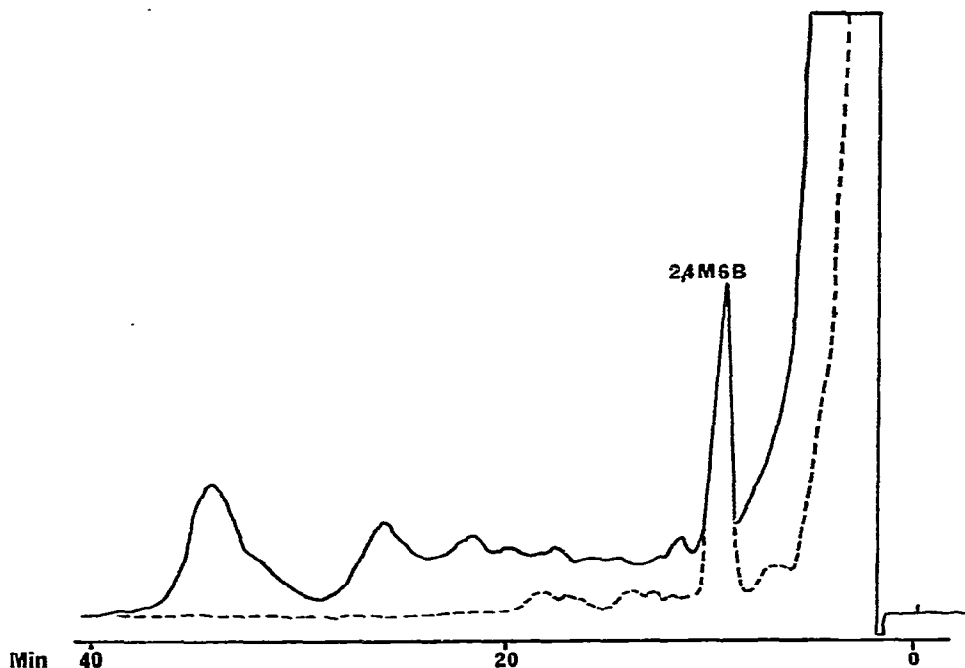


Fig. 2. Chromatograms of reference (—) and sample (---) AVTUR. Conditions: column, 50 cm \times 2.6 mm Cyano-Sil X; solvent, 0.03% isopropanol in isooctane; flow-rate, 1.4 ml/min; detector, UV at 280 nm.

The method was shown to give linear detector peak height response over a 2,4M6B concentration range of 0 to 30 mg/l. One mg/l of antioxidant gave a peak height of 30% full scale deflection at a detector sensitivity of 0.02 a.u.f.s. Using the reference AVTUR, checks for recovery and precision were made against standards prepared in isooctane. The results are given in Table I and show that the method is repeatable to within ± 0.2 mg/l at the 12-mg/l level with a mean recovery of 99%.

Several samples of AVTUR from different sources were run and no interferences from the fuel peak were found. The results on samples with known nominal contents are shown in Table II.

The method is also applicable when a mixed hindered phenolic antioxidant additive of known 2,4M6B content is used.

TABLE I
RECOVERY AND REPEATABILITY OF 2,4M6B IN AVTUR

<i>Added (mg/l)</i>	<i>Found (mg/l)</i>
2.5	2.5, 2.6
12.3	12.3, 12.4, 12.0, 12.4, 12.1
24.5	24.0, 23.8

TABLE II
DETERMINATION OF 2,4M6B IN AVTUR

<i>Sample</i>	<i>Nominal (mg/l)</i>	<i>Found (mg/l)</i>
A	11*	23
B	9	7
C	9	7
D	Nil	<1

* Sample A was analysed by the indirect method (alumina separation and HPLC) described in MQAD Technical Paper No. 572⁵ and found to contain 25 mg/l.

For interest some other types of fuels were examined and the results showed that 2,4M6B could be determined in AVTAG and AVGAS. A sample of DIESO 47/20 fuel, however, gave a complex chromatogram which completely masked the 2,4M6B peak.

CONCLUSIONS

It has been shown that HPLC using a microparticulate column of silica gel modified with an alkyl nitrile (Cyano-Sil-X) can be used to quantitatively determine 2,4M6B directly in aviation turbine fuel. The method is repeatable to within 0.2 mg/l and is applicable over the range 0–30 mg/l with a limit of detection of less than 1 mg/l. A number of fuel samples have been examined and no interference from the fuel peak was found. It has also been demonstrated that the method is applicable to the fuels AVTAG and AVGAS but not to diesel fuel.

REFERENCES

- 1 F. C. A. Killer and R. Amos, *J. Inst. Petrol.*, 52 (1966) 315.
- 2 R. Amos, *J. Inst. Petrol.*, 54 (1968) 9.
- 3 R. Amos and S. G. Perry, *J. Chromatogr.*, 83 (1973) 245.
- 4 R. Amos, in S. G. Perry (Editor), *Gas Chromatography 1972*, Applied Science Publ., Barking, 1973, pp. 235–245.
- 5 A. F. Cunningham and D. E. Hillman, MQAD Technical Paper No. 572.