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Note

Determination of 2,6-di-*tert.*-butyl-4-methylphenol in aviation turbine fuel by liquid chromatography with electrochemical detection

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2,6-Di-*tert.*-butyl-4-methylphenol (2,6B4M), is one of a number of phenolic antioxidants, which are approved for service use in aviation turbine fuel (AVTUR). The specified level for total active material in hydrogen-treated fuel is between 17 and 24 mg/l, and for non-hydrogen-treated fuel the level of total active material should not exceed 24.0 mg/l. 2,6B4M may be present as the sole antioxidant, or as a component of a mixture.

Liquid chromatography with UV detection has been used to measure low levels of the related anti-oxidant, 2,4-dimethyl-6-*tert.*-butylphenol (2,4M6B) in aviation turbine fuel[1,2]. However, previous attempts to determine 2,6B4M by normal or reversed-phase chromatography have failed, owing to the highly hindered structure of this compound, which causes it to elute with the hydrocarbon components of the AVTUR.

Selective detection, by electrochemical means, was also attempted and showed initial promise but failed at the 10–30 ppm level, owing to instability caused by the large excess of fuel components. This report describes the successful use of a more sophisticated dual-electrode detector, used in the oxidative screen mode.

EXPERIMENTAL

The equipment used consisted of a constant-flow solvent delivery system (Waters Assoc. Model 6000A), connected to a Rheodyne injection valve (20-μl sample loop) and a 25 cm × 5 mm I.D. stainless-steel column, packed with Zorbax C_{18} (Dupont) of 10 μm particle size.

The detector used comprised a control module (ESA Model 5100A Coulochem) connected to a guard cell (ESA Model 5020) and a dual-electrode analytical cell (ESA Model 5010). The electrodes were all composed of porous graphite.

The guard cell was placed between the pump outlet and the injection valve, with the electrode potential being set at +1.2 V (all potentials quoted are with respect to a standard calomel electrode). This served to reduce the level of electro-active impurities present in the eluent. In order to keep background interference to a minimum, the eluent was continuously recirculated.

The electrodes of the analytical cell were set at +0.7 V (screen electrode) and +1.1 V (measuring electrode.) The gain was set at 90 × 1, and a response time of 0.1 sec was used.

The composition of the eluent was 90% methanol, 10% 0.05 *M* acetate buffer, pH 4.8. The buffer was prepared by dissolving 6.8 g of sodium acetate trihydrate and 3 ml of glacial acetic acid in 500 ml of deionised water in a 2-l flask, and making up to the mark; 100 ml of this solution were added to 900 ml of methanol. The eluent was filtered through a 0.45-μm filter before use. The flow-rate was 1 ml/min.

A stock solution of anti-oxidant was prepared by adding *ca.* 0.1 g of 2,6B4M, accurately weighed, to a 100-ml volumetric flask, dissolving in additive-free reference AVTUR and making up to the mark. Suitable dilutions were prepared from this stock solution, using the same reference AVTUR as diluent, to give standard solutions in the concentration range 2–30 ppm.

After optimisation of the experimental conditions a series of standard solutions of 2,6B4M were injected onto the column, and the resultant peak heights were plotted against concentration. Sample solutions were injected in a similar way, and the peak heights were compared with the calibration plot. An injection volume of 5 μl was used.

RESULTS AND DISCUSSION

In order to obtain optimum results from an electrochemical detector, it is necessary to investigate the redox behaviour of the analyte of interest. Therefore, the first stage in this investigation involved the generation of a current–voltage (C–V) curve, or voltammogram, by plotting detector response against detector potential for a series of injections of 2,6B4M, at constant concentration (Fig. 1).

The best conditions, with respect to signal-to-noise ratio and selectivity, were obtained by using the oxidative screen mode. When this mode of operation is used, the first (upstream) electrode is set at a potential which corresponds to a point at the base of the C–V curve. Any electro-active material in the sample which has an oxi-

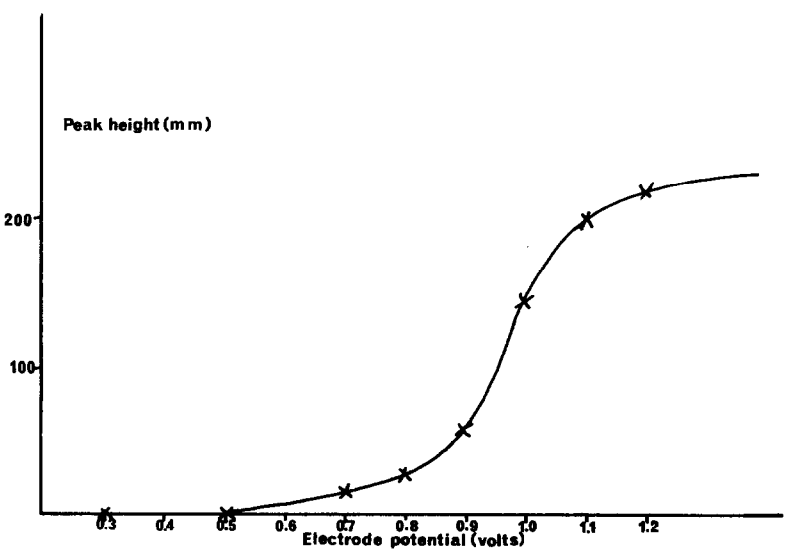

Fig. 1. Voltammogram for oxidation of 2,6B4M.

dation potential up to that of the screen electrode, will be oxidised before coming into contact with the second, measuring electrode.

The measuring electrode is set at a potential that corresponds to a point on the plateau of the C–V curve. This electrode will respond to any component of the sample that has an oxidation potential between that of the screen and measuring electrode potentials. It is, thus, used to detect and quantify the analyte of interest, in this case 2,6B4M. In all of the subsequent work, the screen electrode was set at +0.7 V and the measuring electrode was set at +1.1 V.

A typical chromatogram is shown in Fig. 2. The 2,6B4M is adequately resolved from the later fuel peaks. The less hindered phenolic antioxidant, 2,4M6B, is lost in the major fuel peak and cannot, therefore, be determined.

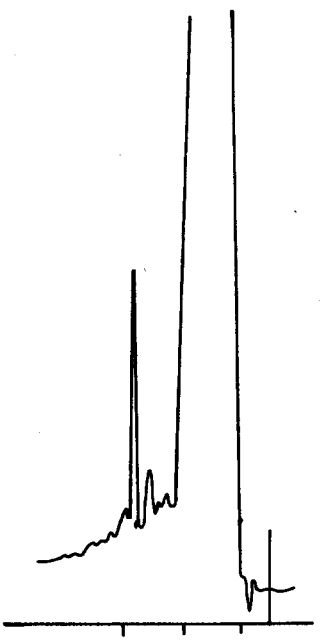

Fig. 2. Chromatogram of 20 ppm of 2,6B4M in reference AVTUR.

Earlier work used a Waters Radial-Pak 5 μm C_{18} packing, but while the separation was generally similar, the 2,6B4M peak exhibited a shoulder due to an unresolved component, which could not be removed by a change in eluent composition. The choice of column packing therefore appears to be very critical.

A number of fuel samples were examined by this method, using the Zorbax C_{18} column and, in all cases, resolution from AVTUR components was satisfactory.

A calibration plot of peak height against 2,6B4M concentration is shown in Fig. 3. Response is linear over the 0–30 ppm range.

The precision of the method was estimated by analysis of four samples of reference AVTUR, to which had been added known amounts of 2,6B4M. A 30-ppm solution was used as a standard. Five separate series of determinations were made and the results show acceptable accuracy and precision at the levels studied (Table I).

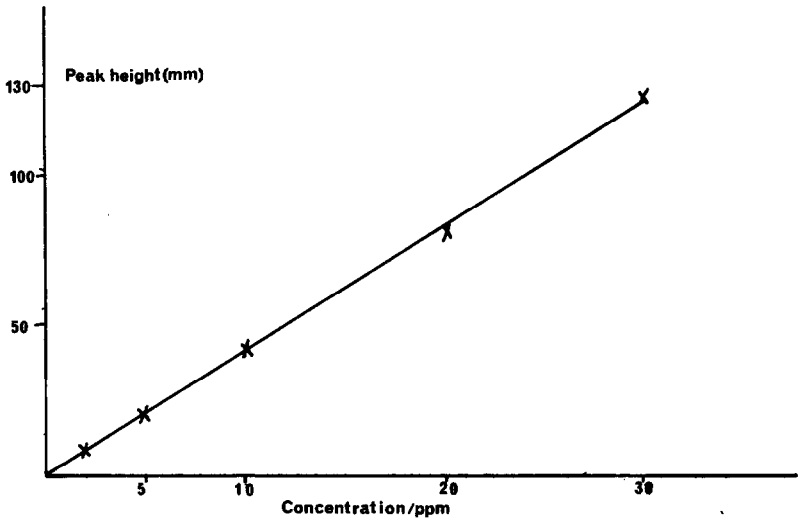

Fig. 3. Calibration curve for determination of 2,6B4M in AVTUR.

TABLE I

ANALYSIS OF SYNTHETIC SAMPLES FOR 2,6B4M CONTENT

Concentration added (ppm)	*Concentration found (ppm)*	*Mean (ppm)*	*Relative standard deviation (%)*
3.0	3.6, 4.0, 3.6, 3.3, 4.0	3.7	8.1
6.0	6.9, 6.6, 6.6, 6.6, 6.9	6.7	2.4
12.0	13.9, 13.5, 13.9, 12.9, 12.9	13.4	3.7
24.0	24.3, 24.4, 24.6, 23.7, 24.7	24.3	1.6

The detector sensitivity to 2,6B4M is very high; however, the limit of detection is determined by the presence of electroactive impurities in the AVTUR, which contribute to the background noise. The estimated limit of detection in this application is 1 ppm.

CONCLUSIONS

It has been shown that liquid chromatography, with electrochemical detection, can be used for the direct quantitative determination of the phenolic antioxidant 2,6B4M in AVTUR at the 2–30 ppm level.

REFERENCES

1 A. F. Cunningham and D. E. Hillman, *J. Chromatogr.*, 148 (1978) 528.
2 *Institute of Petroleum Method IP 343/80*, Wiley, London, 1984.