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Short communication

Determination of phenolic antioxidants in aviation jet fuel

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Abstract

The world-wide aviation jet fuel used for civil and military aircraft is of a kerosene type. To avoid peroxide production after the refinery process a specific antioxidant additive should be added on fuel. The antioxidants generally used are based on hindered phenols in a range of concentration 10–20 μg/ml. In the present work a specific method to measure the concentration of phenolic antioxidants is shown. The method is based on a liquid chromatographic technique with electrochemical detection. The technique, because of its selectivity, does not require sample pre-treatments. The analysis of a 5–10 ml fuel sample can be performed in less than 10 min with a sensitivity of 0.1 μg/ml and a RSD=2.5%. A comparison with another highly selective gas chromatographic technique with mass spectrometric detection with selected ion monitoring (GC–MS-SIM) is reported. The sensitivity of GC–MS-SIM method was 2 μg/ml with a RSD=3.1%. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Kerosene; Antioxidants; Phenols; Alkylphenols

1. Introduction

The world-wide aviation jet fuel used for civil and military aircraft is of a kerosene type, a development of the illuminating kerosene originally used in gas-turbine engines [1]. Aviation turbine fuel, grade Jet A1, is generally manufactured mainly from straight-run kerosene. Straight-run kerosene obtained from sweet crude oil will meet the requirements of the jet fuel specification with some refinery process. One of these processes is "hydrotreating" to reduce the sulphur active compounds present in kerosene to elemental sulphur to obtain a jet fuel with sulphur level according to the present directive [2]. This process generates a peroxidation of some hydrocarbons which can originate a rapid deterioration of nitril rubber and the formation of insoluble deposits with detrimental effects on the jet fuel thermal stability [3]. For this reason a specific antioxidant additive should be added after the refining process. The antioxidants generally used are based on hindered phenols as 2,6-di-*tert*.-butylmethylphenol (AO-1), 2,4-dimethyl-6-*tert*.-butylphenol (AO-2) and 2,6-di-*tert*.-butylphenol (AO-3), (Fig. 1) in a range of concentration 10–20 μg/ml. In the present work a specific method to measure the concentration of phenolic antioxidants is shown. The method is based on a liquid chromatographic technique with electrochemical detection (HPLC–ED) [4–7]. The technique, because of its selectivity, does not require sample pre-treatments. The analysis of a 5–10 ml fuel sample can be performed in less than 10 min.

A comparison with a gas chromatographic technique with mass spectrometric detection in the selected ion monitoring mode (GC–MS-SIM) [8–10] is reported. The internal standard (I.S.) chosen

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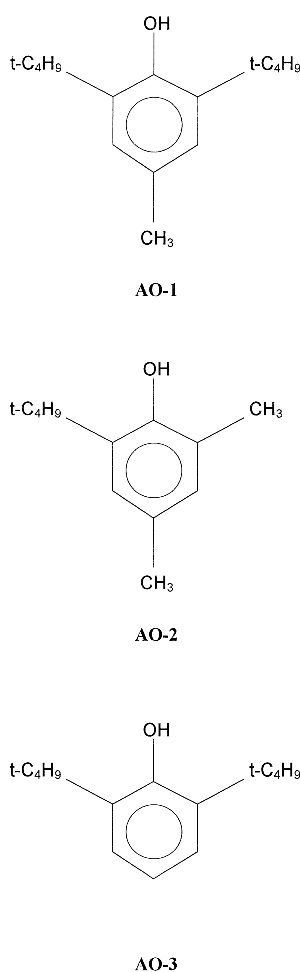


Fig. 1. Phenolic antioxidants.

for the GC–MS-SIM measurement was diphenylamine (DPA).

2. Experimental

2.1. Reagents, standards and samples

The standard solutions were prepared with commercial products: AO-1, AO-2 and AO-3 were in analytical grade (>99%, Octel), DPA (>99%, Aldrich). All the remaining reagents were of analytical grade. The Jet A1 fuel used to prepare the standard solutions was according to present directive for the civil and military aviation.

A stock solution of antioxidants was prepared by dissolving known weight amount of AO-1, AO-2 and AO-3 in jet fuel. Then, from this stock solution, were prepared fuel standard solutions in the concentration range of 5–100 μg/ml.

The fuel samples and standards for HPLC–ED determinations of phenolic antioxidants did not require any treatment and were prepared by dilution $1:10^3$ in methanol.

The fuel standard solutions for the GC–MS-SIM determinations were prepared by the addition in a 10 ml volumetric flask of a known amount of each phenolic antioxidants in the concentration range of 5–100 μg/ml and 10 μl of a 1% (w/v) DPA solution in jet fuel for a final concentration of 10 μg/ml as I.S.

The fuel samples for the GC–MS-SIM determinations were prepared by the addition in a 10 ml volumetric flask of jet fuel and 10 μl of a 1% (w/v) DPA solution in jet fuel for a final concentration of 10 μg/ml as I.S.

3. HPLC determination of phenolic antioxidants

3.1. Instrumentation

The apparatus used for HPLC–ED analysis consisted of a constant flow solvent delivery system (2150 HPLC pump; LKB, Bromma, Sweden), connected to a Rheodyne injection valve (100 μl sample loop) and a 12.5 cm×5 mm I.D. stainless steel column, packed with Nucleosil-120 C_{18} (Nertex) of 5 μm particle size. Between pump and injection valve there was a pulse-dumper.

The detector used comprised a control module (ESA Model 5200 Coulochem II) connected to a conditioning cell (ESA Model 5021) and a dual-electrode analytical cell (ESA Model 5011). The electrodes were all composed of porous graphite. Between column and conditioning cell there was a in line filter (frits 3 mm).

3.2. Conditions

3.2.1. Chromatographic conditions

The composition of the eluent was methanol–0.05 *M* acetate buffer, pH 4.5 (90:10). The buffer was

prepared by dissolving 6.8 g of sodium acetate trihydrate and 20 ml of glacial acetic in 500 ml of deionised water in a 2 l volumetric flask. The eluent was filtered through a 0.45 μm filter before use. The flow-rate was 1 ml/min.

3.2.2. Electrochemical conditions

The conditioning cell was placed between the column outlet and the analytical cell, with the electrode potential being set at +1.2 V. This served to reduce the level of electroactive impurities present in the eluent. In order to avoid background interference, the eluent was continuously recirculated. The electrodes of the analytical cell were set at +0.6 V for AO-1 and AO-2 and +0.4 V for AO-3 (screen electrode) and +1.1 V (measuring electrode) for all. The offset was set at +5%, and a response time of 1 s was used.

3.3. Procedure

The fuel samples for HPLC–ED determinations of phenolic antioxidants did not require any treatment. Fuel sample was prepared by dilution $1:10^3$ in methanol and than 20 μl of the fuel solution was injected.

4. GC–MS determination of phenolic antioxidants

4.1. Instrumentation

The apparatus used for GC–MS-SIM analysis consisted of a gas chromatograph Fisons GC 8000 Series, equipped with a methylsilicone capillary column (25 m×0.25 mm I.D. and 0.25 μm phase film). The GC–MS analysis was carried out by a mass spectrometry detector Fisons MD 800 operating in the mass range of 33–500 u.

4.2. Conditions

The measurements for GC–MS-SIM determinations were carried out with injection temperature at 250°C, initial temperature of 45°C for 1 min to a final temperature of 260°C for 1 min with a rate of 10°C/min. The carrier gas used was helium with a linear speed in column of 24.5 cm/s. The operating conditions of the MS detector were as following described: interface temperature 250°C, electron impact ionization (positive) (EI+) (70 eV ionisation energy), and scan speed 0.8 s for each ion. The following ions were acquired to measure the concentration of phenolic antioxidants: m/z=205, 220 for AO-1, m/z=163, 178 for AO-2, m/z=191, 206 for AO-3 and m/z=168, 169, 170 for DPA as IS.

4.3. Procedure

The GC–MS-SIM determinations of phenolic antioxidants were carried out by injection 1 μl of jet fuel sample prepared as previously described.

5. Results and discussion

The use of dual electrode detector, especially in the oxidative screen mode, allows to describe better the redox behaviour of phenolic antioxidants. In order to obtain the optimum results, the first step involved the generation of a current–voltage (I–V) curve, by recording detector response against detector potential for a series of injections of the analytes, at constant concentration. The best results, in terms of signal-to-noise ratio and selectivity, were obtained by using the oxidative screen mode. The second step involved the generation of a calibration curve, obtained by the injection onto the column of standard solutions at different concentration.

Calibration curves in the range 5–100 μg/ml have been built by injecting standard solutions with a concentration of 5, 10, 20, 50 and 100 μg/ml of each phenolic antioxidants. They show a linear relationship between the instrumental response and the analytes concentration according to the following equations:

$$\text{Area (AO-1)} = 0.4635 \cdot \mu\text{g/ml (AO-1)}$$

$$\text{Area (AO-2)} = 0.4905 \cdot \mu\text{g/ml (AO-2)}$$

$$\text{Area (AO-3)} = 0.3640 \cdot \mu\text{g/ml (AO-3)}$$

A typical chromatogram of the three phenolic

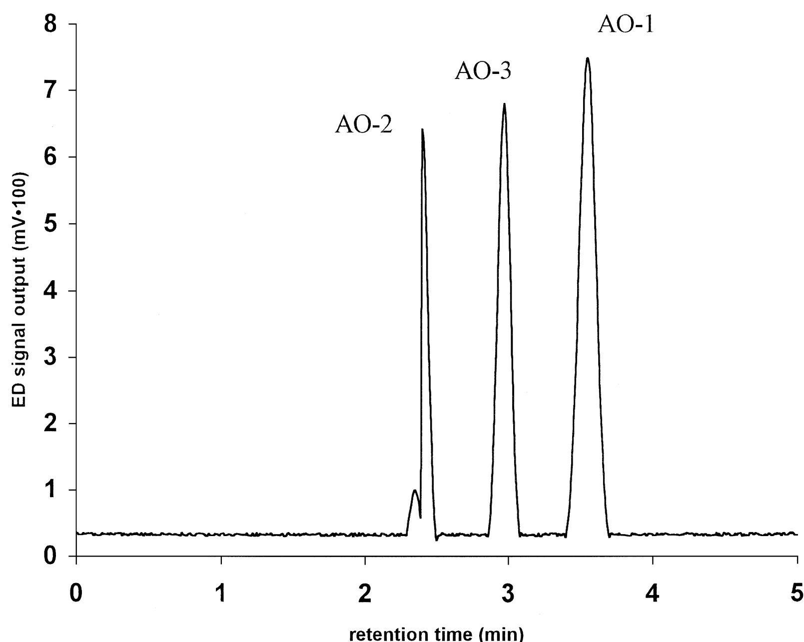


Fig. 2. HPLC–ED chromatogram of a jet fuel sample added with 20 μg/ml of AO-1, AO-2, and AO-3.

antioxidants, obtained in the described experimental conditions, is shown in Fig. 2.

A useful alternative route to the quantitative analysis of phenolic antioxidants is based on the use of GC–MS-SIM.

The mass spectrum of AO-1 (Fig. 3, top) is characterised by the presence of two significant signals for the molecular ion, $m/z=220$, and the base peak originated by a $^{\cdot}CH_3$ lost, m/z 205. The spectrum of AO-2 (Fig. 3 middle) shows a similar behaviour with significant signals for the molecular ion, m/z 178, and the base peak originated by a $^{\cdot}CH_3$ lost, m/z 163. Finally the mass spectrum of AO-3, also, is characterised by the presence of two significant signals for the molecular ion, m/z 206, and the base peak originated by a $^{\cdot}CH_3$ lost, m/z 191 (Fig. 3 bottom).

DPA, having a retention time higher than the phenolic additives, has been chosen as the internal standard (Fig. 4); it shows the mass spectrum reported in Fig. 5.

Calibration curves in the range 5–100 μg/ml have been built by injecting standard solutions with a concentration of 5, 10, 50 and 100 μg/ml of each phenolic antioxidants, all containing 10 μg/ml of DPA as internal standard. They show a linear relationship between the instrumental response and the analytes concentration according to the following equations:

$$\text{Area (AO-1)/Area (DPA)} = 0.4635 \cdot \mu\text{g/ml (AO-1)}/\mu\text{g/ml (DPA)}$$

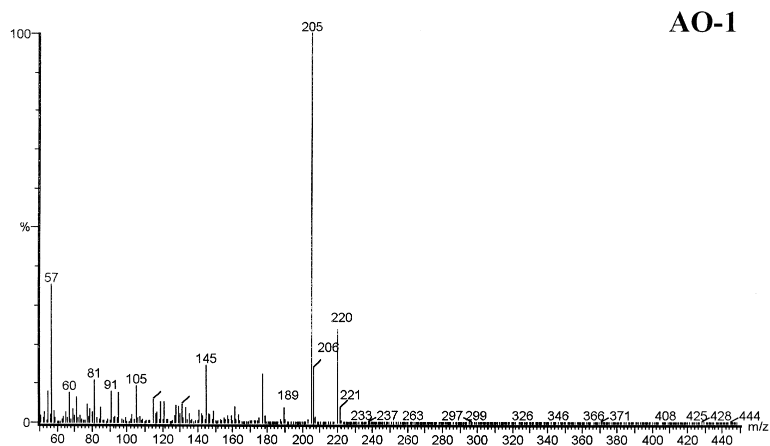
$$\text{Area (AO-2)/Area (DPA)} = 0.4905 \cdot \mu\text{g/ml (AO-2)}/\mu\text{g/ml (DPA)}$$

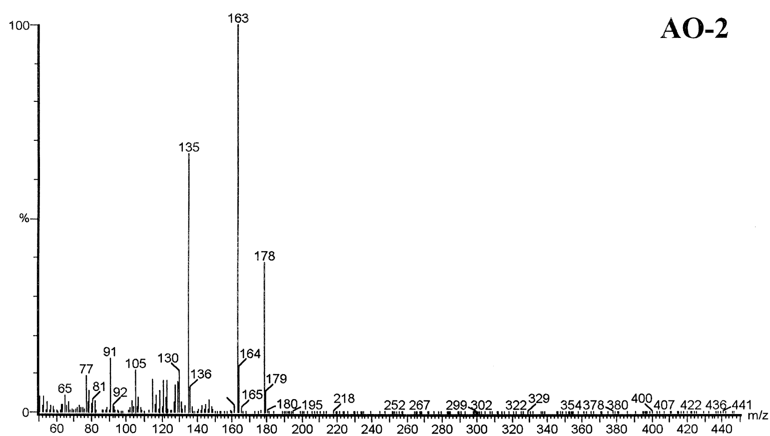
$$\text{Area (AO-3)/Area (DPA)} = 0.3640 \cdot \mu\text{g/ml (AO-3)}/\mu\text{g/ml (DPA)}$$

In Table 1 the validation parameters for the two analytical methods are summarised.

6. Conclusions

Due to its selectivity, HPLC–ED represent an useful tool to measure phenolic antioxidants in an hydrocarbon matrix, such as aviation jet fuels, without pre-treating samples. This characteristic





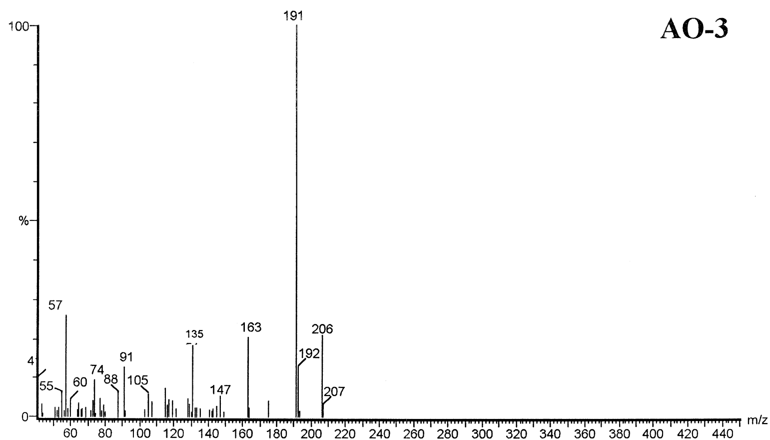


Fig. 3. Mass spectra of AO-1, AO-2 and AO-3.

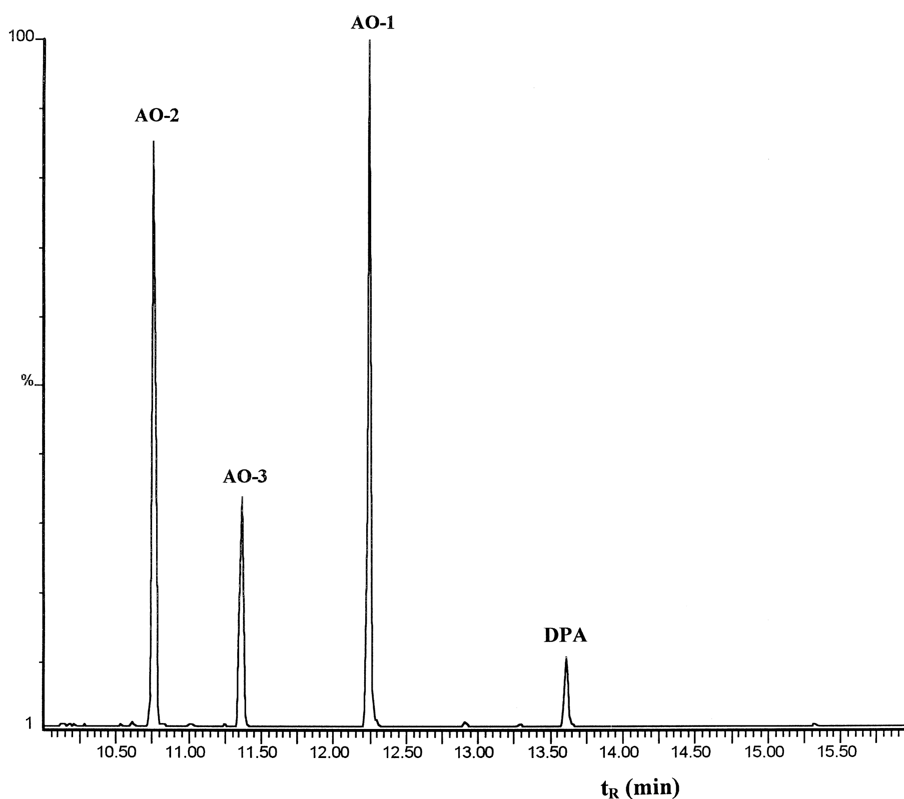


Fig. 4. GC–MS-SIM chromatogram of a jet fuel sample added with 20 μg/ml of AO-1, AO3, 10 μg/ml of AO-2 and 2 μg/ml of DPA as internal standard.

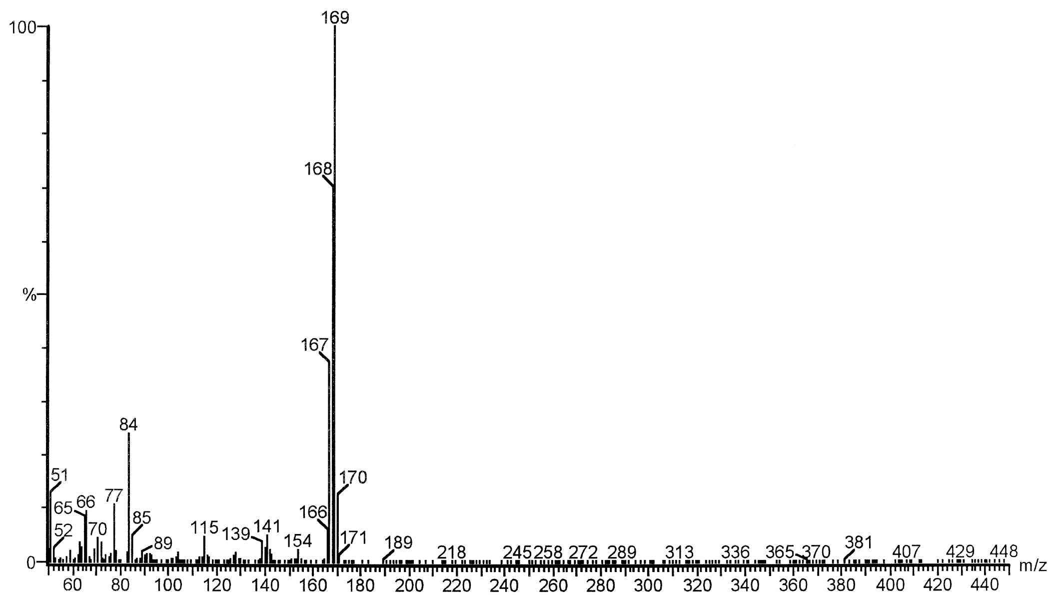


Fig. 5. Mass spectrum of DPA.

Table 1
Quality parameters for HPLC–ED and GC–MS-SIM methods

	HPLC–ED			GC–MS-SIM		
	AO-1	AO-2	AO-3	AO-1	AO-2	AO-3
Linearity range (μg/ml)	5–100	5–100	5–100	5–100	5–100	5–100
Linear regression (R^2)	0.995	0.995	0.995	0.996	0.996	0.996
Sensitivity (μg/ml)	0.1	0.1	0.1	2	3	2
Detection limit (μg/ml)	0.005	0.05	0.002	0.1	0.5	0.1
RSD (%, n=5, 20 μg/ml)/inter-day	2.0	2.1	2.4	1.3	3.1	2.6
RSD (%, n=5, 20 μg/ml)/intra-day	4.0	4.5	5.2	2.5	5.1	4.1

enable to perform accurate determinations (RSD= 2.5%) with sensitivity of 0.1 μg/ml. Using GC–MS-SIM analyses the only pre-treatment samples operation was the addition of the internal standards at a given concentration. These techniques have two relevant advantages: short time needed to carry out the analysis and low amount of sample needed.

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