CHROM. 20 778

Note

Determination of phenolic antioxidants in JP-5 jet fuels by gas chromatography–mass selective detection*

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Throughout the petroleum industry, the desirable light, sweet crudes are increasingly being replaced by heavy crudes containing undesirable amounts of metals, sulfur, nitrogen, and oxygen. This has led to a number of problems with the currently available jet fuels (such as the Navy's JP-5). These fuels can increase in peroxide number, corrosiveness, and viscosity during storage.

Commercial antioxidant mixtures containing hindered phenols are available to protect jet fuels against storage instability, and these contain either fully hindered or partially hindered phenolic types. Because of the current problems with the degradation of stored jet fuels, a project was initiated to study the depletion of antioxidants and changes in chemical composition occurring when stored at elevated temperatures. The project required development of analytical technology that would give accurate measurement of the specified antioxidants down to the 1-ppm level in JP-5 jet fuel. A desirable technique would either analyze the fuel directly or with a minimum of pretreatment.

Techniques for determining phenolic antioxidants in a variety of matrices have been described[1–12]. The majority of these techniques[1–9] was not applicable to the requirements of our particular project either because of a different matrix[1 7], or lack of a low ppm detection limit[8]. One technique[9] applied only to partially hindered phenols. Of the techniques which determined trace antioxidants in jet fuel[9–12], one was directly applicable but required fractionation and concentration of the fractions[10]. Two techniques that appeared to be directly applicable were selected for evaluation and adaptation to our specific uses. Hillman and Hayes[11] described a reversed-phase high-performance liquid chromatographic (HPLC) technique using electrochemical

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detection (ED) that appeared to have potential for detecting all fully and partially hindered phenolic antioxidants with sensitivity and selctivity. Masoud and Cha[7] reported a similar method for non-fuel matrices. Bartl and Schaaff[12], in a brief communication, outlined the use of gas chromatography–mass spectrometry (GC–MS) to identify and detect specific antioxidants in AVTUR aviation turbine fuel. No details concerning linearity or precision were given, and some of the operating parameters of the GC were not discussed.

This report describes work done to extend the use of GC–MS to the determination of antioxidants in a JP-5 jet fuel and to evaluate its usefulness in identifying and quantitating trace levels of specific antioxidants.

EXPERIMENTAL

Instrumentation

The analyses were carried out using a Hewlett-Packard (Palo Alto, CA, U.S.A.) 5890 gas chromatograph with a HP 5970A mass selective detector, and the data were processed with a HP 9825B calculator. The GC column was a Supelcowax 10 (30 m × 0.25 mm) fused-silica capillary column (Supelco, Bellefonte, PA, U.S.A.), and injections were in the splitless mode with a 0.5-min purge. The column enters the detector in the capillary direct mode.

Reagents

The HPLC grade *n*-heptane was obtained from J. T. Baker. Pure phenolic compounds were obtained from Aldrich. Commercial antioxidant A (DuPont AO-29) contained over 99% of 2,6-di-*tert.*-butyl-4-methylphenol (BHT). Commercial anti-oxidant B (DuPont AO-33) contained approximately 66% of 2,4-di-*tert.*-butylphenol plus 14% of 2,4,6-tri-*tert.*-butylphenol, and 12% of 4-*tert.*-butylphenol. The last two compounds were identified by GC and GC–MS data. Commercial antioxidant C (DuPont AO-30) was used as the internal standard in the determination of antioxidants A and B. It contained approximately 82% of 6-*tert.*-butyl-2,4-dimethyl-phenol. A fuel equivalent to a JP-5 fuel but without additives was used to prepare standards and samples for this work.

Standard blends. Blends of antioxidants A and B at the 0.2–0.3% (w/w) level in a JP-5 jet fuel were prepared. The jet fuel used was the same as that used for the preparation of samples for the storage and depletion tests. Dilute blends approxi-mating 20 ppm were prepared from these standards as required.

Internal standard blend. A blend of antioxidant C at the 0.2–0.3% (w/w) level in *n*-heptane was prepared. Dilute blends approximating 20 ppm were prepared from this standard as required.

Calibration blend. Internal standard (2 ml) and standard blend (2 ml) were mixed. The detector was calibrated with these blends before unknown samples were analyzed.

Sample preparation. Sample (2 ml) and internal standard (2 ml) were mixed prior to analysis.

Operating conditions

Gas chromatography. The gas chromatograph was operated with the injection port at 280°C and the detector manifold at 220°C. The column was programmed from 50°C to 220°C at a rate of 5°C/min for antioxidant A and 8°C/min for antioxidant B. The flow through the column was 1 ml/min of helium with a column head pressure of 2 p.s.i.

Mass selective detector. The detector was operated using a dwell time of 200 ms and a mass window of 1.0 a.m.u. For antioxidant A, ions monitored were at m/z 205.1 and 135.1, and for B they were at m/z 191.1 and 135.1. Also for antioxidant B, the ion at m/z 247.2 was sometimes monitored to allow measurement of the 2,4,6-tri-*tert.*-butylphenol impurity.

RESULTS AND DISCUSSION

The majority of the analyses were carried out on samples from a stability storage test at 60°C. In each case, only the major component of each of the commercial antioxidants under study was monitored, and the analytical technology was developed to determine only this major component. Information about other phenols in each commercial mixture is included only as background information.

Choice of suitable ions

With the mass selective detector in the peak finder mode (scanning), blends of each of the three antioxidants in *n*-heptane were used to determine their most abundant ions. The most abundant ions and their relative abundances are shown in Table I. The molecular ion M^+, $[M - 15]^+$ and $[M - 43]^+$ fragments are common to hindered phenols (13) and other *tert.*-butyl substituted aromatics.

The usefulness of each particular ion was evaluated with blends prepared in jet fuel. The criterion was to be able to monitor the ion and detect and measure the antioxidants without interference from jet fuel components. It was found necessary to use a Carbowax-type (Supelcowax 10) fused-silica capillary column to separate the antioxidants from components of the jet fuel. A program rate of 8°C/min successfully separated the antioxidant B (2,4-di-*tert.*-butylphenol), which is partially hindered, from the jet fuel components, but a program rate of 5°C/min was required to separate

TABLE I

RELATIVE ABUNDANCE OF MOST ABUNDANT IONS

M is the molecular ion in each case.

Compound	M^+ (%)	m/z	$[M - 15]^+$ (%)	m/z	$[M - 43]^+$ (%)	m/z
2,6-Di-*tert.*-butyl-4-methylphenol (antioxidant A)	25	220	100	205	10	177
2,4-Di-*tert.*-butylphenol (major component of antioxidant B	16	206	100	191	16	163
6-*tert.*-Butyl-2,4-dimethylphenol (antioxidant C)	39	178	100	163	51	135

antioxidant A from the jet fuel components. Being completely hindered, antioxidant A (2,6-di-*tert*.-butyl-4-methylphenol) eluted much earlier than antioxidant B and required a slower program rate.

Choice of internal standard

Another hindered phenol, 6-*tert*.-butyl-2,4-dimethylphenol (antioxidant C), was chosen for the internal standard. This eluted between antioxidants A and B in the GC program. Two ions that were abundant showed jet fuel interference (see Table I), so the ion at *m/z* 135.1 was selected as it did not have interfering jet fuel components in the chosen jet fuel.

Analytical parameters

Typical chromatograms of antioxidants A and B in jet fuel are shown in Figs. 1 and 2. These show clearly the separation of the selected ion peaks from the interfering jet fuel components. The absence of interfering fuel components is further demonstrated in Fig. 3 which shows selected ion chromatograms of the jet fuel used in this study without added antioxidants.

Over the range of 0–40 ppm of antioxidant in the jet fuel, satisfactory linearity was demonstrated with a linear regression analysis that gave a correlation coefficient of 0.9998 for antioxidant A and 0.9996 for antioxidant B. The precision of the technique was determined by preparing ten aliquots of one sample with internal standard and analyzing each portion. Relative standard deviations of 2.3% for antioxidant A and 3.9% for antioxidant B were obtained. The accuracy of the
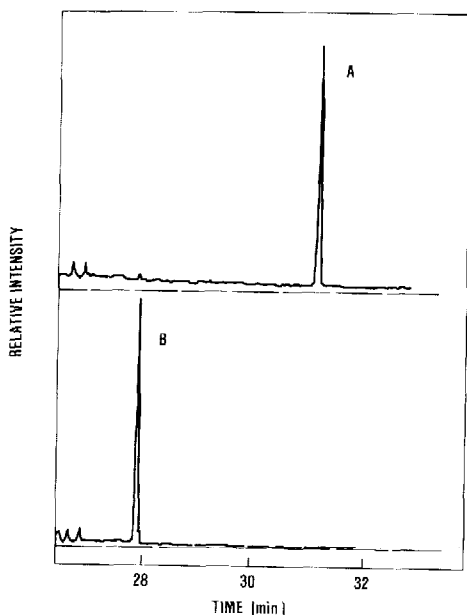

Fig. 1. GC–MSD of antioxidant A in jet fuel 1, monitored at (top) *m/z* 135.1, (bottom) *m/z* 205.2. Peaks: A = internal standard (antioxidant C, 25 ppm), B = antioxidant A (17 ppm). Conditions as described in Experimental.
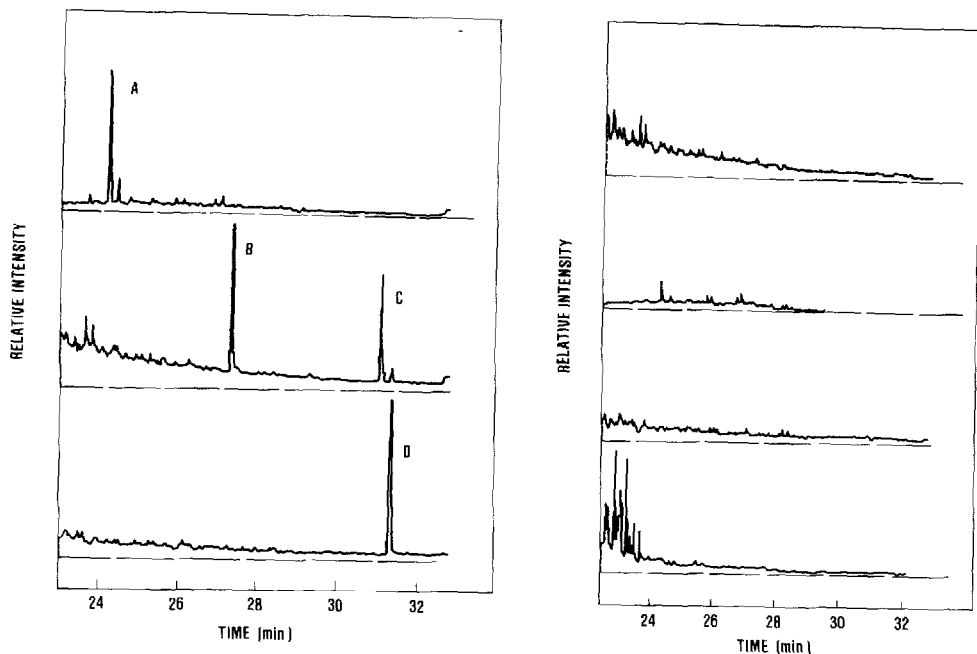
Fig. 2. GC–MSD of antioxidant B in jet fuel 1, monitored at (top) *m/z* 247.2, (middle) *m/z* 135.1, (bottom) *m/z* 191.1. Peaks: A = tri-*tert.*-butylphenol, B = internal standard (antioxidant, 19 ppm), C = impurity in antioxidant B (4-*tert.*-butylphenol), D = antioxidant B (20 ppm). Conditions as described in Experimental.

Fig. 3. GC–MSD of jet fuel 1 without additives, monitored at (from top to bottom) *m/z* 135.1, *m/z* 247.2, *m/z* 191.1, and *m/z* 205.1. Conditions as described in Experimental.

technique should be similar to the precision. The minimum detection level is 0.2 ppm with a 0.2-μl splitless injection, or approximately 0.2 ng of each antioxidant (assuming a signal-to-noise ratio of 3).

Analysis of samples from storage at 60°C

For the storage stability test, large quantities of blends of antioxidants A and B at 12 and 24 μg/g in a JP-5 jet fuel were prepared and stored at 60°C. Samples were withdrawn and the antioxidant level determined at two-week intervals. During the first twelve weeks, no reduction in antioxidant level was found within the limits of precision of the method. These data were averaged and are shown in Table II. It can be seen that the values agree well with the theoretical values.

Interference from oxidation products

A brief, two-week storage test of this jet fuel at 90°C rapidly caused antioxidant depletion. When these samples were analyzed, a large number of new components (see Fig. 4) appeared on the select ion at *m/z* 135.1 (used to monitor the internal standard). These oxidation products are quite polar and are probably hydroxy compounds. The internal standard peak was overlapped by interfering compounds in the analysis of antioxidant B. This problem was overcome by reducing the programming rate from 8°C/min to 6°C/min which eluted the components over a longer period and gave

TABLE II

COMPARISON OF MEASURED *VERSUS* THEORETICAL LEVELS OF ANTIOXIDANT IN JP-5
JET FUEL

Antioxidant A (µg/g)			Antioxidant B (µg/g)		
Theory	Measured	n	Theory	Measured	n
12	11.9	6	12	11.8	5
24	24.1	6	24	23.8	5

complete resolution of the internal standard peak. The other ions at m/z 191.1, 205.1, and 247.2 did not show any new components. If, in future work, interference with the internal standard ion becomes worse, it would be quite feasible to use antioxidant A as the internal standard for B, and *vice versa*.

Another phenomenon that emerged during the analysis of these (90°C storage) samples was the depletion of antioxidant A, apparently during vaporization in the injection port. This problem was uncovered when antioxidant A was used as an internal standard. This loss of antioxidant is thought to be due to reaction with peroxides (1170 ppm) and/or the newly formed oxygenated compounds that were in the jet fuel. At the injection port temperature of 280°C, reaction could occur rapidly. Antioxidant B, however, was not affected in this manner.
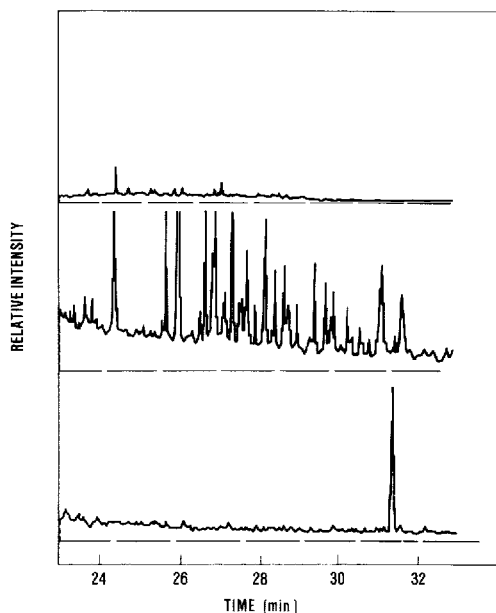

Fig. 4. GC–MSD of jet fuel 1 with antioxidant B after storage at 90°C, monitored at (top) m/z 247.2, (middle) m/z 135.1, (bottom) m/z 191.1. Many new components are present on the m/z 135.1 trace. Compare with Fig. 2. Conditions as described in Experimental.
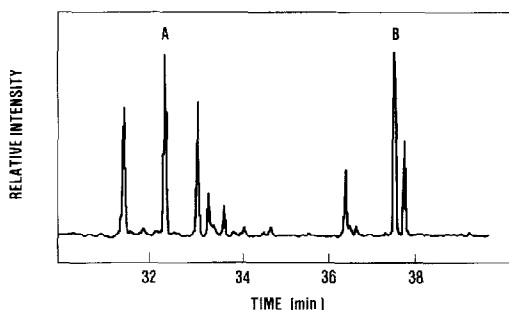
Fig. 5. GC–MSD of jet fuel 4, monitored at m/z 163.1. Peaks: A = internal standard (antioxidant C), B = major component of antioxidant D. Conditions as described in Experimental.

After the above occurrence, the injection technique was switched to a cool, on-column injection. This eliminates exposure of the sample to high temperatures. The work reported below used the cool, on-column technique.

Extension of technique to other fuels and another antioxidant

Three other JP-5 jet fuels that were on hand have also been examined by GC–mass selective detection (MSD) to establish if they contained interfering impurities. No impurities were found for ions at m/z 135, 191, and 205.

Other phenolic antioxidants can be determined by this technique. Three outside samples of JP-5 jet fuels were submitted for determination of their specified antioxidants. The first and second contained antioxidants B and C, respectively, and the third contained antioxidant D, which GC–MSD showed was predominantly *tert.*-butyldimethyl or *tert.*-butylethylphenols concentrated mainly in three major components. Although these components were isomeric with antioxidant C, they all eluted later than C (see Fig. 5) suggesting that they are less hindered than antioxidant
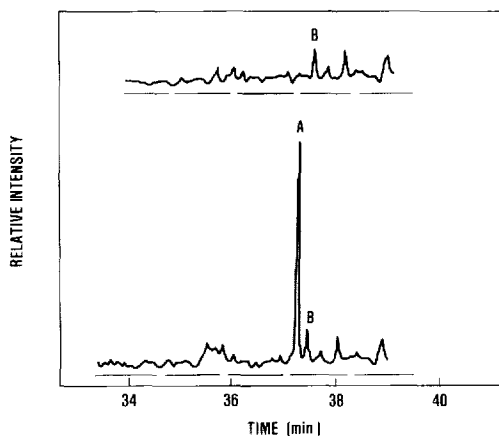

Fig. 6. GC–MSD of jet fuel 2, monitored at m/z 191.1. (Top) Neat fuel, (bottom) fuel containing 3.4 ppm of added antioxidant B. Peaks: A = antioxidant B, B = reference peak. Conditions as described in Experimental.

C (more polar). The latter was used as an internal standard, and measurement for both antioxidants (the largest component was used to quantitate D) were made using ion of m/z 163. The level of antioxidant D was found to be 18.5 ppm.

A different quantitation technique was developed for the other two samples of JP-5 jet fuels. A GC–MSD scan revealed that none of the specified antioxidants were present, but in each case a broad fuel component eluted at the same retention time as the antioxidant. Addition of ppm levels of antioxidant to the fuel resulted in a narrow peak riding on a broad peak (see Fig. 6). Calculation of detection limit was made by using an adjacent fuel component to correlate sample size and measuring peak heights with and without the added antioxidant. In both cases, the antioxidant level was found to be less than 1 ppm.

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