

## ANALYSIS OF PHENOLIC ANTIOXIDANTS IN JP-5 AVIATION FUELS

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### ABSTRACT

The Navy requires the addition of antioxidants to prevent the degradation of JP-5 aviation fuel in storage. Monitoring phenolic compounds commonly used for this purpose is essential to determine the quality of prepositioned aviation fuel supplies. The large number of chemical constituents in JP-5 fuels provides complex chromatograms which, for most approaches, hinder the detection of antioxidants. In this study, however, liquid chromatography with electrochemical detection and a judicious choice of the mobile phase provided good resolution of many antioxidants. Several phenolic antioxidants are evaluated in fuels originating from different crude sources and processing techniques.

### INTRODUCTION

The jet fuel supply and distribution system is very complex and unpredictable. The refineries supplying the U.S. Navy with JP-5 fuel change annually depending upon cost, logistics and the political situation in the oil industry. JP-5 properties within a given geographic area, therefore, are becoming more variable.<sup>1</sup>

Trends indicate future crude sources will have higher unsaturated hydrocarbon, heteroatom and metallic contents. All of these properties require increased hydroprocessing to produce an acceptable JP-5 product. Jet fuel is changing from a product made by simple distillation to a variable blend of streams from different processing units.<sup>2</sup>

The Navy is becoming increasingly concerned with the properties of the JP-5 now available for consumption and is relying less on property/performance relationships which existed ten years ago. The Naval Air Propulsion Center (NAPC) has initiated a Fuels Diagnostics Program to facilitate the measurement of JP-5 properties and interpretation of their relationship with aircraft engine performance. An integral part of this program is to collect, modify and/or develop analytical methods which will allow us to make evaluations.

The stability of our current JP-5 supplies must be periodically monitored. This is especially true for fuels placed in strategic storage locations for extended periods. Due to the shortage of pristine, straight distillate fuels, storing fuels with known less-than-desirable stability characteristics is becoming more of a reality. Presently, the Navy does not have regulations to prohibit the storage of fuels processed by techniques other than straight distillation. The Navy must rely heavily upon the addition of antioxidants to

prevent fuel degradation. The additives currently accepted in Specification MIL-T-5624 are phenolic in structure and serve to inhibit the degradation of fuel components by breaking the reaction chain of the peroxy radical which occurs during the hydrocarbon auto-oxidation process.<sup>3</sup>

A study conducted<sup>4</sup> had shown that peroxidation will occur only after the additive has been depleted. Therefore, tracking an additive's depletion pattern would give forewarning of fuel degradation. Having this information prior to degradation could assist the Navy in making decisions regarding when to rotate JP-5 stock. This could reduce the number of potential JP-5 fuels which may have to be downgraded to Diesel Fuel Marine (DFM) due to high peroxide content, thus not meeting military aviation fuel stability requirements.

Gas chromatographic and liquid chromatographic techniques for determining commercial phenolic antioxidants in aviation turbine fuels have been reported.<sup>5-8</sup> Unfortunately, only a few antioxidants were investigated in these papers. Pearson<sup>5</sup> presented an internal standard technique using gas chromatography-mass selective detection for two antioxidants. Cunningham and Hillman<sup>6</sup> reported a liquid chromatographic method with ultraviolet detection that can be applied to measure several hindered phenolic antioxidants. Also in this paper, an extractive procedure was developed to remove part of the "main fuel peak" from the chromatogram. Hayes and Hillman<sup>7</sup> used liquid chromatography with electrochemical detection (LCEC) for determining a single antioxidant in turbine fuel. A modified LCEC procedure to determine the retention time of several antioxidants was presented by Vogh.<sup>8</sup> However, the results were obtained with severely hydroprocessed neat (additive-free) jet fuels. Further modifications to this LCEC method were carried out in our study at NAPC to measure additional commercial phenolic antioxidants in actual refinery-produced JP-5 fuels.

## EXPERIMENTAL SECTION

The isocratic liquid chromatographic system consisted of a solvent delivery pump (SSI Model 222B Single-Piston) with the flow rate set at 0.5 ml/min., a pulse damper (SSI Model LP-21 Lo-Pulse Damper), a Rheodyne 7176 injector with 20 microliter sample loop, a Rheodyne 73XX column inlet filter, and a 4.6 mm I.D x 25 cm stainless steel Du Pont Zorbax C<sub>8</sub> reversed phase column of 5 micron particle size.

The detector was a flow-by type electrochemical (EC) detector (EG&G Princeton Applied Research Model 400). The EC detector contained a glassy carbon working electrode and a reference electrode. The reference cell was filled with a solution containing 3 M sodium chloride and saturated silver chloride. The EC detector was operated in the DC mode at 1000 mV, a current of 100 nA, a 1.0 second time constant, and a cathodic output. A Perkin-Elmer LCI-100 integrator was used for peak area measurements.

The mobile phase consisted of a mixture of 30% of 0.02 M potassium acetate buffer, 60% of 2-propanol, and 10% methanol. This solution was vacuum filtered through Millipore HVHP 0.45 micron filter paper and degassed for at least ten minutes (sonicated with vacuum).

The response factor and the retention time for each antioxidant in JP-5 fuel samples varied slightly from day to day. This was probably due to slight variances of conditions of the analytical instrumentation and the composition of the mobile phase. Therefore, it was necessary to run a standard solution every day for calibration prior to the analysis of each fuel sample. If more analyses needed to be run the following day, it was essential to pump the mobile phase continuously overnight at a low flow rate. If this was not done, the system might become clogged and damaged by the deposits that could be formed by the buffer solution in the mobile phase. If the instrument was going to be turned off for long period, distilled water with 10% methanol had to be pumped through the system for few hours, followed by acetone for at least half an hour prior to turning off the pump.

## RESULTS AND DISCUSSION

Hindered phenolic type antioxidants are typically added into JP-5 fuel at a concentration of 17 to 24 ppm during the refining process. At this level, analytical methods with commonly used detectors do not provide sufficient sensitivity for identifying and quantifying the antioxidants. An electrochemical (EC) detector was chosen in this study due to its selectivity and sensitivity for phenolic compounds. With EC detection, compounds that contain either electro-oxidizable or electro-reducible organic functional groups will be detected. Thus, many hydrocarbon fuel components can be conveniently eliminated from detection making it easier to isolate antioxidant peaks.

Based on initial testing, it was determined that improvements could be made to the mobile phases that had been used and reported in other papers.<sup>7,9</sup> A variety of solvents and combinations of solvents were evaluated. The mobile phase that was found to be most effective in this study (see Experimental Section) provided much improved resolution of many antioxidants and minimized the miscibility problem between JP-5 fuel and the mobile phase.

Seven antioxidants that are commonly added to JP-5 aviation fuels were studied in this work. The chemical compositions of these antioxidants are listed in Table 1. Most antioxidants that are added to JP-5 fuels at the refinery are phenolic mixtures. Of the antioxidant structures that are or had been used in the military specification, only three antioxidants (AO-A, AO-B, and AO-E) are single component additives.

In the preliminary phase of this study, antioxidants were added at the 17 to 25 ppm level into a "clean" fuel to prepare standards. A hydrocracked JP-5 type additive-free fuel (Fuel X) was used as the "clean" fuel. It was selected

because the high intensity region in its chromatogram (Figure 1) is much narrower than a typical JP-5 fuel (Figure 2, Fuel #1) due to differences in refinery processing (e.g. hydrocracking vs straight run). The antioxidants in the prepared standards were then characterized by their chromatogram retention time (Figures 3 and 4). This "preliminary" information for each antioxidant was then applied to the analyses of "actual" JP-5 fuel samples.

A number of actual JP-5 fuels originating from different crude sources and processing techniques were evaluated. Examples of their typical chromatograms are shown in Figure 5 (Fuel #2) and Figure 6 (Fuel #3). Unfortunately, for most of these fuels, the "main fuel peak" that elutes during the first fifteen minutes retention time completely masks the peaks of a number of the antioxidants in this study. Antioxidants AO-B, AO-C, AO-D, the minor peak for antioxidant AO-F, and the minor peaks for antioxidant AO-G are completely blocked by this "main fuel peak". It is impossible to positively identify antioxidants AO-B, AO-C and AO-D in JP-5 fuel samples unless the "main fuel peak" can be eliminated partially or completely from the chromatogram.

The major component of antioxidant AO-F has the same chemical composition as antioxidant AO-E. Therefore, they will be detected with the same retention time. Thus, when this peak is detected in "real" JP-5 with the large "main fuel peak", it is not known if the minor peak for antioxidant AO-F is being masked. In this case, it is impossible to determine whether antioxidant AO-E or AO-F is present in the JP-5 fuel sample.

Regardless of the difficulty in identifying some antioxidants as mentioned above, antioxidant AO-E (or the major component of antioxidant AO-F), a component of antioxidant AO-G, and antioxidant AO-A in JP-5 fuel samples still can be detected by HPLC analysis. Peak retention times for antioxidant AO-E and antioxidant AO-G are very close to each other (Figure 7, Fuel #4). However, these two antioxidants will never be added simultaneously into JP-5 fuel by the manufacturer. Therefore, the antioxidant which is actually present in the fuel can be identified by spiking one of these antioxidants into the fuel.

Not all fuels contain the large "main fuel peak" in their chromatogram. The intensity of the "main fuel peak" in Figure 7 is much narrower than the one for most typical JP-5 fuel samples as shown in Figure 2. This difference is most likely due to the fact that JP-5 Fuel #4 was produced by different refinery processing. The antioxidant peaks in this chromatogram did not originate from the fuel sample. Antioxidants AO-A, AO-E, and AO-G were added into the fuel before running the chromatogram.

Quantitative analysis of "actual" JP-fuels involved several steps. A chromatogram was run on the as-received JP-5 fuel for a "preliminary" identification of antioxidant peaks. Next, a standard was prepared from a "blank" fuel. Because "actual" JP-5 fuels vary in chemical composition which affects the peak area measurement in the analysis, it is necessary to prepare

a standard for each fuel sample. A "blank" fuel was obtained by filtering the JP-5 fuel through either a silica gel column or an Alumina N Sep-Pak cartridge. This step removed the antioxidant from the fuel and their peaks from the chromatogram. An antioxidant at a concentration of 10 to 25 ppm was added into a "blank" fuel to prepare a standard. The prepared standard was then analyzed to calculate the response factor for each corresponding antioxidant. With the response factor for each antioxidant and the fuel chromatogram that was obtained in the first step, the amount of antioxidant in the JP-5 fuel sample was determined by the external standard technique.

For most fuel samples, there was only a very small peak shown at the chromatogram retention time that corresponds to antioxidant AO-A (Figure 2). It is very difficult to accurately measure such a low concentration directly. However, in this case, the amount of antioxidant AO-A in JP-5 fuels could be more accurately determined by an addition technique than with an external standard technique. The addition method was conducted as follows: A known amount of antioxidant AO-A was added into a "blank" fuel to calculate its response factor. The "blank" fuel was prepared by the same filtration technique described earlier. After spiking a known amount of antioxidant AO-A into an actual JP-5 fuel sample (Figure 8), the total concentration of antioxidant AO-A in the spiked fuel sample was determined. The difference between this measured total amount of antioxidant AO-A and the known amount that was added into the fuel sample was the original concentration of antioxidant AO-A in the JP-5 fuel sample.

The effects of interferences occurring at the location of an antioxidant peak may also be minimized by using the addition technique described in the preceding paragraph. When Fuel #1 was filtered through an Alumina N Sep-Pak cartridge, a small shoulder remained at the prior location of the antioxidant AO-A peak (Figure 9). This demonstrates that care must be taken to account for interferences in quantitative analyses. This process effectively subtracts out baseline interferences since the response factor is determined on a "blank" fuel containing interferences.

## CONCLUSIONS

A number of JP-5 aviation fuel samples were examined by liquid chromatography with electrochemical detection. A mobile phase was found which provided good resolution. All antioxidant peak locations were identified and quantitative analysis demonstrated at use levels (17-24 ppm). A detection limit of about 1 ppm was found for all antioxidants. However, many JP-5 fuels have a "main fuel peak" which masks some of the antioxidant peaks. Thus, a complete qualitative/quantitative analysis of actual JP-5 fuel samples was greatly dependent on the location of the antioxidant peaks with respect to the "main fuel peak". A technique for eliminating the "main fuel peak" (partially or completely) from the chromatogram needs to be developed to analyze the antioxidant peaks which are located in that region and will be the objective of subsequent work.

## ACKNOWLEDGEMENT

The authors wish to thank Dr. M. N. Sundberg for helpful discussions on this project. Also, the authors would like to express their thanks to Dr. E. Florio for technological assistance.

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**TABLE I**  
**Antioxidants Commonly Used in JP-5 Aviation Fuels**

<u>Antioxidant</u>	<u>Chemical Composition</u>
AO-A	2,6-di- <u>tert</u> -butyl-4-methylphenol
AO-B	6- <u>tert</u> -butyl-2,4-di-methylphenol
AO-C	72% min 6- <u>tert</u> -butyl-2,4-dimethyl-phenol 28% max <u>tert</u> -butyl-methylphenols and <u>tert</u> -butyl- dimethyl-phenols
AO-D	60% min 2,4-di- <u>tert</u> -butylphenol 40% max mixture of <u>tert</u> -butylphenols
AO-E	2,6-di- <u>tert</u> -butylphenol
AO-F	75% min 2,6-di- <u>tert</u> -butylphenol 25% max <u>tert</u> -butylphenols and tri- <u>tert</u> -butylphenols
AO-G	55% min butylated ethyl phenols 45% max butylated methyl and dimethyl-phenols

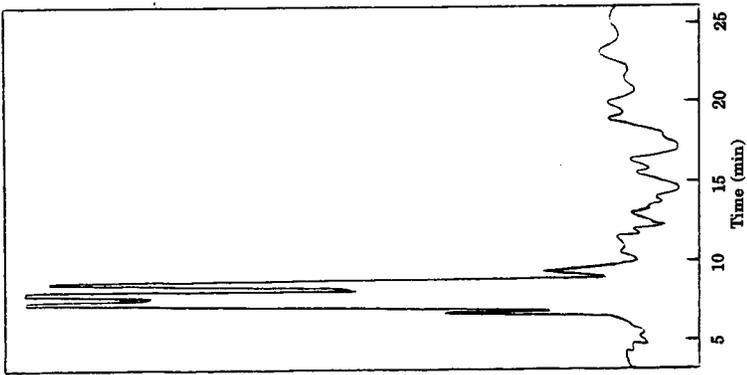


FIGURE 1: Chromatogram of "Clean" Fuel X  
(with no antioxidants)

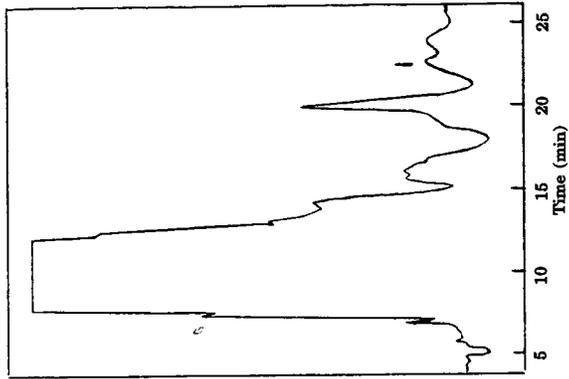


FIGURE 2: Chromatogram of "Typical" JP-5  
Fuel #1 containing AO-A (1)

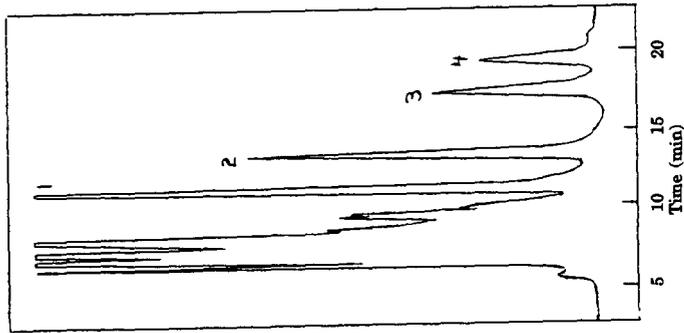


FIGURE 3: Chromatogram of "Clean" Fuel X containing AO-A (4), AO-B (1), AO-C (1), AO-D (2), AO-E (3) and AO-F (3)

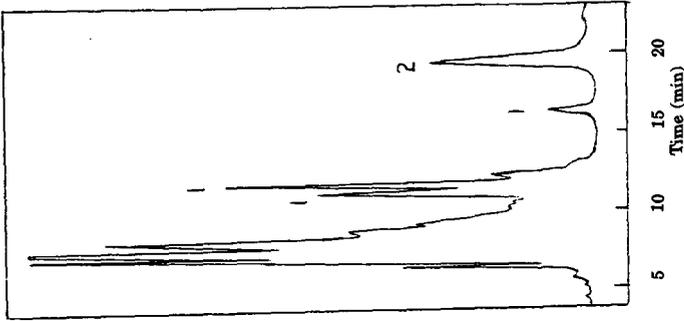


FIGURE 4: Chromatogram of "Clean" Fuel X containing AO-A (2) and AO-G (1)

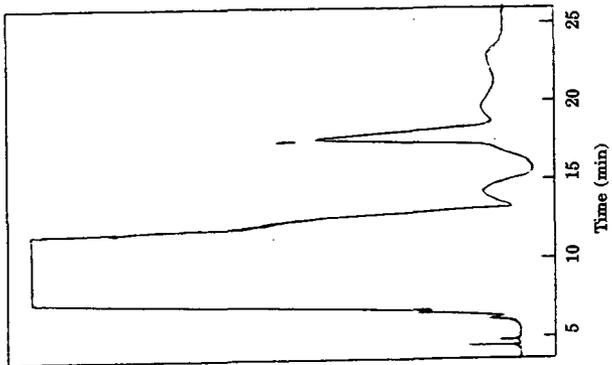


FIGURE 6: Chromatogram of JP-5 Fuel #3 containing AO-E (1) or AO-F (1)

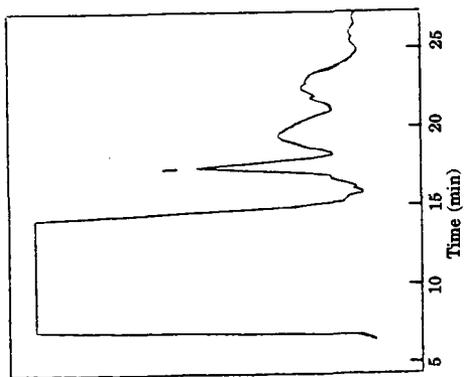


FIGURE 5: Chromatogram of JP-5 Fuel #2 containing AO-E (1) or AO-F (1)

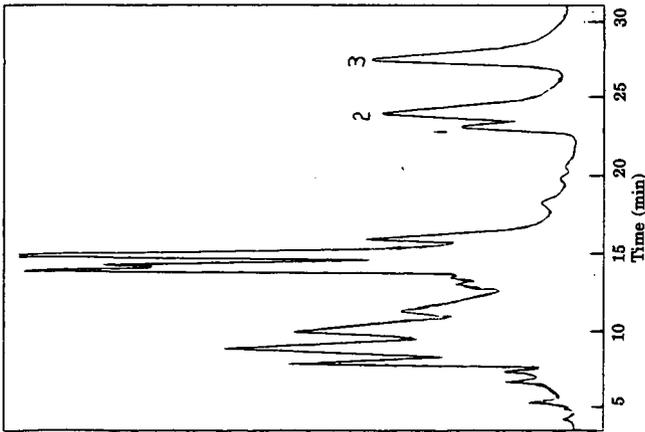


FIGURE 7: Chromatogram of JP-5 Fuel #4 containing AO-A (3), AO-E (2), and AO-G (1)

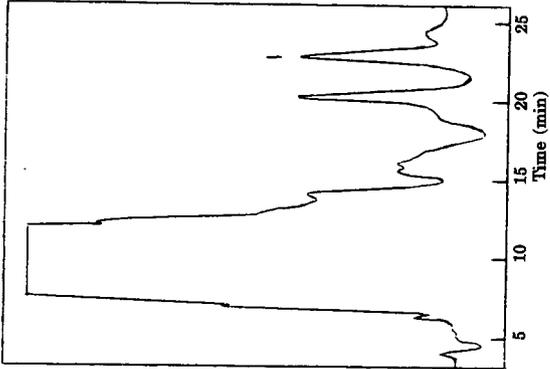
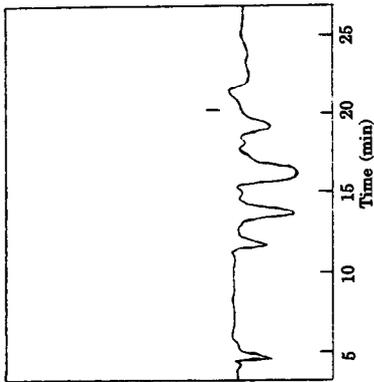


FIGURE 8: Chromatogram of JP-5 Fuel #1 spiked with AO-A (1)



**FIGURE 9:** Chromatogram of JP-6 Fuel<sup>1</sup> filtered through an Alumina N Sep-Pak cartridge showing interferent (1).