

CHARACTERIZATION OF AUTO-OXIDATION PRODUCTS OF AVIATION JET FUELS BY GAS CHROMATOGRAPHY COUPLED WITH MASS SPECTROMETRY

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ABSTRACT

Hydroperoxides are important products in the liquid phase oxidation reactions of jet fuel hydrocarbons. For better understanding of the reasons for the differences in oxidative stability between different jet fuels, it would be useful to monitor the formation of oxidation products, especially hydroperoxides, from individual hydrocarbons. In this work, hydroperoxides were analyzed from fresh, long-time stored and high temperature oxidized jet fuel samples. The analytical procedure includes extraction of the hydroperoxides into deionized water, re-extraction into diethyl ether, subsequent trimethyl silylation and GCMS analysis. Tentative identification of two isomeric cymene hydroperoxides, the tetralin 1-hydroperoxide, isomeric methylindan hydroperoxides, and higher molecular weight substituted tetralin and indan hydroperoxide trimethylsilyl derivatives was obtained. Assignment of individual hydroperoxide isomers was not possible by mass spectra.

INTRODUCTION

Development of the aircraft and particularly of the jet engines seems to place more and more demands on the heat-sink efficiency of the jet fuel. The hydrocarbon mixture should resist higher fuel system component temperatures without thermal oxidative degradation or pyrolysis. Strategic long-term storing, also, places high demands for auto-oxidative and microbial degradation resistance of fuels.

Hydroperoxides are the principal primary auto-oxidation products of most hydrocarbons.¹ Oxidative degradation of jet fuel, which may appear as development of gums and insoluble deposits, unpredictable changes in lubricity, increased corrosiveness, poor water separation properties etc., correlates strongly with the formation of hydroperoxides, at least as intermediates. Soluble oxygen containing products may have useful effects on formation of boundary lubrication films chemically bonded on fuel system surfaces like the friction surfaces of fuel pumps but small amount of insoluble small molecular weight or polymeric secondary products may be harmful by causing fouling of critical engine components like fuel nozzles, augmentors etc. If the role of each oxidation-susceptible molecule in the degradation of the jet fuel could be understood, modifications of the refinery processes or design of more specific antioxidants could be possible, which in turn would result in better thermal and long term stability for the fuel.

Standard jet fuel oxidation tests do not give information about which individual chemical compounds are oxidized most rapidly. A jet fuel is comprised of at least hundreds of saturated paraffin, alicyclic (naphthenic) and aromatic hydrocarbons and may also contain some unsaturated olefinic hydrocarbons and trace amounts of sulfur, oxygen and nitrogen compounds. It is known that olefinic and several aromatic hydrocarbons oxidize much more rapidly than the saturated hydrocarbons. However, there is deficiency of even qualitative information about the individual products formed in oxidative degradation of jet fuels.

Direct detection of individual hydroperoxides and other oxidation products in a jet fuel is very difficult due to the complexity of the product mixtures and low concentration of each product. On the other hand, hydroperoxides are labile compounds and often decompose rapidly at optimal temperatures for GCMS analysis² or when treated with acids or bases.³ Analysis of hydroperoxides by GCMS generally requires derivatization or other conversion into more thermally stable compounds.⁴

The objectives of this investigation were 1) to develop a practical method for the enrichment of hydroperoxides from oxidized jet fuels, and 2) to characterize the molecular structures of the enriched hydroperoxides by conversion into thermally stable derivatives followed by GCMS analysis. The aim of this article is to describe an analytical procedure for hydroperoxides based on water extraction of oxidized fuel samples followed by trimethyl silylation

of the hydroperoxide -OOH groups to the more stable -OOSi(CH₃)₃ groups⁴ and application of GCMS technique for characterization of molecular structures of the most abundant hydroperoxides found in differently oxidized Jet A-1 samples.

EXPERIMENTAL

Materials. A fresh and differently oxidized Jet A-1 fuel samples were treated by procedures described below to obtain samples for GCMS analysis of hydroperoxides as their corresponding peroxytrimethylsilanes. One Jet A-1 sample (obtained from Sabena Airlines Depot, Brussels Airport, Belgium) was allowed to stand 2.5 years at room temperature in a sealed glass flask which was occasionally opened to air (to take samples for NMR). A 10 ml sample of this was extracted once with 50 ml of deionized water. The extract was then allowed to evaporate into dryness at room temperature. The evaporation residue was trimethylsilylated as described below to obtain Sample 1.

Other samples were a 100 ml fresh Jet A-1 (obtained from Finnish Air Force, Satakunnan lennosto, Tampere, Finland), a 50ml Jet A-1 sample oxidized 24 hours at reflux under oxygen atmosphere and a similarly oxidized 50 ml sample of a Jet A-1 sample that had been extracted three times with identical volume of deionized water. The corresponding GCMS samples (Sample 2, Sample 3 and Sample 4) were obtained as described below.

Jet A-1 samples (except the aged one) was extracted three times with identical volume of deionized water, the water phases were combined, saturated with sodium chloride (p.a., Riedel-De Haen, Seelze, Germany) and extracted three times with one third volume of diethyl ether (glass distilled grade, Rathburn, Walkerburn, UK). Ether phases were combined and ether was evaporated with rotatory evaporator. 50 ml acetone (nanograde, Mallinckrodt, Paris, Kentucky, USA) was then added and evaporated with rotatory evaporator to dry the residue.

Derivatization and GCMS analysis. Trimethylsilylation: a 100 μ l sample (for Sample 3 and Sample 4) or the whole evaporation residue (for Sample 1 and Sample 2) was mixed with 100 μ l of BSTFA (Merck, Darmstadt, Germany) and 1 ml of toluene (nanograde, Mallinckrodt, USA) or diethyl ether (for Sample 1) was then added. At least two hours of reaction was allowed prior to analysis by GCMS. Analyses were conducted with a GC (HP 5890) equipped with a quadrupole mass selective detector (HP 5970A series). For all analyses the EI electron energy was 70 eV and the ion source temperature 280 °C. All samples were introduced as 1.0 μ l aliquots by autosampler. Sample 1 was analyzed with a 25 m x 0.2 mm capillary column (HP-1, polydimethylsiloxane, 0.11 μ m film thickness), 90 °C injector temperature, split injection at 1:8.4 split ratio, and scan range from 30 to 300 amu. The temperature program for Sample 1 was 4 min at 60 °C, then to 200 °C at 5 °C/min, then to 280 °C at 20 °C/min, and 3 min hold at 280 °C. Sample 2, Sample 3 and Sample 4 were analyzed with a 30 m x 0.2 mm capillary column (RTx-200, trifluoropropylmethyl polysiloxane, 0.10 μ m film thickness), 200 °C injector temperature in splitless injection mode. For these samples the temperature program was 1.0 min at 70 °C, then to 120 °C at 2 °C/min, then to 200 °C at 4 °C/min and then to 280 °C at 8 °C/min, and the mass analyzer was scanned from 33 to 300 amu the first 10 min and from 33 to 500 amu the rest of the analysis time.

RESULTS AND DISCUSSION

Extraction into water was found to be a useful method for the isolation of hydroperoxides from hydrocarbons of the jet fuel. Many other oxidation products were also water extractable, and the extracts from the oxidized samples were actually quite complicated mixtures, especially those that were oxidized at high temperature (Sample 3 and Sample 4). On the other hand, the yield of the extraction from the fresh Jet A-1 sample (Sample 2) was so low that individual components could not be identified due to low signal to noise ratio (data not shown). Analysis of Sample 2 thus confirmed that the water extractables of the oxidized Jet fuel samples were essentially oxidation products. The water extraction for Sample 4 differed from the other samples in that considerable amount of insoluble gum was formed when water was added into oxidized mixture.

There may have been decomposition of hydroperoxides in the water extracts due to presence of carboxylic acids that were detected among the oxidation products. Partially because of this possibility, Sample 2, Sample 3 and Sample 4 were immediately re-extracted into diethyl ether. The other reason for the re-extraction was that azeotropic evaporation with water of some extracted components was detected in early experiments. Evaporation of diethyl ether can also be

done rapidly at a low temperature. Removal of the residual moisture by azeotropic distillation with acetone has the same benefits.

The effectiveness of the silylation reagent BSTFA was tested with cumene hydroperoxide (data not shown). MSTFA has been successfully used for trimethylsilylation of cumene hydroperoxide⁴ and the product obtained by using BSTFA was confirmed to be the same by comparing the mass spectra. No side products were detected and the reaction appeared to be complete within an hour.

The trimethylsilyl derivatives of hydroperoxides, or more shortly, peroxytrimethylsilanes seem to usually yield, at best, weak molecular ions by 70 eV EI ionization. Loss of the trimethylsilyloxy radical from molecular ion usually produces abundant $[M - 105]^+$ ion.⁴ Important lower mass fragments often appear at m/z values 89 $[C_3H_9SiO]^+$, 75 $[C_2H_7SiO]^+$, 73 $[C_3H_9Si]^+$, 59 $[C_2H_7Si]^+$ and/or $[CH_3SiO]^+$, and 45 $[CH_3Si]^+$ and/or $[HSiO]^+$. Peak m/z 91 which appears in EI mass spectra of cumylperoxytrimethylsilane and 1-tetralylperoxytrimethylsilane may have contribution from ion $[C_2H_7SiO_2]^+$.

TIC chromatogram of Sample 1 is represented in Figure 1. The most abundant analyte peaks in the chromatogram of Sample 1 correspond silylated products that have the fragmentation characteristics of peroxytrimethylsilanes. Examples of the mass spectra are represented in Figures 2 and 3. In Figure 3 there is also a reference spectrum of 1-tetralylperoxytrimethylsilane obtained by trimethylsilylation of tetralin hydroperoxide in an auto-oxidized tetralin sample. Mass spectrum in Figure 2 (RT 10.93 min) is interpreted to correspond a TMS derivative of an unknown isomer of cymene hydroperoxide. Peak assignments: M^+ at m/z 238, m/z 133 (-105 amu, loss of trimethylsilyloxy radical), m/z 119 ($[CH_3C_6H_4CO]^+$ and/or $[C_3H_9SiOOCH_2]^+$ and/or $[CH_3C_6H_4CHCH_3]^+$), low mass ions as described in the previous paragraph. A TMS derivative of another isomer of cymene hydroperoxide at RT 11.78 min yielded almost identical mass spectrum (not shown). There are other significant analyte peaks in the TIC chromatogram of Sample 1 that are due to products that produce mass spectra consistent with peroxytrimethylsilanes with indan and tetralin ring structures up to molecular weight 264 which corresponds compounds with trimethylindan/dimethyltetralin moieties (data not shown).

Figure 1. TIC chromatogram of Sample 1

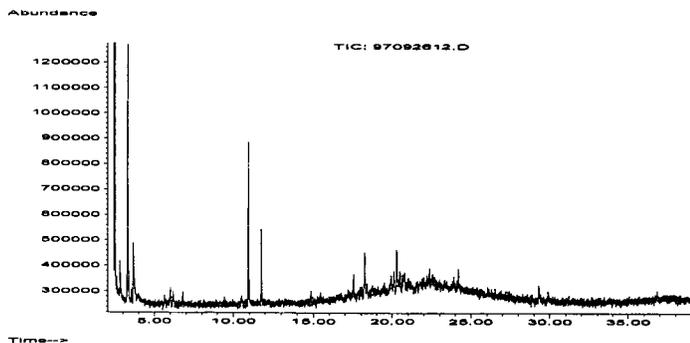


Figure 2. Mass spectrum of a compound (RT 10.93min) tentatively identified as a TMS derivative of an unknown isomer of cymene hydroperoxide.

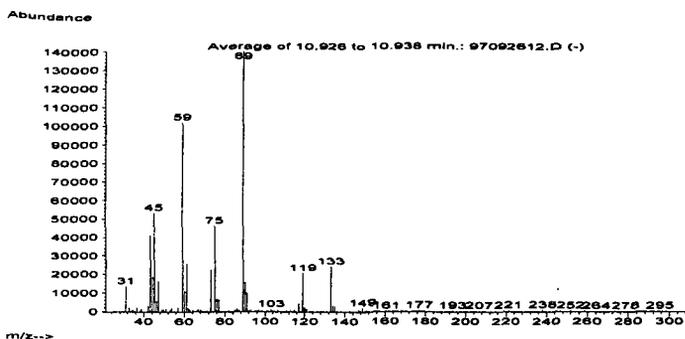
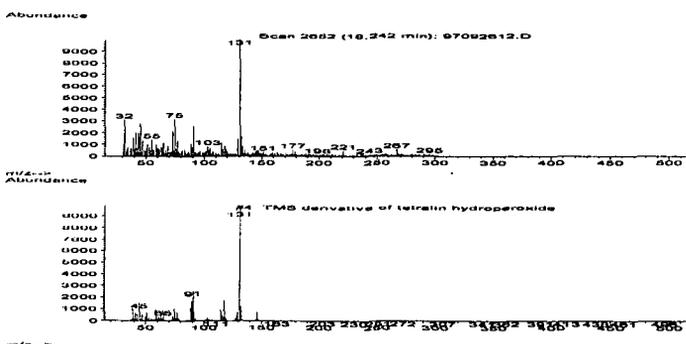


Figure 3. Mass spectra of a compound tentatively identified as tetralin hydroperoxide from Sample 1 and from an auto-oxidized tetralin sample.



TIC chromatogram of Sample 3 is represented in Figure 4. In this sample only one distinct peroxytrimethylsilane peak was detected (Figure 5), and it appeared to be a cymene hydroperoxide derivative. Many types of silylated and nonsilylated oxidation products were found in Sample 3. Among the most abundant peaks were those of TMS ethers of phenols (Figure 6) indicating that phenols are important oxidation products. The phenols are probably formed by decomposition of benzylic alkylbenzene hydroperoxides via hydrolytic mechanism catalyzed by carboxylic acids which were also detected among the oxidation products in Sample 3.

Figure 4. TIC chromatogram of Sample 3.

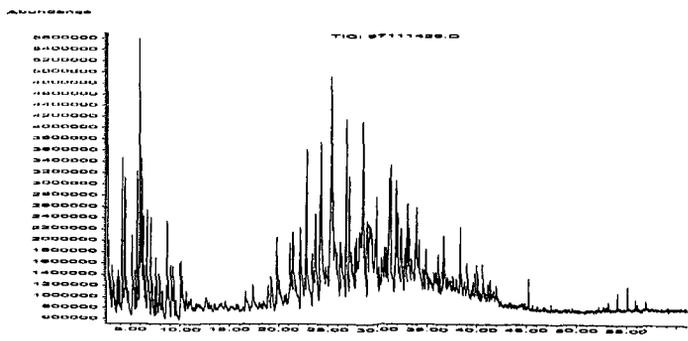


Table 1. Summary of the Experiments.

Samples	Oxidation Conditions	Results
<u>Sample 1:</u> Brussels Jet A-1 Oxidized as such	Two and a half years under air at ambient temperature	Several cymene, tetralin and indan hydroperoxides
<u>Sample 2:</u> Tampere Jet A-1 fresh	Not oxidized	No oxidation products could be identified due to low yield of extraction
<u>Sample 3:</u> Tampere Jet A-1 Oxidized as such	Refluxed 24 h under oxygen atmosphere.	Low on hydroperoxides, various other oxidation products, small amount of insolubles formed
<u>Sample 4:</u> Tampere Jet A-1 water extracted	Oxidized like sample 3	Dark brown product with deposits, oxidation products in the extract similar to as in Sample 3

The water extract of the fresh jet fuel served as the zero sample. The oxidation of the water extracted fuel produced a sample with the characteristics of heavily oxidized fuel, and indicated that separation of water may reduce the antioxidative resistency of Jet A-1 fuel and that presence of water may increase the amount of insolubles formed. The hydroperoxides formed during long-time storing are accumulated since they decompose slowly at low temperatures. In the water extract of the aged sample hydroperoxides were thus the main products. At fuel reflux temperatures the hydroperoxides were no more stable but mostly decomposed producing large variety of secondary products.

Jet fuel samples and oxidation procedures of this investigation are just examples of sample materials where analysis of individual hydroperoxides and other oxidation products could produce useful information about the chemical and tribological condition of the fuel in the molecular level. The four samples described in Table 1 represent examples of different crude oils, different refinery processes and different auto-oxidation conditions (oxidation time and temperature, presence and absence of antioxidant) that may be found in practical applications where determination of individual hydroperoxides would give useful information.

The present work by us is aimed for refinement of the GCMS method for quantitative determination of individual hydroperoxides with the emphasis of elucidation of molecular structures of the isomeric compounds by different spectroscopic techniques as well as characterization of secondary products.

Although all oxidation products cannot be analyzed by the method described, we believe that application of this method can result in better understanding of oxidative degradation and chemical change in long-term storing of middle distillate fuels in general. The method can be routinely applied to monitor of certain key hydroperoxides and other important oxidation products like phenols in the fuels. Effects of fuel additives into oxidation stability of the fuel can be now monitored in molecular level.

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