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Detection and Identification of Sulfur Compounds in an Australian Jet Fuel

Lance C. Kelly¹ and Paul Rawson

Air Vehicles Division
¹Maritime Platform Division
Defence Science and Technology Organisation

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ABSTRACT

Jet fuel contains a wide range of sulfur compounds which may contribute to a number of detrimental fuel characteristics such as corrosion of silver and copper fuel system components, fuel stability and environmental concerns. A range of methods for isolation and identification of sulfur compounds for specific chemical classes of sulfur were examined. Suitable methods were chosen to further elucidate the sulfur compounds in a representative Australian jet fuel. Methods for isolation and characterisation of thiol, sulfide, thiophene and condensed thiophene classes were developed and applied successfully to the jet fuel. The sample examined was found to contain a distribution of sulfides, thiophenes and complex thiophenes. Additionally, no thiols were observed in the jet fuel examined.

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Executive Summary

Jet fuel contains a wide range of sulfur compounds that affect the properties and performance of the fuel in a number of ways, including corrosion of uncoated metals, effects on fuel lubricity, and on both thermal and storage stability properties. All of these properties are ongoing concerns for the ADF. Jet fuel used by the ADF has its sulfur content controlled through specification DEF(AUST) 5240, however, sulfur compounds other than thiols are not controlled by chemical class. A range of methods to isolate, identify and speciate sulfur compounds in fuel were examined and used to elucidate the types of sulfur compounds found in a representative fuel. Methods for isolation of thiols, sulfides, thiophenes and condensed thiophenes were successfully performed. These methodologies are now available for further characterisation of sulfur compounds to assist in ongoing issues of corrosion and stability in ADF jet fuels.

Authors

Lance C. Kelly

Maritime Platforms Division

Lance C Kelly graduated with a Bachelor of Science (Hons.) in Chemistry from Monash University in 1996. He joined Orica in 1997 and completed a Graduate Certificate in Surface Coatings Technology in 1998. As a Senior Research Chemist, his research background includes surface coatings technology, emulsion polymerisation, surfactant synthesis, emulsion explosive development, fuel quality monitoring and product scale-up. He joined DSTO in 2006 in the Fuels & Lubricants group and then moved to the Coatings & Sealants Technology Group in 2007.

Paul Rawson

Air Vehicles Division

Paul Rawson graduated with Degree in Applied Science from the University of South Australia in 1986. He began work at Mobil Port Stanvac Oil refinery in 1987 for two years before joining DSTO's WSD in the propellants group. He joined the AVD Fuels & Lubricants team in 1991. The duties in his current position include research and field problem solving for all aspects of aviation fuel and lubricants for ADF equipment including oil chemical condition monitoring.

Contents

ABBREVIATIONS

1. INTRODUCTION	1
1.1 Aviation fuel and sulfur content	1
1.2 Separation techniques and analysis for sulfur compounds.....	2
1.2.1 Sulfur compounds in petroleum.....	3
1.2.2 Equipment used in sulfur specific detection.....	3
1.2.3 Detection and identification of thiols	4
1.2.4 Detection and identification of sulfides	5
1.2.5 Detection and identification of disulfides	5
1.2.6 Detection of thiophenes and polyaromatic sulfur compounds.....	6
1.3 Project aims.....	6
2. METHOD	8
2.1 Equipment	8
2.1.1 Carbon and sulfur specific GC-AED analysis	8
2.1.2 GC-MS analysis	8
2.2 Oxidation reactions.....	8
2.2.1 Oxidation of thiols by iodine	8
2.2.2 Oxidation of thiols, disulfides and sulfides by hydrogen peroxide	9
2.3 Sulfide extraction	9
2.3.1 Extraction with aqueous sulfuric acid.....	9
2.3.2 Spent Jet A-1 analysis.....	9
2.4 Disulfide analysis with UOP 202-00.....	9
2.5 Thiophene and condensed thiophene extractions	10
3. RESULTS	12
3.1 Thiols in MOBIL Jet A-1	12
3.1.1 Examination of MOBIL Jet A-1 for thiols	12
3.1.1.1 Broad chromatogram examination.....	12
3.1.1.2 Early elution examination	13
3.1.2 Thiol identification	14
3.2 Sulfides in MOBIL Jet A-1.....	14
3.2.1 Examination of Jet A-1 for sulfides.....	14
3.2.2 Sulfide extraction with aqueous sulfuric acid	15
3.2.2.1 Choice of 86% or 91% sulfuric acid.....	18
3.2.3 Sulfide compound analysis using GC-MS	19
3.2.3.1 Identification of sulfur containing peaks by mass spectrum	19
3.2.3.2 Sulfide analysis with chemical ionisation (CI) MS.	20
3.2.4 Sulfide analysis with EI-MS	21

3.3 Thiophenes and condensed thiophenes in MOBIL Jet A-1	23
3.3.1 Assignment of thiophenes identified using HPLC silver Ag-SCX chromatography.....	23
3.3.2 Assignment of thiophenes from sulfuric acid extraction	25
3.3.3 Assignment of thiophenes from isolation by silver loaded column HPLC.....	26
4. CONCLUSIONS.....	27
5. REFERENCES.....	27

Abbreviations

ADF	Australian Defence Force
AED	Atomic Emission Detector
AgNO₃	Silver nitrate
amu	Atomic Mass Unit
ASTM	American Standard Test Method
AVTUR	Aviation Turbine Fuel
CI	Chemical Ionisation
EI	Electron Impact
eV	Electron Volt
FID	Flame Ionisation Detector
FPD	Flame Photometric Detector
FSII	Fuel System Icing Inhibitor
GC	Gas Chromatography
HDS	Hydrodesulfurisation
HPLC	High Performance Liquid Chromatography
i.d.	Internal Diameter
JP	Jet Propellant
KOH	Potassium hydroxide
LEC	Ligand Exchange Chromatography
MS	Mass Spectrometry
ppm	parts per million
PAH	Polycyclic aromatic hydrocarbon
RAAF	Royal Australian Air Force
SCD	Sulfur Chemiluminescence Detector
SCX	Strong Cation Exchange

1. Introduction

1.1 Aviation fuel and sulfur content

Jet A-1 is an aviation fuel used worldwide and is classed as a kerosene type fuel with product specifications stipulated by documents such as DEF(AUST) 5240, ASTM D1655-06b, or Defence Standard 91-913 for reliable performance.^{1,2,3} Chemically, Jet A-1 is a complex hydrocarbon mixture containing hydrocarbons in the distillation boiling range of nonane to hexadecane with a maximum final boiling point of 300°C.⁴ Jet A-1 that is doped with special performance enhancing additives is known as Aviation Turbine Fuel, (AVTUR)/FSII (also known as JP-8 and within NATO as F-34) and is required by many military aircraft as well as being the fuel used by the Royal Australian Air Force (RAAF).

Like all hydrocarbon-based fuels, jet fuel consists of low concentrations, normally less than 1% by mass, of organic molecules that contain nitrogen, oxygen or sulfur atoms. Sulfur compounds in fuel can contribute to a range of quality, performance, stability and environmental issues which are of concern to fuel users. During the combustion process sulfur compounds are either oxidised to sulfur oxides or converted to particulates containing polycyclic heteroaromatic compounds. Through further atmospheric chemistry sulfur oxides convert to acid rain, while polycyclic heteroaromatic compounds are a potential health risk due to their respiratory harm and carcinogenic properties.⁵

Sulfur concentrations in most mobility fuel, such as automotive diesel, is controlled to low concentrations to reduce the amount of acid rain and sulfur particulate pollutants in the air. Australia has set sulfur limits to 50 ppm from 2006 for diesel (from the previous 500 ppm maximum) and then to 10 ppm from 2009⁶, while for premium unleaded petrol a 50 ppm limit was to be achieved by 2008.⁷

Sulfur compounds, such as mercaptan sulfides (thiols), may also give a strong offensive or sour odour to fuel. Sulfur compounds in fuel may also cause corrosion of some components of fuel systems such as elastomers and components that contain silver or copper metal. Even cadmium coated fasteners in aircraft fuel tanks may potentially suffer from the effects of sulfur corrosion. The total sulfur content of RAAF AVTUR/FSII procured against the DEF (AUST) 5240 specification is currently stipulated at less than 3000 ppm with a 30 ppm limit on thiols. No date has been set for the reduction of sulfur in Jet A-1 or AVTUR/FSII but it is likely that aviation fuels will be the next type of fuel to have tighter regulations on the amount and possibly on specific types of sulfur compounds present.

A range of processes are available to refiners to reduce sulfur levels or to specifically reduce mercaptan sulfur levels. Mercaptan removal processes are often called sweetening processes and converts sulfide into non-corrosive disulfides through processes such as mercaptan oxidation (MEROX).

The most often used process for removal of sulfur compounds is hydrodesulfurisation (HDS).⁸ HDS is a process that uses hydrogen with a transition metal catalyst to convert organic sulfur compounds into hydrogen sulfide that is then removed from fuel. In the HDS process not all

sulfur compounds are removed equally. Thiols, sulfides, and simple thiophenes are easier to remove with the HDS process than benzothiophenes, dibenzothiophenes and condensed thiophenes due to the aromatic components protecting the sulfur atom. The type of molecules removed also depends on the refinery, the type of catalyst and the reaction time. To obtain levels of sulfur down to 50 ppm or lower requires a process known as Deep HDS. Other treatment processes to reduce sulfur levels in fuel are also available to remove some of the heteroatoms that are difficult to remove by the hydrotreatment process. These processes include biotreatment and adsorption techniques.

Due to sulfur not being fully removed during HDS, the remaining sulfur compounds must be considered in the behaviour of fuel. Apart from a source of chemical energy, fuels used in aircraft also act as a heat sink by transferring heat from the avionics. Fuel subjected to high temperatures can allow dissolved oxygen to accelerate the formation of gums and other deposits in the fuel that can accumulate in fuel tanks which may lead to poor performance. Determining the types of sulfur compounds present in the fuel by chemical analysis may assist with an understanding of the interaction of sulfur compounds in the gum forming thermal degradation process and how these compounds influence fuel properties and performance.

The chemical composition of fuels, the concentrations and type of sulfur compounds have been studied. Some sulfur compounds were found to inhibit the oxidation of hydrocarbons by reacting with hydroperoxides but the inhibition efficiency depends on the compound structure and reactivity.⁹ JP-5 (a fuel with a higher flashpoint than JP-8) doped with sulfur compounds showed thiols were the best at controlling peroxidation, but disulfides and phenyl disulfide were ineffective in controlling peroxidation.¹⁰

The effect of sulfur compounds on deposit and gum formation has also been studied. Early studies showed that the addition of various thiols, sulfides, disulfides and condensed thiophenes at 1000 ppm sulfur added to sulfur free hydrocarbon fuel increased the rate of deposits in fuel tanks by a factor of twenty. Sulfur compounds such as dibenzothiophene or diphenyl sulfide had no effect on deposit formation.¹¹ Hydrotreated Jet A-1 (<10 ppm sulfur) with added mercaptan, sulfide or disulfide compounds were shown to inhibit fuel oxidation but increased fuel deposits.¹²

Methods exist for measuring total sulfur and thiol/mercaptan compounds in jet fuel. None exist for rapid discrimination of sulfur species. Jet fuels (JP-8), sourced from refineries in the USA, have been previously examined for the types of sulfur compounds present.¹³ JP-8 was found to contain mostly thiols, sulfides and disulfides. For the higher boiling point materials, benzothiophenes were the main fraction. The results obtained did not give specific types of thiols, sulfides or disulfides but only compounds identified by retention time matching of compounds using gas chromatography. As jet fuels from around the world vary greatly due to petroleum source and refining processes, these results may be useful but may not contain all the information required about the sulfur compounds in aviation fuels in regions outside the USA.

1.2 Separation techniques and analysis for sulfur compounds

To determine the composition of sulfur compounds in AVTUR appropriate methods must be selected. The chemistry of each sulfur compound class is different and therefore requires

different separation techniques to isolate them from the hydrocarbon fuel matrix. Methods for isolating specific compound types are available and a range of them were examined to determine the most appropriate to assist in characterisation of sulfur in Australian jet fuel as used by the RAAF.

1.2.1 Sulfur compounds in petroleum

The main classes of sulfur compounds that are present in fuel have been described by the broad classification of thiols (mercaptans), sulfides, disulfides, thiophenes, benzothiophenes and dibenzothiophenes. Each type of sulfur compound found in fuels is shown in Table 1.

1.2.2 Equipment used in sulfur specific detection

Many papers have been published on the isolation or extraction, then identification of sulfur compounds from hydrocarbon distillates. No single method has been developed for the simultaneous extraction and analysis of all sulfur compounds from fuels.

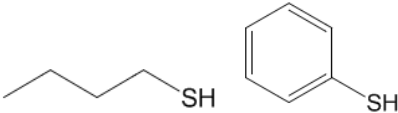
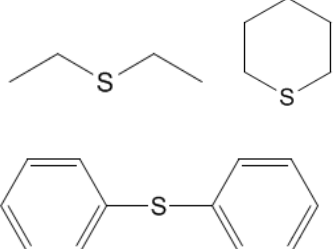
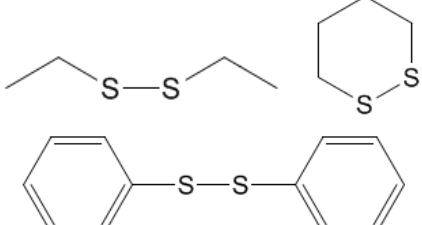

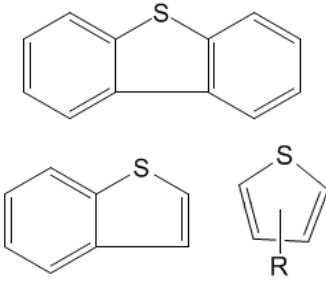
Gas chromatography-mass spectrometry (GC-MS) is the ultimate tool that is used to identify unknown compounds. However, in a fuel complex, the hydrocarbon matrix and fragmentation pattern of the hydrocarbon carbon compounds will interfere with those of the sulfur compounds of interest due to the hydrocarbon content being several orders of magnitude greater than and similar chemical structures to the sulfur compounds.¹⁴

To distinguish the sulfur containing compounds with petroleum products, several types of sulfur detecting equipment exists for GC such as the Flame Photometric Detector (FPD), the Atomic Emission Detector (AED) and the Sulfur Chemiluminescence Detector (SCD).

The use of an SCD coupled with high performance liquid chromatography (HPLC) has been successful in identifying various sulfur containing compounds and thiophenes in hydrotreated gas oil whilst FPD exhibits interferences from hydrocarbons.^{15, 16}

Gas Chromatography-Atomic Emission Detector (GC-AED) is an excellent tool for sulfur compound characterisation as it can be sensitive to low amounts of sulfur, is element specific without hydrocarbon compound interferences and multi-element analysis can be run simultaneously. This makes it suitable for analysis of petroleum products. The GC-AED has been used for the study of sulfur compounds in both gasoline and diesel,¹⁷ the study of sulfur heterocycles in Egyptian crude and the analysis of jet fuels and JP-8.^{18,13,19} One method of sulfur analysis requires the fuel sample run through a gas chromatograph (GC) attached to a sulfur selective detector such as FPD or AED.²⁰ The resulting peaks are then matched against the retention times of a library of known sulfur standards. This method requires hundreds of sulfur compound standards for comparison and the user needs to know in advance what type of sulfur compounds will be present in the distillate. Matching retention times to a standard is not an absolute guarantee the compound is structurally similar. A more thorough approach to identifying sulfur compounds in hydrotreated fuel is to analyse samples with a sulfur selective GC-AED and GC-MS operating with identical conditions with or without any an enrichment process.²¹

Table 1: Sulfur compound classes found in petroleum products

Sulfur compound	General structure	Structural examples
Thiols	R-SH	
Sulfides	R-S-R	
Disulfides	R-S-S-R	
Simple and condensed thiophenes		

Note: R denotes any alkyl or aryl group

1.2.3 Detection and identification of thiols

Extraction and identification of thiols from hydrocarbons has been conducted in many ways. Total thiol concentration can be quantified by the use of titration methods, such as ethanolic sodium acetate potentiometrically titrated with silver nitrate.²² This method yields the total amount of thiols but no structural information of thiols present. It is used by petroleum refineries to determine the final amount of thiols in their products.

Another method of determining the presence of thiols in a fuel is the oxidation of thiols with iodine to form disulfides as shown in Equation 1:¹⁴

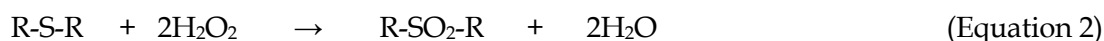


The removal of thiols is then detected by comparison of sulfur specific GC-AED chromatograms of the hydrocarbon matrix before and after oxidation with iodine. Iodine does not react with sulfides or thiophenes under these conditions.

Selective thiol extractions has been completed using aqueous ethanolic sodium hydroxide solutions to extract thiols from hydrocarbon mixtures, back extracted with isopentane and removal of ethanol to yield thiols.⁹ Selective extraction of thiols was also reported by the extraction of naphtha with MDS-KOH-H₂O (under nitrogen) in a naphtha to extractant ratio of 1:1.3. The thiols obtained were then characterised by GC-MS compared against thiol reference compounds.²³ Thiols can also be extracted by selective chemical reaction. The formation of hydrocarbon insoluble mercaptides by reaction with mercury or silver salts has been reported.⁹ The thiols are then obtained by acidic hydrolysis of these complexes. Thiols have also been derivatised with pentafluorobenzoyl chloride to form thiol esters (sulfides and thiophenes are unreactive) and identified by GC-MS fragmentation patterns after separation by solid phase extraction.²⁴

1.2.4 Detection and identification of sulfides

Determination of sulfides in hydrocarbons by oxidation via hydrogen peroxide has been reported.¹⁴ The sulfides were oxidised to sulfones as shown in Equation 2.



The absence of sulfides is detected in a sulfur specific GC-AED. The sulfide peaks there are then identified by comparison against a set of sulfur compounds by retention time matching in a GC.

Sulfides have been reported to be selectively extracted from hydrocarbon mixtures. Diluted sulfuric acid dissolves the sulfides without extracting other sulfur compounds or hydrocarbons.⁹ This process was utilised by refineries in Russia. Best results were achieved with a two stage extraction, 86% aqueous sulfuric acid used first, then 91% aqueous sulfuric acid. The optimal hydrocarbon ratio to dilute sulfuric ratio ranges from 5:1 to 10:1. Two stage systems are used as the 86% aqueous sulfuric acid extracts out aliphatic and cyclic sulfides that decompose in stronger acid solutions whereas 91% aqueous acid extracts the aromatic sulfides. The use of aqueous sulfuric acid solutions of 80 to 90% strength to extract sulfides has also been reported for Chinese gasoline and Chinese naphthas.^{25, 26} In all cases the sulfides were obtained by diluting the sulfuric acid and back extraction with an organic solvent to extract out the sulfides. The sulfides were then identified by GC-MS.

Separation of low molecular weight sulfides from mixtures of organic compounds have been reported using a zinc chloride stationary phase.²⁷ The separation of all sulfides in aromatic hydrocarbons has been also reported to be achieved by the use liquid chromatography on a copper loaded carboxylic exchange resin.²⁸ The collected sulfides were obtained by washing the column with a 90% pentane and 10% ethyl ether solution without loss of any sulfides.

1.2.5 Detection and identification of disulfides

Disulfides are products usually formed by oxidation of thiols during the sweetening process of fuels.²⁹ Determination is based on reducing the disulfide to the thiol by zinc, or lithium borohydride. The amount of disulfides present in a fuel sample can be measured by the tests described in standard UOP202-00.³⁰

1.2.6 Detection of thiophenes and polyaromatic sulfur compounds

The separation of the benzothiophenes, dibenzothiophene and other polyaromatic sulfur compounds from hydrocarbons has been documented. The use of ligand exchange chromatography (LEC) has been the most successful in this area. The first work used silica gel covered with 20% silver nitrate to separate sulfur compounds from mono or di-aromatics.³¹ 5% silver nitrate on 200 mesh silica was used to separate thiophenic compounds that were identified by GC-AED and compound retention time matching.³² Silver nitrate on Kieselgel 60G has been used to extract out the polyaromatic sulphur compounds from Egyptian crude and identified with AED.¹⁸ Greater success was found with the use of LEC utilising 5% palladium(II) chloride on silica gel activated at 200°C, with aromatic fractions of coal and petroleum, it resulted in extraction of polyaromatic sulfur compounds having two to six aromatic rings.³³ These fractions were then analysed by GC-MS and compared to standards for identification. Problems with this method were that the benzothiophenes eluted with polycyclic aromatic hydrocarbons (PAHs) and some compounds showed low recoveries. Later LEC methods have become more selective by using silica gel immobilised with 2-amino-1-cyclopentene-1-dithiocarboxylic acid (ACDA) that was packed into columns with hexane as the mobile phase.³⁴ The silica gel ion exchange is made attaching ADCA to amino functionalised silica,³⁵ the ADCA is made by the literature method.³⁶ Complexed with palladium(II) chloride or silver(I) cations to form the Pd-ACDA or Ag ACDA complexes, the palladium complex showed better retention recoveries. The use of Pd-ACDA in separating PASH from polycyclic aromatic hydrocarbons (PAH) in the aromatic fraction of gasolines and heavy distillates was demonstrated.³⁷ The use of ionic liquids (IL) has also been investigated and it was shown the selective extraction of dibenzothiophenes from alkanes occurred but encountered difficulties using diesel in this process.³⁸

1.3 Project aims

The AVTUR/FSII delivered to the RAAF may be sourced from a number of Australian and south-east Asian refineries that have different fuel finishing processes and methods for sweetening or desulfurising the fuel. Figure 1 shows the difference in distribution of sulfur compounds in three fuels used by the ADF, note the almost complete removal of sulfur from the hydrotreated AVCAT sample.

The aim of this project is to establish a range of isolation and characterising methodologies to determine what classes of sulfur compounds and their structures are in AVTUR/FSII sourced to RAAF. The database of sulfur compounds discovered can then enable comparison to sulfur species that remain in deep hydrodesulfurised or alternate desulfurisation processed AVTUR/FSII fuels of the future. This work will provide guidance to which sulfur molecules influence corrosion, fuel lubricity, storage and thermal stability or other fuel performance properties. The feasibility of the methods chosen will be used on MOBIL Jet A-1 fuel.

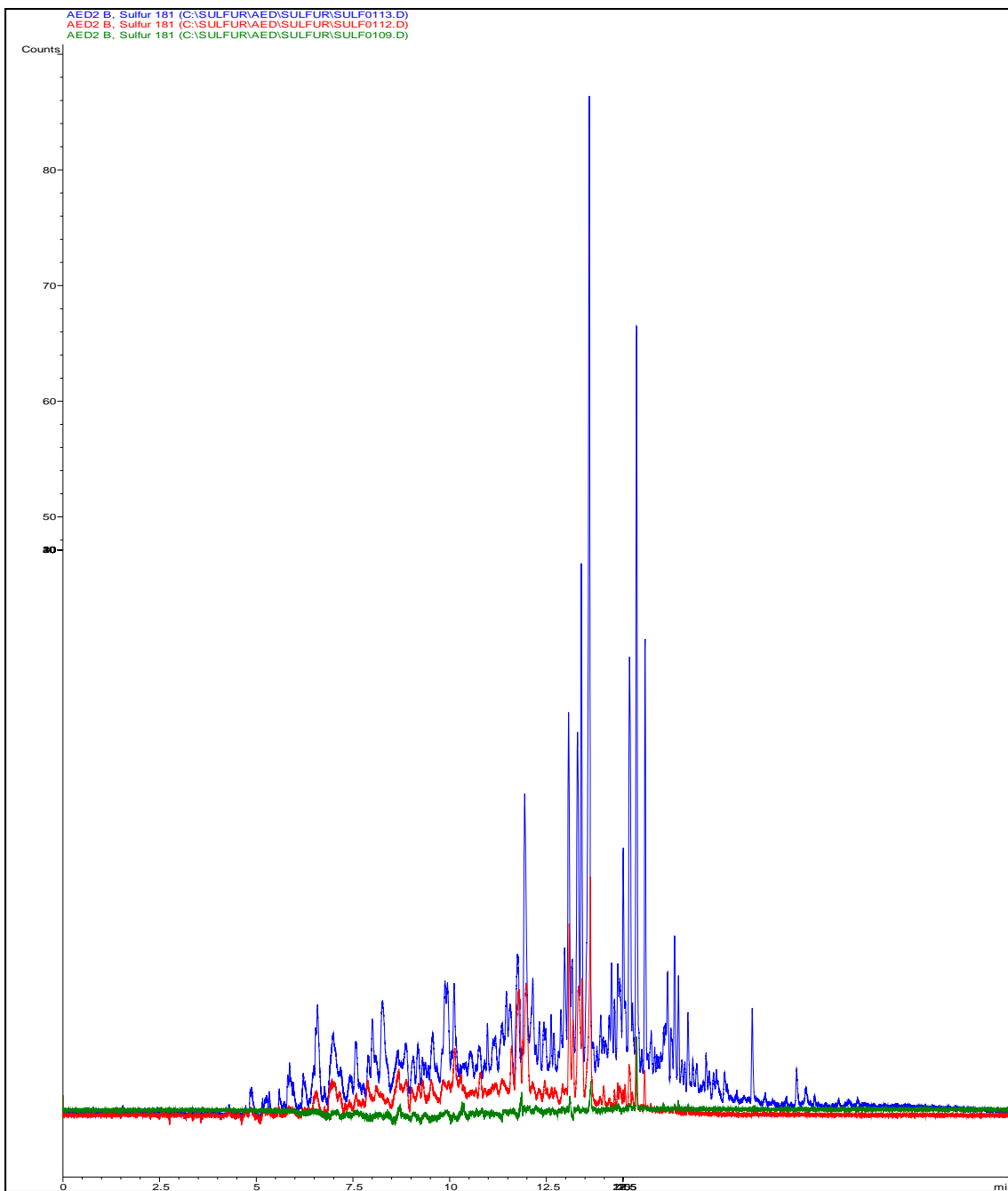


Figure 1: Sulfur compound distribution from three RAAF fuels using GC-AED sulfur S181 nm channel (Blue = RAAF Pearce, Red = RAAF Amberley, Green = AVCAT)

2. Method

2.1 Equipment

2.1.1 Carbon and sulfur specific GC-AED analysis

Gas Chromatography-Atomic Emission Detector (GC-AED) of samples was conducted with an Agilent Technologies 6890N Network GC System equipped with a 7683 Series Autosampler and coupled to a JAS G2350A Atomic Emission Detector. The AED was configured to monitor emission lines carbon 179 nm and sulfur 181 nm. Following the method of Quimby *et al.*¹⁷, carrier gas was helium (Ultra High Purity, BOC), reagent gases hydrogen (Linde) at 45 psi, oxygen (Linde) at 55 psi, make-up gas set at 100 ml/min. The GC-AED system was fitted with Agilent Technologies BD-5 SMS-1 column, 30 m x 0.32 mm i.d. x 0.25 μ m. Conditions used were: injection volume 2 μ L, injection temperature 40°C, injection split ratio 1:50, ramp rate 2°C/min to 300°C, constant flow 1.2 ml/min, pressure 13.6 psi. Cavity temperature 280°C and transfer line 280°C.

2.1.2 GC-MS analysis

GC-MS analyses were performed on a Varian Saturn 2000R 3800 Gas Chromatogram connected to a Varian 2000R Mass Spectrum. 1 μ L samples were injected onto a Varian CP-WAX 52 CB (50 m x 0.32 mm i.d., DF=0.4 μ m), held at 50°C for five minutes, then programmed at 10°C/min to 230°C and then held for 20 min at 230°C. Helium flow rate 1.2 ml/min, linear velocity 33 cm/s, total flow 22 ml/min, split ratio 100:1. m/z range from 40 to 600, 70 eV ionising voltage for electron impact (EI). Chemical ionisation (CI) impact was conducted with the same conditions except the Varian 2000R Mass Spectrometer was switched to CI mode using a methanol as the reagent gas.

2.2 Oxidation reactions

2.2.1 Oxidation of thiols by iodine

The method of Stumpf *et al.* was used.¹⁴ To 3 ml of Jet A-1 was added 3 ml of iodine solution (made by dissolving 0.64 g of iodine (Aldrich) in 16 ml of acetone (HPLC Grade, B&J)). The mixture was then shaken for 10 min at room temperature followed by the addition of 2 ml of a basic sodium thiosulfate solution (made by 2.51 g of Na₂S₂O₃·5H₂O (M&B) dissolved in 20 ml of 0.05 M NaOH). The phases were separated and the yellow aqueous phase removed. The Jet A-1 layer was washed four times with 4 ml of distilled water, each time the water phase was removed. Comparison of Jet A-1 and the sample that reacted with iodine was then conducted to observe peak loss in GC-AED on the sulfur 181 nm wavelength.

2.2.2 Oxidation of thiols, disulfides and sulfides by hydrogen peroxide

Following the method of Stumpf *et al.*¹⁴, to 6 ml of Jet A-1 was added 6 ml of hydrogen peroxide solution, followed by 2 ml of acetic acid and 2 ml acetone (HPLC Grade, B&J). The mixture was then warmed for 60 min at 60°C with shaking every 5 min. The phases were separated and the fuel layer washed four times with 4 ml of distilled water, each time the water phase was removed. Comparison of Jet A-1 and the sample that reacted with iodine was then conducted to observe peak loss in GC-AED on the sulfur selective 181 nm wavelength.

2.3 Sulfide extraction

2.3.1 Extraction with aqueous sulfuric acid

120 ml of Jet A-1 fuel was added to a separating funnel and shaken thoroughly for 5 min with 30 ml of 86% aqueous sulfuric acid cooled to 10°C. The phases were allowed to separate over 10 min and the bottom orange sulfuric acid fraction collected. This extraction process was repeated twice more (the acid washed Jet A-1 fuel was set aside for further work) and the three sulfuric acid extractions were then combined. This was then slowly added to 60 ml of chilled distilled water in a 500 ml flask. This produced a hazy 42% aqueous sulfuric acid solution. The above process was then repeated using the acid washed Jet A-1 with 91% aqueous sulfuric acid cooled to 10°C but to yield a 45% aqueous sulfuric acid solution on dilution.

The 45 and 42 % aqueous sulfuric acid solutions obtained were then combined and placed in a separating funnel with an equal volume of isopentane and shaken for five minutes. The isopentane fraction was then collected and the process repeated with fresh isopentane. The two isopentane fractions were combined. The isopentane was then removed at 35°C to yield approximately 1 ml of a purple liquid containing the sulfides.

2.3.2 Spent Jet A-1 analysis

Jet A-1 fuel washed with aqueous sulfuric acid was placed in a separating funnel and washed with an equal volume of distilled water four times to remove acid residues. Samples were then injected with the same method as Section 2.1.2 into carbon specific 179 nm GC-AED to examine any hydrocarbon loss from the Jet A-1.

2.4 Disulfide analysis with UOP 202-00

Jet fuel will not normally contain disulfides.³² They are normally found only in fuel that has undergone a specific sulfur oxidation sweetening processing. The fuel examined in this report had not undergone such oxidation processing and thus was not examined for disulfide content. A Universal Oil Products (UOP) method for determining total concentration of disulfides was examined to determine its potential for disulfide analysis in jet fuel.³⁰

The method required determination of total mercaptan sulfur concentration then reducing the disulfides to mercaptans using an acid reflux procedure. The mercaptan sulfur concentration is remeasured and the disulfide content determined by subtraction of the original mercaptan concentration from the post reduction concentration. The specific disulfide compounds are not determined using this method. The UOP method is also for determining the disulfide content of

gasoline, liquefied petroleum gas and other light petroleum distillates, it does not state it is possible to determine the disulfide content of middle distillates.

2.5 Thiophene and condensed thiophene extractions

To examine the simple and condensed thiophene content and compound distribution in the fuel a technique based on adsorption liquid chromatography was used. The fuel was first fractionated into three fractions containing saturates, monoaromatics and di/polycyclics. These three fractions were further fractionated on a silver loaded column by a mechanism of charge transfer with the sulfur compounds for further identification of sulfur compounds. The subsequent fractions were examined by both GC-MS and GC-AED techniques.

The first series of fractionation on the fuel was done by HPLC using a matrix simplification technique to enhance detection and characterisation of the sulfur compounds.³⁹ The samples fractionation times were generated using a 1/100 sample dilution and a 1/20 sample dilution was then fractionated ten times and each fraction collected, combined and concentrated before subsequent analysis and silver loaded column fractionation (Figure 2). HPLC set up: Column:- CN spherisorb 5 μ m 250 x 4.6 mm, solvent: n-heptane, flow: 1 ml/min, detector UV 210 nm.

To examine the success of the initial broad fractionation of the fuel into the three broad classifications of saturates, mono aromatics and di/polycyclics, the fractions were examined for hydrocarbon and sulfur compound distributions by GC-AED.

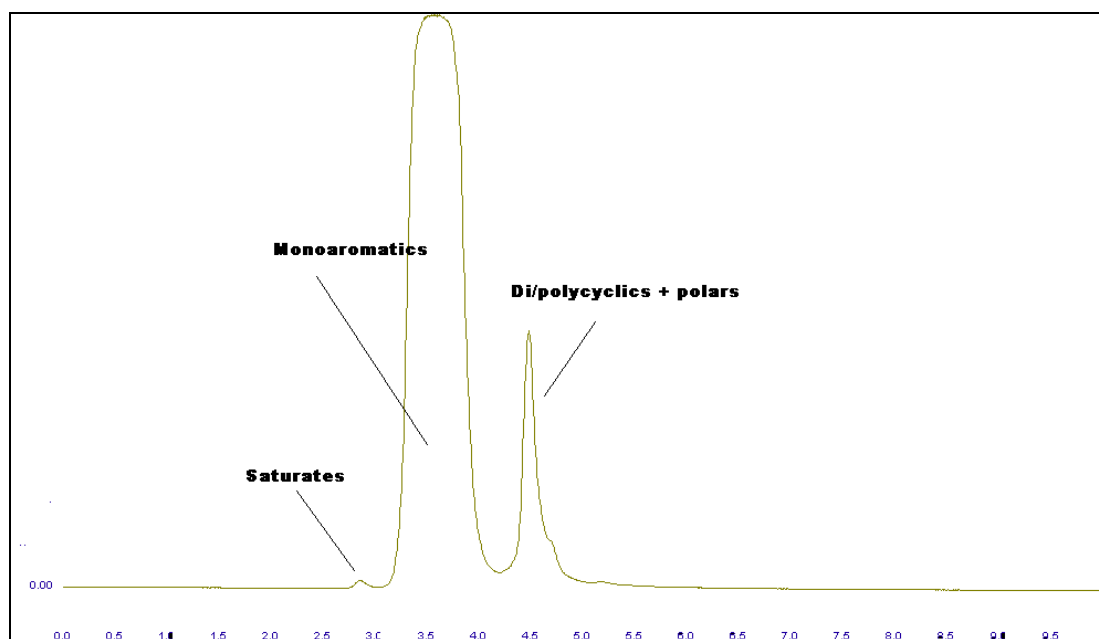


Figure 2: Fuel fractionation into three components by HPLC to obtain the polycyclic fraction

Sulfur compounds coordinate strongly with a range of metal salts. A method immobilising silver onto a strong cation exchange (SCX) column was developed forming a ligand exchange system capable of selective retention of sulfur compounds simplifying the sample matrix enabling identification of specific sulfur compounds and compound types in prefractionated fuel samples.³² A spherisorb 5 μm strong cation exchange column 250 x 4.6 mm (propylbenzenesulfonyl- hydrogen form) was loaded with silver by the following method. One ml of 20% AgNO_3 in water was prepared, the column then loaded with 15 x 50 μl injections of the AgNO_3 and flushed with water for 1 hour. The column was then washed with 60 ml of methanol and 60 ml of dichloromethane at a flow rate of 1.0 ml/min.⁴⁰ Standards were used to develop fraction cut times to isolate simple and condensed thiophenic compounds.

3. Results

3.1 Thiols in MOBIL Jet A-1

3.1.1 Examination of MOBIL Jet A-1 for thiols

3.1.1.1 Broad chromatogram examination

Analysis of peak shifts in sulfur 181 nm selective GC-AED chromatograms of MOBIL Jet A-1 before and after reaction with elemental iodine can discern if thiols are present due to the chemical conversion of thiols to disulfides. Examination of the chromatograms before and after reaction with iodine shows near identical chromatograms (Figure 3). Therefore the majority of the sulfur compounds present in Jet A-1 are not thiols. This is as expected due to the control of maximum concentration of thiols in fuel via the DEF (AUST) 5240 specification.

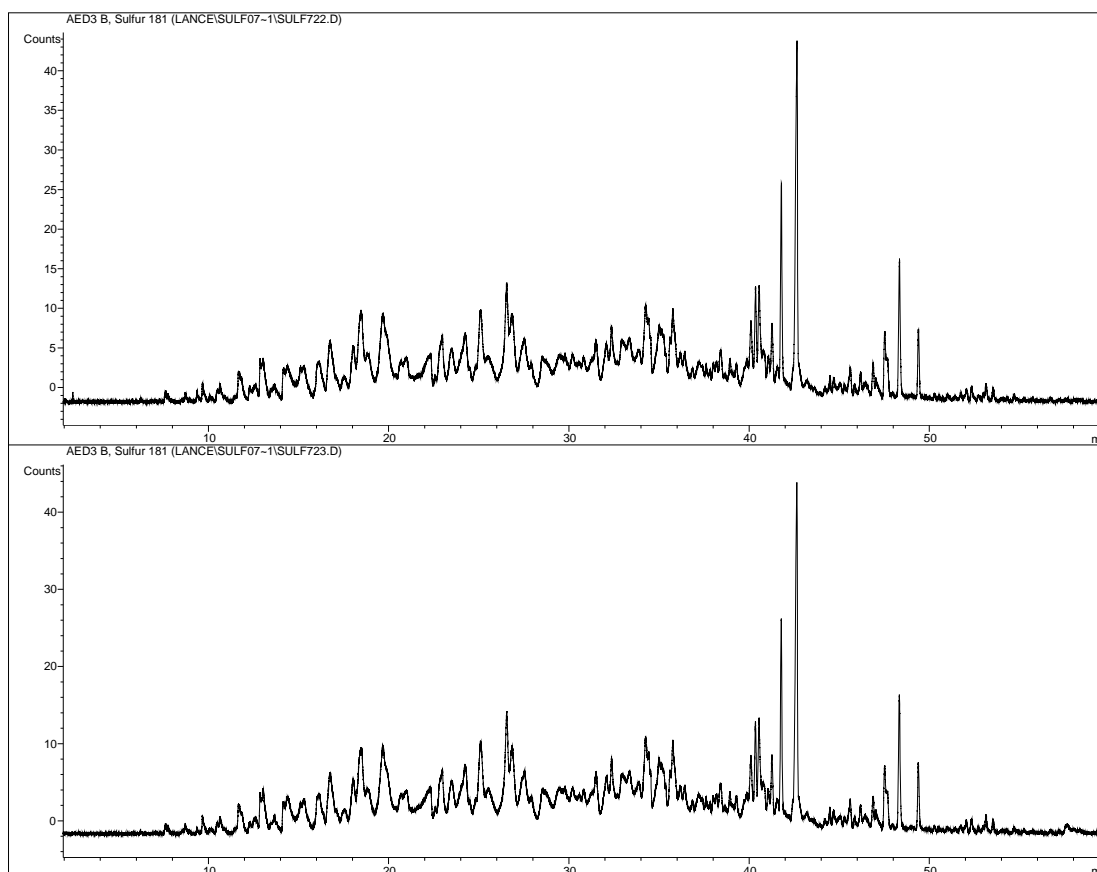


Figure 3: Sulfur 181 nm selective GC-AED chromatograms of Jet A-1 (top) and after oxidation with iodine (bottom)

3.1.1.2 Early elution examination

Closer analysis of the GC-AED chromatogram shows that in the early elution period three thiols are initially present in MOBIL Jet A-1. They are subsequently removed by oxidation with iodine as shown in Figure 4. As these compounds eluted in the early part of the chromatogram, this indicates they are low molecular weight thiols as the BD-5 column used in the chromatography relies on the differences in boiling point for compound separation.

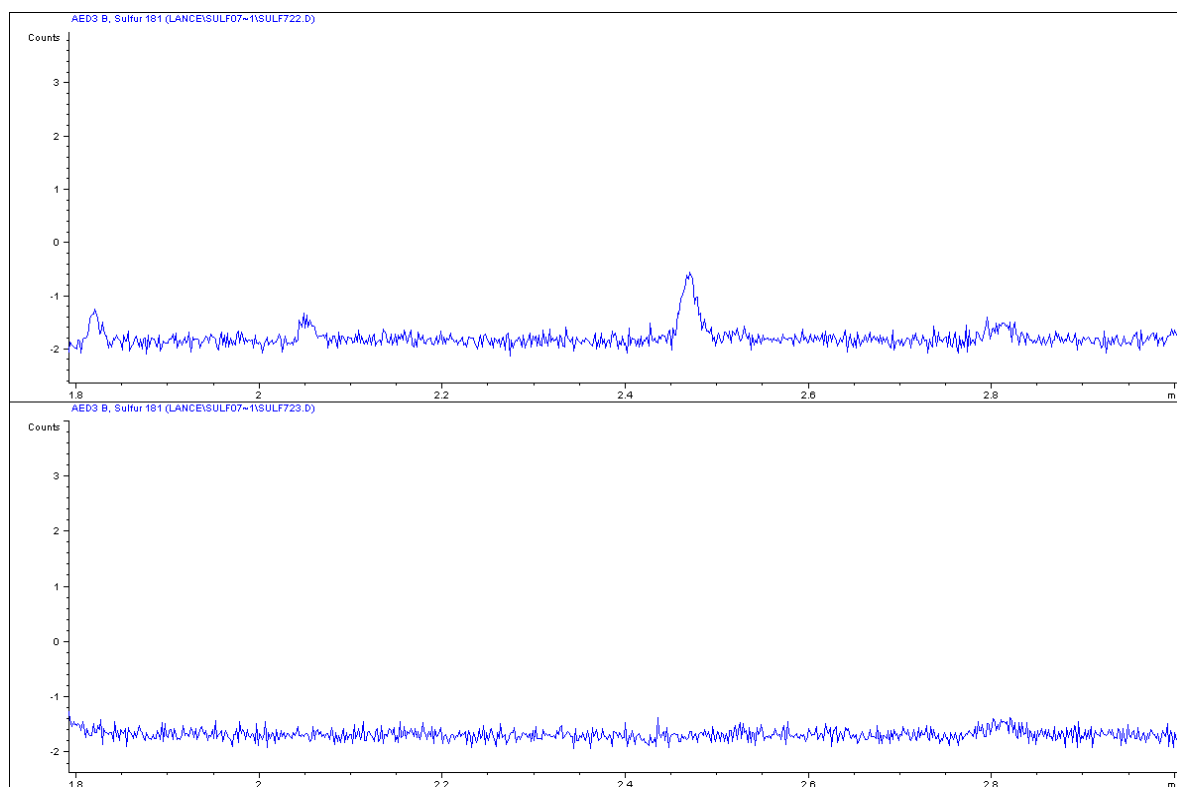


Figure 4: Sulfur 181 nm selective GC-AED chromatograms of MOBIL Jet A-1 (top) and after oxidation with iodine (bottom) in retention time 1.8 to 3.0 min to reveal thiols

As thiols are oxidised to disulfides, these disulfides formed must be present in the chromatogram. Analysis of the chromatograms (Figure 5) reveals the formation of a new peak at a retention time of 57.6 min that may be a disulfide formed by the oxidation of a thiol.

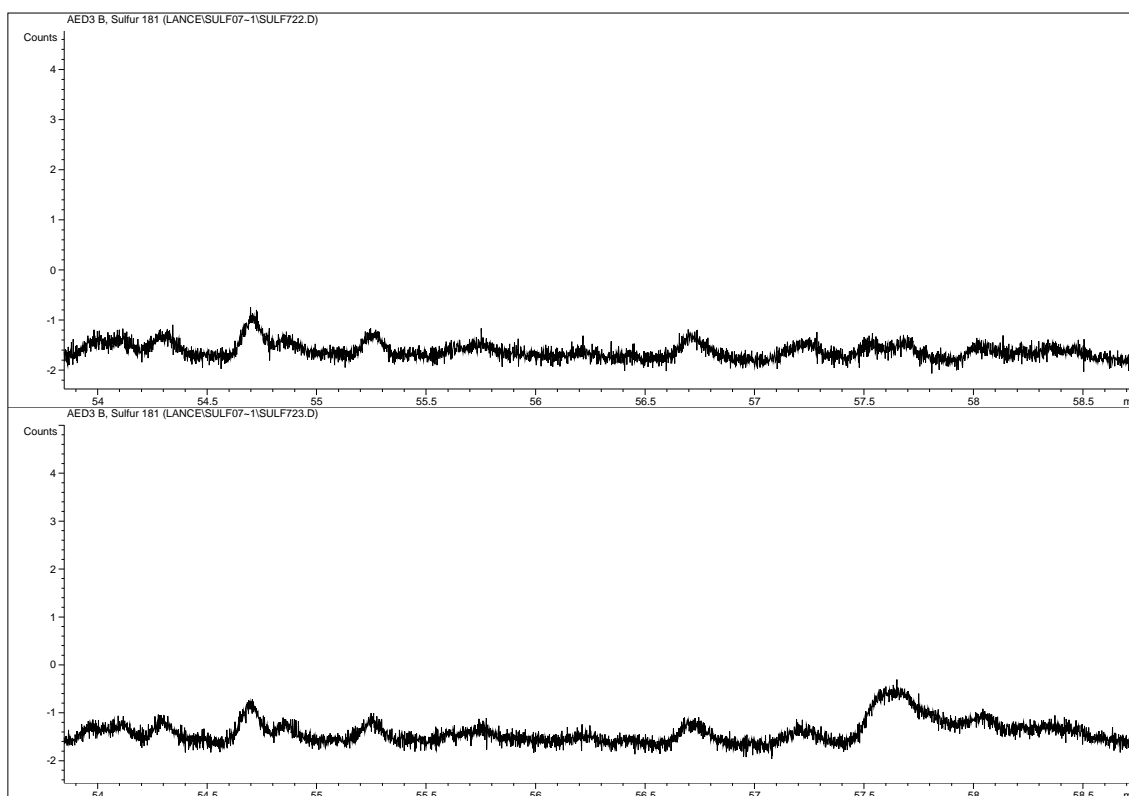


Figure 5: Sulfur 181 nm selective GC-AED chromatograms of MOBIL Jet A-1 (top) and after oxidation with iodine (bottom) showing the formation of a new peak at 57.6 min, a possible disulfide

3.1.2 Thiol identification

The identities of the three thiols found can't be elucidated as their signals are swamped in a GC-MS by hydrocarbon molecules in Jet A-1. Identification would require retention time matching with a series of known thiols and then comparing a 181 nm sulfur specific spectrum, or extraction of the thiols from the Jet A-1 fuel with caustic ethanolic solution.

The findings are that MOBIL Jet A-1 does contain thiols but the amounts are minor. This is in agreement with the manufacturers claim that Jet A-1 has less than 30 ppm in the form of thiols.⁴ The thiols observed had very short retention times when examined by the GC method, this indicated that they are volatile molecules and if future isolation and analysis is required care must be taken to ensure volatiles are not lost from the sample during the isolation and concentration procedure.

3.2 Sulfides in MOBIL Jet A-1

3.2.1 Examination of Jet A-1 for sulfides

Existence of sulfides in MOBIL Jet A-1 can be examined by the analysis of the peaks in sulfur 181 nm selective chromatograms from the GC-AED of MOBIL Jet A-1 before and after reaction with hydrogen peroxide (with an acid catalyst). Examination of the chromatograms (Figure 6) shows a large number of peaks have disappeared in the first half of the elution. This information from the oxidation reaction proves many of the sulfur compounds in Jet A-1 are sulfides. New peaks are

formed that have retention times of 50 min or greater and are the sulphones produced by the oxidation of sulfides to sulfones by hydrogen peroxide. The oxidation of Jet A-1 with hydrogen peroxide has also left many peaks unaltered. These compounds are believed to be simple and condensed thiophenes that are unreactive to oxidation by hydrogen peroxide. Subsequent analysis for condensed thiophenes determined the remaining sulfur compounds post oxidation with the peroxide were substituted benzothiophenes and alkyl thiophenes (Figure 6 and 7, bottom chromatograms).

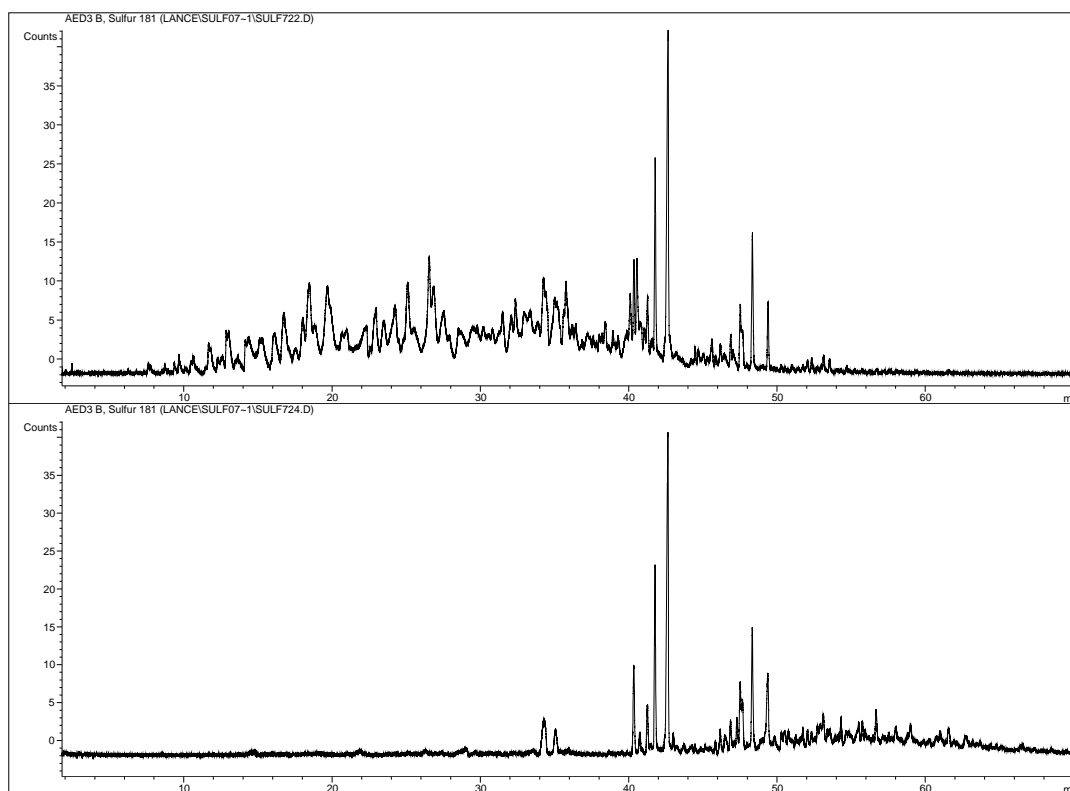


Figure 6: Sulfur 181 nm selective GC-AED chromatograms of MOBIL Jet A-1 (top) and after oxidation with hydrogen peroxide (bottom) showing the loss of sulfides and the formation of sulfones

3.2.2 Sulfide extraction with aqueous sulfuric acid

MOBIL Jet A-1 was washed with 86% aqueous sulfuric acid, followed by washing with 91% sulfuric acid. After extracting the sulfuric acid with pentane to re-extract the sulfides, the sulfur 181 nm chromatograms of MOBIL Jet A-1 before and after washing with sulfuric acid are shown in Figure 7. The chromatograms show the use of aqueous sulfuric acid is an excellent method for the selective removal of sulfides from hydrocarbons such as Jet A-1, as shown by the similarities in peak losses between the chromatograms of MOBIL Jet A-1 oxidised with hydrogen peroxide and that washed with sulfuric acid. In contrast to the reaction with hydrogen peroxide, the use of aqueous sulfuric acid does not leave behind oxidation products like sulfones that remain in the Jet A-1 that elute later in chromatographs.

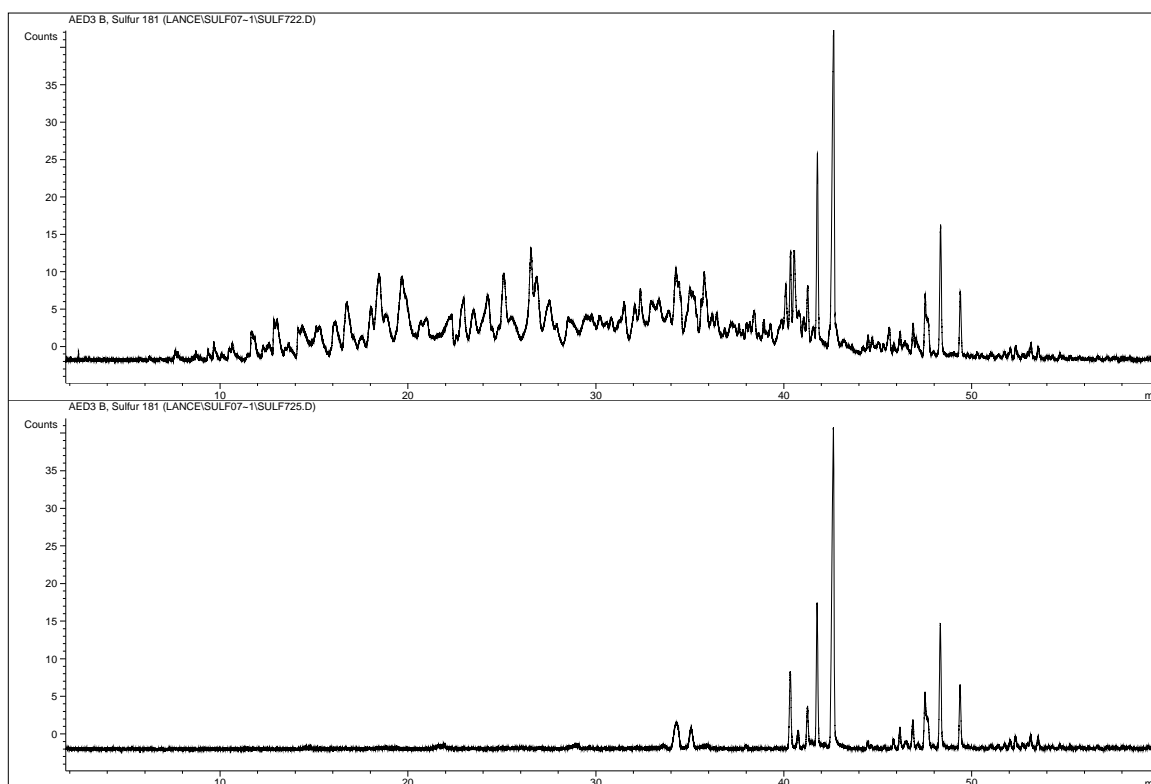


Figure 7: Sulfur 181 nm selective GC-AED chromatograms of MOBIL Jet A-1 (top) and after washing with aqueous sulfuric acid (bottom) showing the removal of sulfides

The sulfides extracted out of MOBIL Jet A-1 with sulfuric acid were then obtained by back extraction with pentane. Figure 8 shows the sulfur 181 nm selective chromatograms from the GC-AED of Jet A-1 washed with acid, and the sulfides obtained by back extracting with pentane. Note the differences in scale in sulfur counts showing the concentrating of the sulfide species by this method.

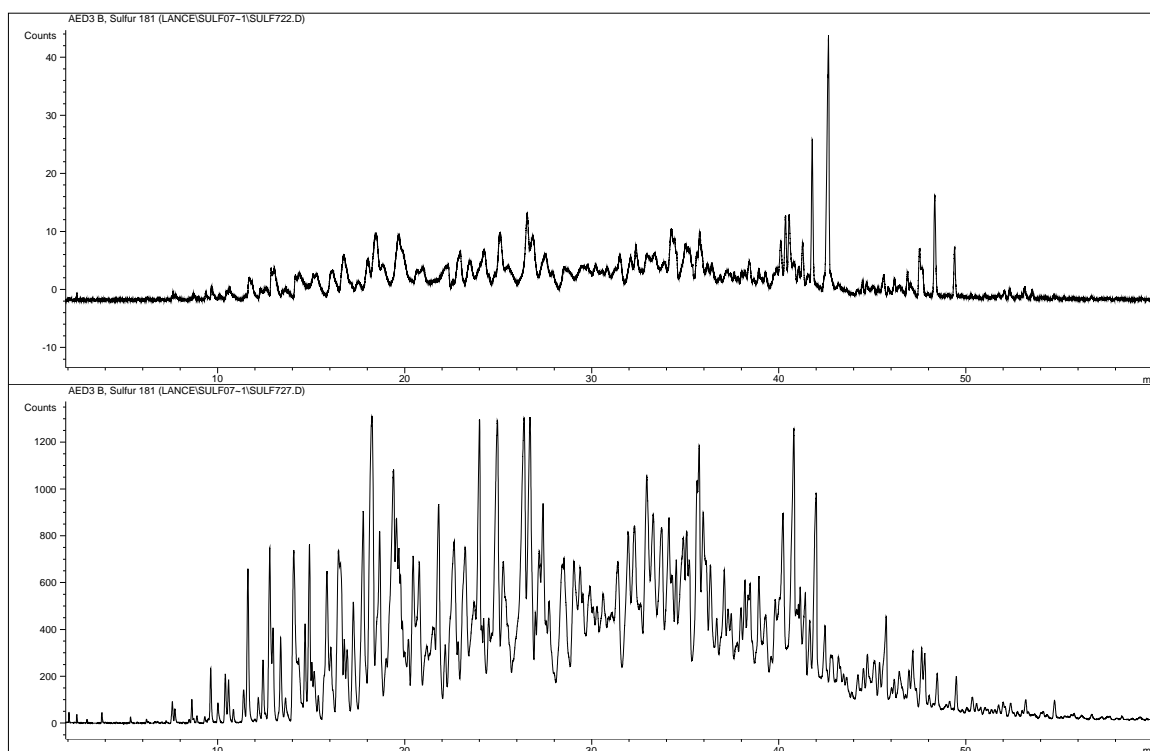


Figure 8: Sulfur 181 nm selective GC-AED chromatograms of MOBIL Jet A-1 (top) and pentane extraction of sulfuric acid (bottom) used to wash Jet A-1 showing the selective extraction of sulfides

The sulfuric acid extraction is selective as a comparison of chromatograms in the carbon 179 nm specific chromatogram show no changes in the carbon peak distribution or intensity (Figure 9). Like the hydrogen peroxide oxidation of MOBIL Jet A-1, the sulfur compounds remaining in MOBIL Jet A-1 after washing with aqueous sulfuric acid were subsequently found to be condensed thiophenes with only two simple thiophenes.

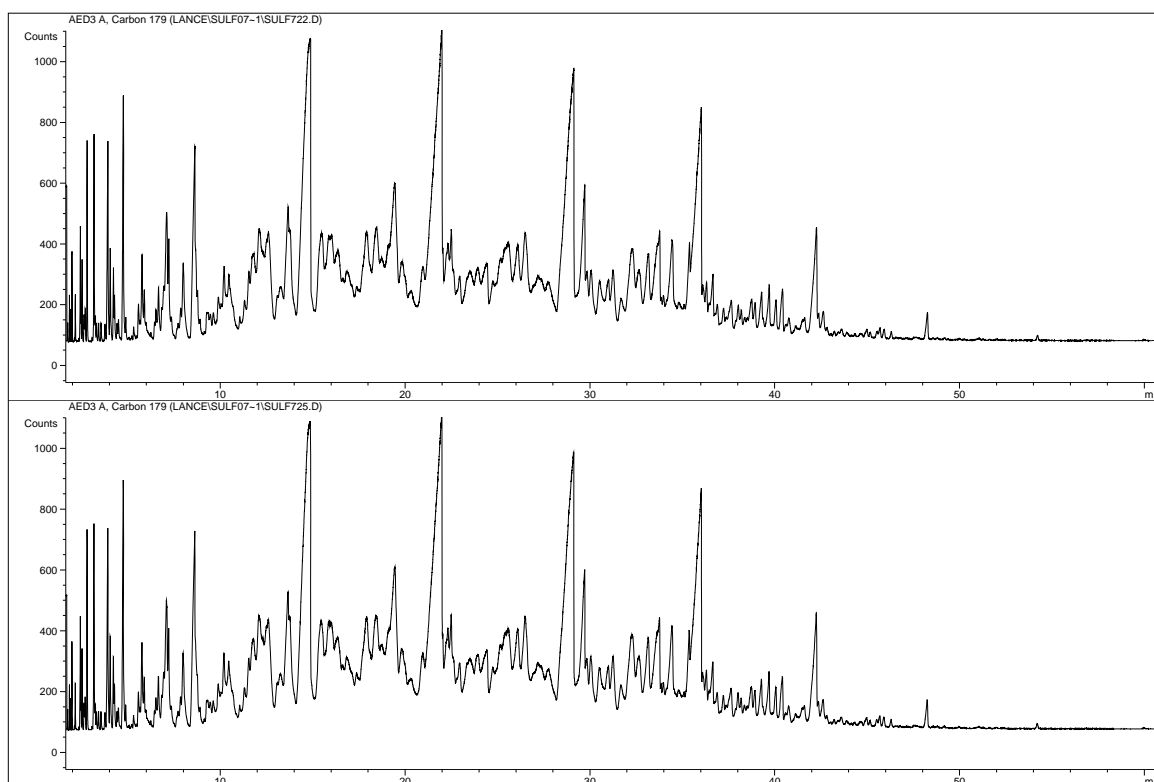


Figure 9: Carbon 179 nm selective GC-AED chromatograms of MOBIL Jet A-1 (top) and after washing with 86% showing no observed change in hydrocarbon distribution

3.2.2.1 Choice of 86% or 91% sulfuric acid

The sulfide extraction process used a process consisting of five sulfuric acid washes, three with 86% sulfuric acid and two with 91% sulfuric acid. This may be considered time consuming as there is not much difference between the two strengths of aqueous acid, and three washes with 86% sulfuric acid may be sufficient to extract out the sulfides.

Chromatograms of MOBIL Jet A-1 washed with 86% and then 91% aqueous sulfuric acid solutions were compared on the sulfur 181 nm selective GC-AED (Figure 10). The chromatograms show that after three washes with 86% sulfuric acid, the sulfides have been removed from MOBIL Jet A1. With 91% acid, the differences in the chromatogram shows a reduction in peak intensities of compounds not removed by the 86% sulfuric acid. It is not known if the higher strength acid is more efficient at removing these compounds from a hydrocarbon matrix, or destroying them due to incompatibility with the higher acid strength.

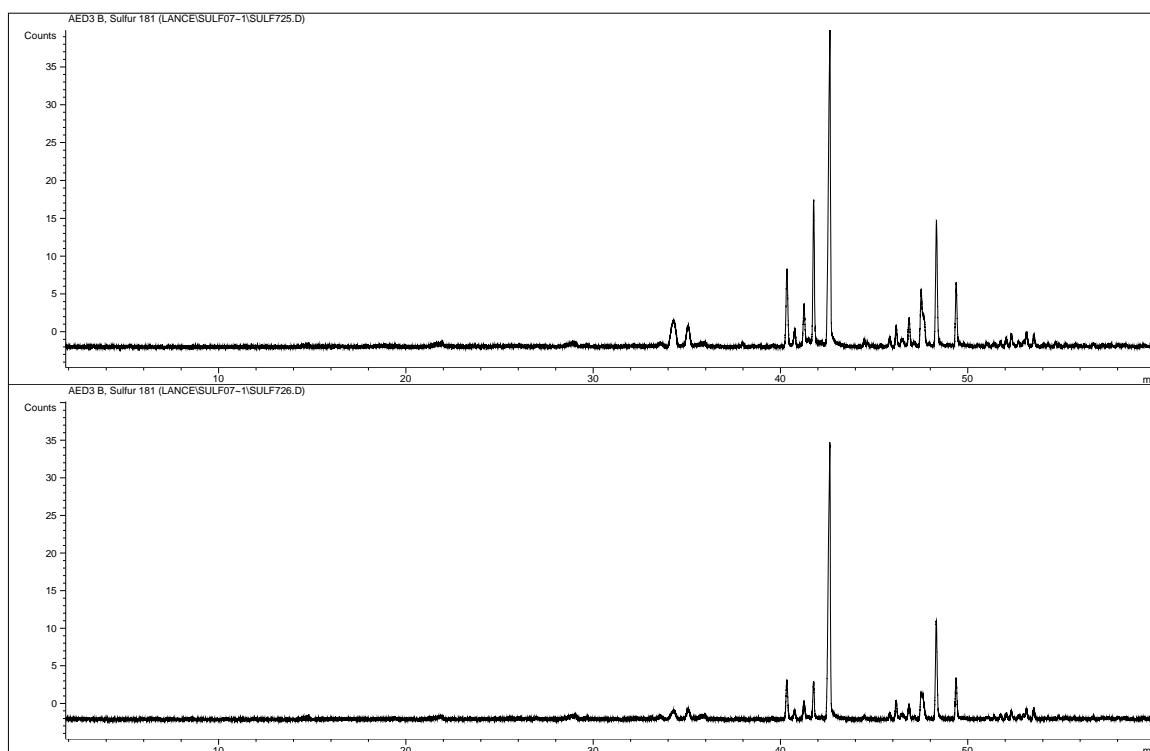


Figure 10: Sulfur 181 nm selective GC-AED chromatograms of Jet A-1 and after washing with 86% sulfuric acid (top) and then 91% sulfuric acid (bottom)

3.2.3 Sulfide compound analysis using GC-MS

The sulfides that were extracted were then injected on a GC-MS to determine their identities. The GC-MS were run on both CI and EI modes to determine the parent ion (molecular weight) and the structure of the compound from the breakdown components in the electron impact.

3.2.3.1 Identification of sulfur containing peaks by mass spectrum

Compounds containing sulfur were identified by observing the mass spectral pattern of the parent molecular ion in CI-MS. Only peaks in the chromatogram that contained mass spectra consistent with the presence of a sulfur atom were assigned as a sulfide. This was required as some hydrocarbons may have entered the sulfuric acid phase during the extraction and thus entered the final product during iso-pentane re-extraction. For sulfur, the isotope distribution is shown in Table 2.

Table 2: Isotope distribution for the sulfur atom⁴¹

Sulfur isotope	³² S	³³ S	³⁴ S
Natural abundance (%)	95.0	0.8	4.2

To test this hypothesis, pure samples of butyl sulfide and diphenylsulfide (nominal weight of 146 and 186 daltons respectively) were tested in CI-MS conditions (Figure 11) to form their respective parent ions. With both sulfides the distribution of the protonated parent ion (MH⁺) shows the existence of three lines, indicating the three isotopes of the sulfur atom. The form of the parent ion

being protonated is due to the proton transfer reaction with methanol. Hydrocarbon molecules can be differentiated as the parent ion will only show two lines due to ^{13}C and ^{12}C isotopes.

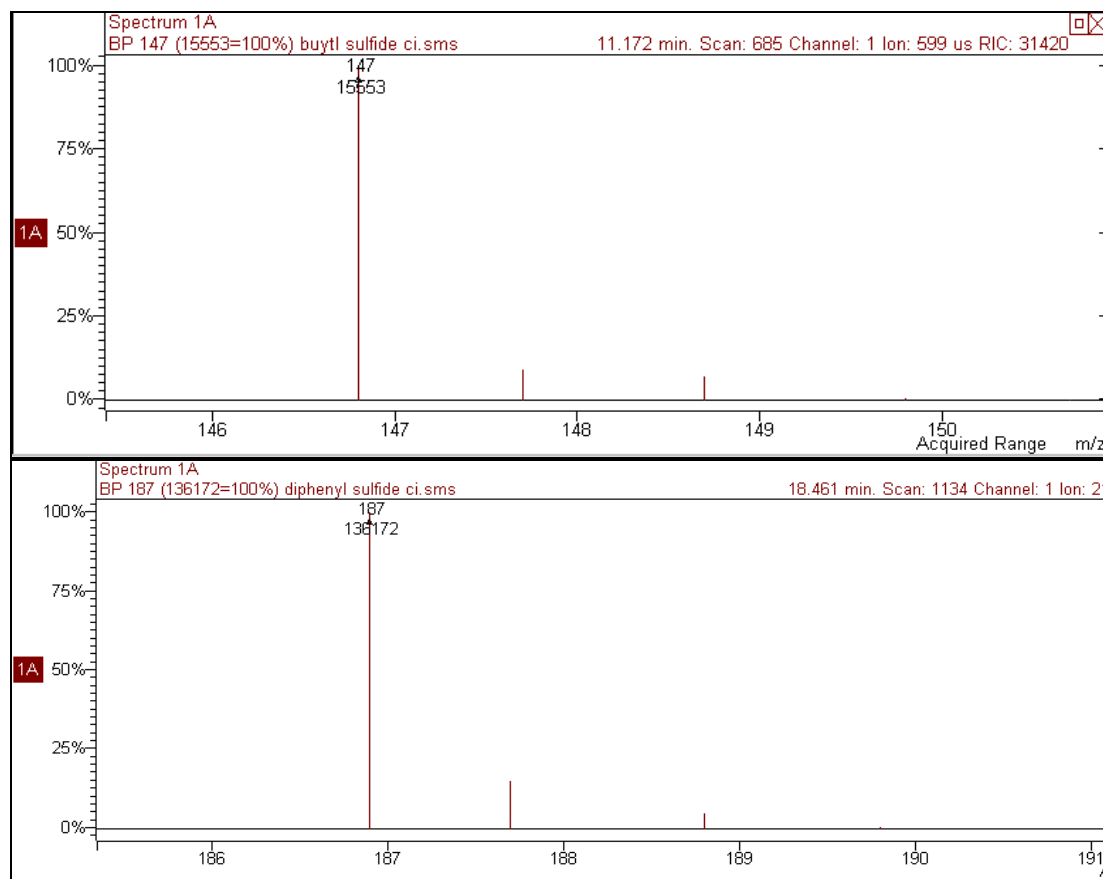


Figure 11: Distribution of molecular ions in butyl sulfide (top) and diphenyl sulfide (bottom) in CI-MS spectroscopy

3.2.3.2 Sulfide analysis with chemical ionisation (CI) MS.

Extraction with sulfuric acid yielded 234 sulfide. CI-MS showed the sulfides extracted exist in a range of C6 to C14, the distribution peaks with C9 molecules. Each carbon compound has many isomers and these are listed in Table 3. Sulfides can exist as either linear or cyclic structures that have the general formulas $\text{C}_n\text{H}_{(2n+2)}\text{S}$ and $\text{C}_n\text{H}_{2n}\text{S}$ respectively (where n is an integer). The parent molecular ions obtained indicated the sulfides extracted are cyclic in nature as linear compounds would be two daltons heavier.

Table 3: Sulfides extracted from MOBIL Jet A-1 observed in chemical ionisation mass spectroscopy

CI Mass spectrum (MH ⁺)	Formula	Isomers found
C_nH_{2n}S series		
116	C ₆ H ₁₂ S	7
131	C ₇ H ₁₄ S	19
145	C ₈ H ₁₆ S	32
159	C ₉ H ₁₈ S	44
173	C ₁₀ H ₂₀ S	38
187	C ₁₁ H ₂₂ S	34
201	C ₁₂ H ₂₄ S	29
215	C ₁₃ H ₂₆ S	24
229	C ₁₄ H ₂₈ S	5
Others		
194	C ₁₂ H ₁₆ S	1
198	C ₁₂ H ₁₉ S	1

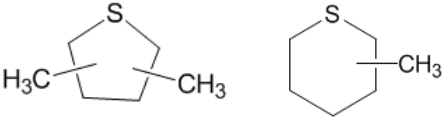
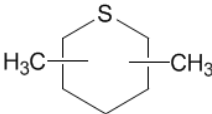
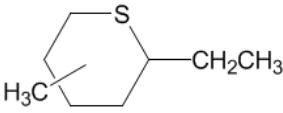
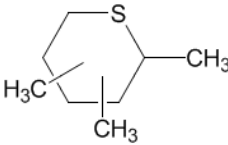
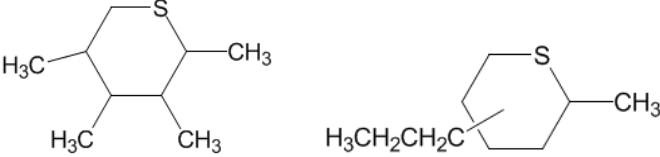
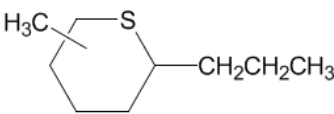
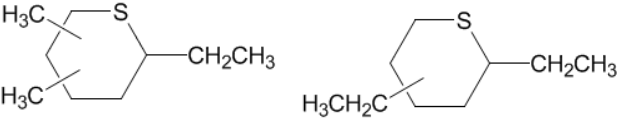
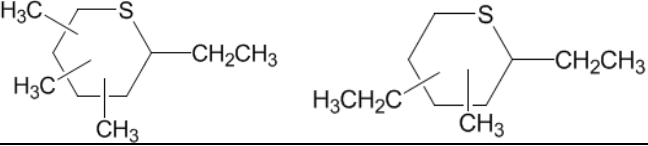
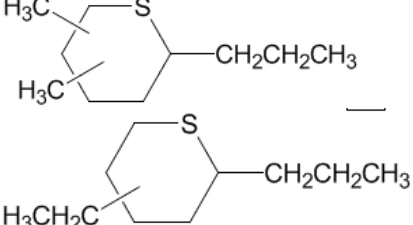
3.2.4 Sulfide analysis with EI-MS

The use of EI mass spectroscopy is a useful tool for structure determination of sulfides as sulfides follow set rules. EI-MS can be used to provide structural information in conjunction with CI-MS. CI-MS provides the parent ion, while EI-MS provides the daughter ions formed by the higher EI energies.

The fragmentation of cyclo sulfides in EI-MS occurs mostly via beta cleavage as the cyclic ring is very stable resulting in the loss of alkyl side chains such as methyl, ethyl, propyl groups or other combinations from the sulfide ring.^{42, 43}

An examination of 234 sulfides extracted from MOBIL Jet A-1 would require large time resources, so a random selection of retention times were chosen. Structures were elucidated by the CI-MS to produce the parent ion and EI-MS results provided information on the most stable daughter ions. Each eluted compound and the proposed structures are shown in Table 4. Cyclic six member rings were postulated instead of seven or eight membered rings as for the higher molecular weight molecules as six membered rings are the most stable due to minimal strain energy.⁴⁴

Table 4: Sulfide compounds extracted from MOBIL Jet A-1 and possible related compound structures

CI-MS (Daltons)	EI-MS (Daltons)	Loss	Possible structures (isomers of)
115	101	CH ₂	
130	115	CH ₂	
145	115	CH ₂ CH ₃	
145	129	CH ₂	
158	144	CH ₂	
158	115	CH ₂ CH ₂ CH ₃	
158	130	CH ₂ CH ₃	
172	143	CH ₂ CH ₃	
172	129	CH ₂ CH ₂ CH ₃	

187	143	$\text{CH}_2\text{CH}_2\text{CH}_3$	
187	115	$\text{CH}_2\text{CH}_2\text{CH}_2\text{C}$ H_2CH_3	
201	172	CH_2CH_3	
215	159	$\text{CH}_2\text{CH}_2\text{CH}_3$	
194	194	None	
198	198	None	

3.3 Thiophenes and condensed thiophenes in MOBIL Jet A-1

3.3.1 Assignment of thiophenes identified using HPLC silver Ag-SCX chromatography

The distributions of thiophenic compounds in the Jet A-1 were determined by initially dividing the fuel into three fractions, saturate, mono-aromatic and di/polyaromatic fractions. The mono and di-aromatic fractions were then further fractionated using the silver loaded HPLC technique. These sub fractions were then examined using CG-AED (Figure 12) to attempt to identify the individual sulfur compounds in each fraction. It was found that most of the sulfur compounds were alkyl, dialkyl and trialkyl benzothiophenes. No dibenzothiophenes were observed. Identification of the compounds was found to be significantly improved due to the fractionation procedures effectively simplifying the sample matrix.

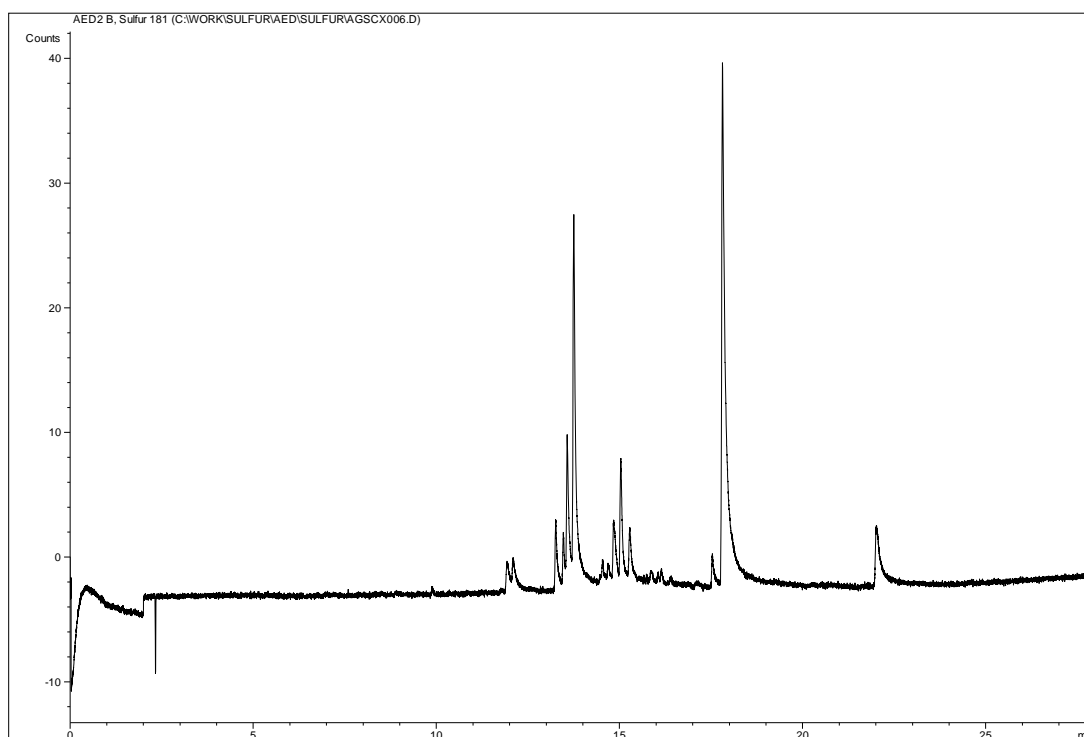


Figure 12: GC-AED chromatogram of condensed thiophenic compounds isolated from MOBIL Jet A-1 then fractionated on a silver loaded SCX column

No simple thiophenes were found in any of the sub fractions which was considered unusual. To examine the isolations methods capacity for correctly isolating these compounds thiophene and 2-methyl thiophene were doped into the fuel. The dosed fuel was then processed through the isolation procedure and both compounds were successfully isolated and identified (Figure 13). It is possible that the simple thiophenes may have been removed during hydrodesulfurisation of this Jet A-1 at the refinery, or they were in the fuel at very low concentration and being more volatile than the condensed thiophenes were removed during the concentration stages of the isolation procedure.

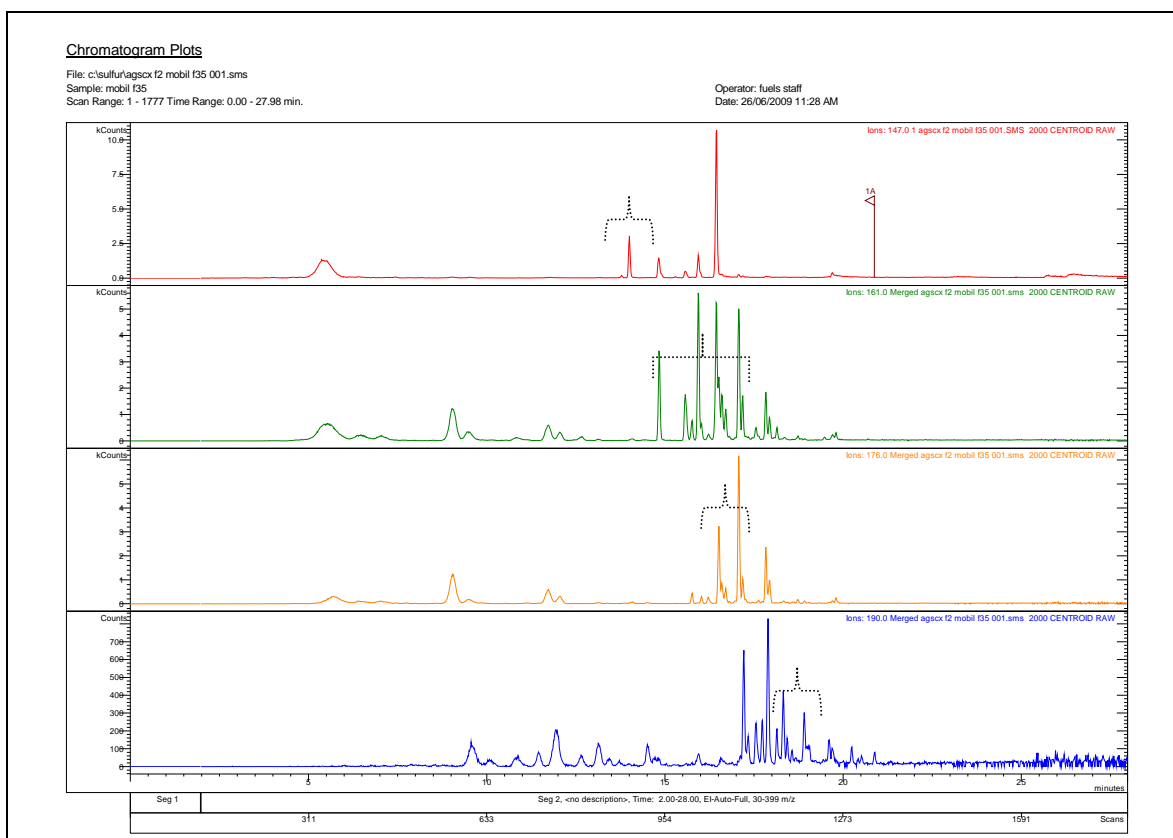


Figure 13: GC-MS BP90 column analysis and identification of thiophenic sulfur components as fractionated by Ag-SCX HPLC fractionation procedure. Red = ethyl thiophene (147 amu), green = dialkyl thiophenes (161 amu), orange = trialkyl thiophenes (176 amu) and blue = tetraalkyl thiophenes (190 amu)

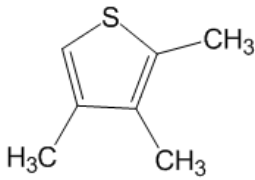
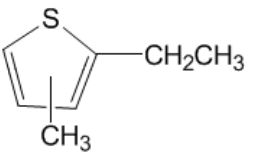
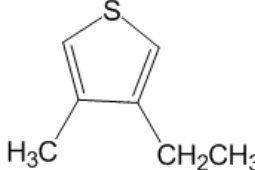
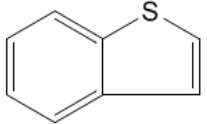
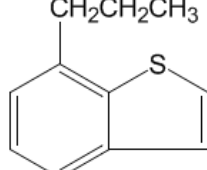
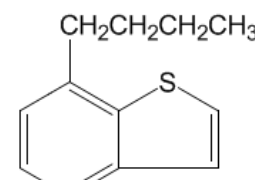
3.3.2 Assignment of thiophenes from sulfuric acid extraction

Thiophenes and condensed thiophenes can also be extracted out using sulfuric acid solutions as shown with Chinese naphtha.²⁶ The types of thiophenes that can be extracted into sulfuric acid solutions are ones containing two or more alkyl groups. The number of thiophenes and condensed thiophenes was less than sulfides (Table 5). Structural assignments for the thiophenes were made with the same methods as the sulfides (Table 6).

Table 5: Simple and condensed thiophenes extracted from MOBIL Jet A-1 by sulfuric acid

CI-MS (Daltons)	Formula	Isomers
Simple thiophenes		
110	C ₆ H ₈ S	3
125	C ₇ H ₁₁ S	15
Condensed thiophenes		
134	C ₈ H ₅ S	1
176	C ₁₁ H ₁₂ S	2
190	C ₁₂ H ₁₅ S	1

Table 6: Simple and condensed thiophenes extracted from MOBIL Jet A-1 and possible related compound structures

CI-MS (Daltons)	EI-MS (Daltons)	Loss	Possible Structure
124	110	CH ₂	
124	95	CH ₂ CH ₃	
124	124	None	
134	134	None	
176	176	None	
190	190	None	

3.3.3 Assignment of thiophenes from isolation by silver loaded column HPLC

The fractions collected using the silver loaded HPLC column method were dominated by condensed thiophenes. The compounds were grouped into ethyl thiophenes, benzothiophene, a distribution of alkyl benzothiophenes, dialkyl thiophenes, trialkyl thiophenes and tetra alkyl thiophenes.

4. Conclusions

A range of techniques for isolating and identifying sulfur compounds from a Jet A-1 fuel sample sourced from a local refiner were examined. Laboratory techniques for isolating thiols, sulfides and thiophenes were successfully used to characterise the fuel's sulfur compound distribution. The method for quantification of disulfides was not attempted as the fuel was not expected to contain disulfides and the method gives only total disulfide concentration rather than detailed compound speciation. The isolation methods were found to be selective for each of the specific sulfur types and GC-AED in combination with GC-MS was found to be a suitable technique for characterisation of the sulfur compounds in each sub fraction of the fuel.

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19. ABSTRACT Jet fuel contains a wide range of sulfur compounds which may contribute to a number of detrimental fuel characteristics such as corrosion of silver and copper fuel system components, fuel stability and environmental concerns. A range of methods for isolation and identification of sulfur compounds for specific chemical classes of sulfur were examined. Suitable methods were chosen to further elucidate the sulfur compounds in a representative Australian jet fuel. Methods for isolation and characterisation of thiol, sulfide, thiophene and condensed thiophene classes were developed and applied successfully to the jet fuel. The sample examined was found to contain a distribution of sulfides, thiophenes and complex thiophenes. Additionally, no thiols were observed in the jet fuel examined.					