

Safety Regulation Group



CAA PAPER 2004/04

Cabin Air Quality

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CAA PAPER 2004/04

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February 2004

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ISBN 0 86039 961 3

Published February 2004

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Foreword

The Civil Aviation Authority initiated its research programme into cabin air quality in 2001 after a small number of events, including two on UK registered aircraft, where flight crew were partially incapacitated. Evidence from these incidents indicated that contamination of the ventilation systems by engine oil fumes was the most likely cause. This was also supported by the determinations of 'likely cause' from previous investigations made in Sweden and Australia and discussion with the UK AAIB. Although the CAA research was targeted in this direction, it was also necessary to keep an open mind on other potential causes. However, subsequent CAA investigations found no weight of evidence indicating that other causes were involved.

The research described in this report addresses the effect of cabin air contamination on the pilot's ability to safely fly and land the aircraft.

The research programme was conducted in two parts, aimed at investigating the existence of noxious or toxic products generated at the engine level and the aircraft level. Phase 1 of the research, detailed in chapter one of this report, was a toxicological review conducted by Defence Science & Technology Laboratory (DSTL) Porton Down of the products of 'pyrolised' oil, (i.e. heated to and beyond the temperatures experienced in the engine), that had been identified by test and analysis at Defence Evaluation & Research Agency (DERA) Pyestock. The review concluded that 'no single component or set of components can be identified which at conceivable concentrations would definitely cause the symptoms reported in cabin air quality incidents'. However, the presence of short chain organic acids was identified, which could cause irritant effects. No quantitative information on the concentrations in inspired air necessary to cause irritancy was available.

Phase 2 of the research detailed in Chapter 2 of this report was analysis by DSTL Porton-Down of contaminated cabin air supply ducts removed from two different BAe146 aircraft. The research investigated the chemical content of the accumulated and absorbed products. In addition, airflows of varying temperature and relative humidity were passed through the ducts to identify any products that could be liberated in the aircraft air conditioning system and delivered into the cabin and flight deck. The conclusions from Phase 2 were that the ducts were contaminated with a carbonaceous material containing chemicals entirely consistent with the pyrolysis products of aircraft engine oil. Short chain organic acids were present and the odour of the duct was similar to pentanoic acid, one of the acids that can produce irritant effects. Basic toxicology surmises that increase in exposure time or concentration of an irritant can cause an increase in the severity of symptoms and this fits the variable nature of the reported incidents as they have affected individual aircrew. Some additional compounds were found in Phase 2, including the ortho isomer of tricresyl phosphate (known as TOCP), but toxicological review of these previously unrecorded chemicals indicates that they are most unlikely to be present in sufficient concentration to have a physiological effect and, in any case, the specified symptoms were not the same as those associated with exposure to TOCP.

The CAA has reviewed the results of concurrent and similar research conducted by the aircraft and engine manufacturers. This, together with the CAA research indicates that fumes from engine oil leaking into the bleed air system and hence into the cabin air supply, is the most likely cause of the incidents. There are over 40 different chemicals contained in oil breakdown products and many have no published toxicity data, so it is not possible to be certain whether any of these products contribute to, or are the sole cause of the recorded incidents. However, scientific advice is that the smaller more volatile molecules are most likely to give toxic effects, although many of these also have no published exposure limits. Any or all of the small molecular compounds discovered could possibly be responsible for the symptoms experienced by flight crew, but the most likely are the short chain organic acids such as pentanoic and valeric acid, acting as irritants.

As a result of this investigation the CAA has required operators and manufacturers of particular aircraft types to make a number of changes including modifications to minimise oil leaks into the bleed air. Maintenance procedures to monitor, clean, or replace air ducts that are contaminated have been introduced along with enhanced troubleshooting procedures. As at the date of this report, service experience shows that these actions have controlled any airworthiness risk by reducing both the number and the severity of reported events. However, even with these actions, oil leaks will occasionally occur on all aircraft types. Therefore, in the event of experiencing any suggestive symptoms or unusual odours in the flight deck, the flight crew procedures have been emphasised. Finally, it is important to note that, although some references are made concerning long term health effects, the scope of this research did not include an attempt to determine the extent of any such risk. The recommendations made by DSTL are to be raised by the CAA Aviation Health Unit with the Department for Transport Aviation Health Working Group.

Chapter 1 **The Toxicity of Aircraft Lubricant Pyrolysis Products Related to Cabin Air Quality Incidents (UC)**

1 Introduction

- 1.1 The occurrence, in recent years, of a variety of symptoms in aircrew and cabin crew on commercial airlines has stimulated the investigation of the quality of cabin air [1,2,3]. Some of the reported incidents have been associated with odours in the cabin and "haze" or "mist" which may indicate a leak of oil pyrolysis products into the cabin air supply. Several aircraft types including the BAe 146 have been the subject of reports. All the aircraft have a common method of handling the air supply to the passenger cabin. Air is bled off the engines and supplied to the Environmental Conditioning System (ECS) for air conditioning before entering the cabin, a proportion of which is re-circulated. This system enables the cabin to be pressurised and at cruise altitudes the atmosphere within the cabin can be adjusted to a maximum apparent altitude of 8000 feet with a consequent reduction in the partial pressure of oxygen (pO_2). In the event of oil leakage there is the opportunity, therefore, for the pyrolysis products of engine lubricant/fuel to enter the cabin air supply and exert toxic effects on both passengers and crew.
- 1.2 The symptoms have been widely reported and are diverse in nature. There are two major classes of symptoms, which are reported as being associated with odours in the cabin, irritation of the eyes and nasal passages and feelings of nausea followed by dizziness. Many other symptoms have been reported and are summarised in Tables 1 and 2. The symptoms themselves do not suggest any specific chemical toxicity nor are they definitely associated with odours of any kind (Table 1). Various components of the lubricating oil, which can potentially exert neurotoxic effects, have been implicated but to date have not been shown to be present in cabin air at sufficient concentrations to produce toxicity. These include the tricresyl phosphates additives, of which the tri ortho isomer is an organophosphate cholinesterase inhibitor capable of inducing a delayed neuropathy.
- 1.3 The purpose of this report is to make a general assessment of the toxic potential of the components and thermal degradation products of a synthetic ester gas turbine lubricant used in the BAe 146 carried out at DERA Pyestock and reported by Marshman [4].

2 Methods

- 2.1 Several toxicological databases were interrogated for information of the inherent toxic effects of the chemicals identified in the analysis of both new and used engine lubricating oil under four different temperature conditions. In addition, a search of open literature databases was conducted for reports of studies of the toxicology of aircraft lubricating oils as background information.
- 2.2 Toxicological databases interrogated were:
- Toxicology, Occupational Medicine & Environmental Series (TOMES) including The Hazardous Chemical Database [5]
 - Sax's dangerous properties of industrial materials [6]
 - National Institute of Occupation Safety and Health (NIOSH) [7]

- 2.3 Where sufficient information existed, it was used to determine if the inherent toxicity of the oil pyrolysis products might produce the symptoms reported in incidents where cabin air quality had been implicated in ill health. Where possible, a concentration or dosage was identified above which toxic effects of the chemicals might be observed.
- 2.4 Where Occupation Exposure Standards are quoted in this report, they refer to long term exposure limits published by the UK Health and Safety Executive. This is the level to which a workforce may be exposed for 8 hours per day, 5 days per week without ill effect.

3 Results and Discussion

3.1 Symptoms Reported in Cabin Air Quality Incidents

- 3.1.1 A wide variety of symptoms have been reported as being associated with contamination of aircraft cabin air. The acute symptoms fall broadly into two categories, those of irritation such as sore eyes, burning throat and nose, and those associated with a possible effect on the central nervous system such as nausea, dizziness and inability to concentrate. The chronic symptoms are more diverse and also affect the gut and peripheral nerves. There is no common pattern of symptoms which can readily be identified as being characteristic of "cabin air quality incidents" and the symptoms are not in themselves characteristic and, therefore, suggestive of any specific form of chemical toxicity.
- 3.1.2 It is important to note that the only evidence which links any of these symptoms with chemical contaminants in the air supply as indicated by odours is that they occur at the same time, but this does not occur in all cases. The incident on a BAe 146 (5 November 2000) is a typical example [1]. An odour was detected in the passenger cabin during take-off, but the crew showed no symptoms until the descent to landing. This supports the conclusions of other authors [3,8,9] that the odour is not always associated with symptoms (as summarised in Table 1).

3.2 Constituents and Pyrolysis Products of Aviation Lubricants

- 3.2.1 The components of new and used oils reported by Marshman [4] fell into four general categories. Two major types of chemical esters make up the lubricant itself, trimethylolpropane (TMP) esters and pentaerythritol (PE) esters. The other two groups comprise the additives, i.e. the cresylphosphates and N-phenyl-1-naphthylamine, and relatively low molecular weight organic acids, esters and ketones which are reported as thermal breakdown products of the lubricant esters or contaminants present after manufacture. The percentage of the total analytes categorised into the above four groups in oils pyrolysed at 350°C, 350°C at high humidity and at 450°C are summarised in Figures 1-4. (Data used is the property of BAE Systems).
- 3.2.2 The major change in the oil constituents from new to used and from cold to thermally degraded oil was a small increase in the percentage of low molecular weight organic acids and esters. The percentage of the anti-oxidant N-phenyl-1-naphthylamine and the additive agents such as tricresylphosphates appeared to be only slightly reduced by either use or thermal degradation.

3.3 Trimethylolpropane Esters (TMP) and Pentaerythritol (PE) Esters

No information on the toxicology of either of the lubricant ester classes was found in any of the databases interrogated. Several studies have been conducted to investigate the delayed neurotoxicity of Mobil oils. These were conducted in chickens as the most sensitive species to these effects and showed that animals fed 1g of oil

per day, orally, for several weeks showed no toxic effects. The inhalation toxicity of Mobil Jet Oil II, Mobil Jet Oil 254 and Mobil Jet Oil 291 is given in the manufacturer's datasheets as $>5000 \text{ mg.m}^{-3}$ [10,11,12] and as such is classified on the basis of this criteria as practically non-toxic. The oils in the cases we have examined are broadly similar and are also composed of predominately TMP and PE esters.

3.4 **Organic Acids**

The toxicology information found is summarised in Table 3. The small quantities of decanoic and octanoic acids which were found are known to be irritants and could produce the stinging of the eyes and nasal membranes as reported. Organic acids also have characteristic odours which are described by some as "acid", "old socks", "body odour" and are not dissimilar to the descriptions of cabin odours given in some of the incident reports. Information on the effective concentrations of decanoic and octanoic acids has not been found but the odour threshold for octanoic acid is given as 0.008 ppm or 0.0052 mg.m^{-3} .

3.5 **Organophosphates**

3.5.1 The tricresyl phosphates are organophosphates and the ortho isomer is an anti-cholinesterase which can induce "Organophosphate Induced Delayed Neuropathy" (OPIDN). The meta and para isomers of cresyl phosphate are not as toxic as the ortho isomer and are not reported as inducing OPIDN. The delayed peripheral neuropathy is a progressive condition where the peripheral nerves become unable to transmit impulses. This produces a characteristic set of symptoms which are not consistently present in the symptom profiles reported in the cabin air quality incidents. Significantly, no tri-ortho-cresylphosphate was detected in the new, used or pyrolysed oil analysed by Marshman [4].

3.5.2 The occupational exposure limit for tricresylphosphate should be interpreted in the light of the ortho isomer of tricresyl phosphate (TOCP) being the most toxic and the meta and para isomers being listed as relatively non-toxic. The occupational exposure limit for tricresylphosphates of 0.1 mg.m^{-3} is based on the toxicity of the ortho isomer and is not indicative of the toxicity of the meta and para isomers. No definite toxicity estimates for the meta and para isomers were found in any of the databases interrogated. However, Dautrey *et al* [13] tested three types of aviation lubricants containing 3% (w/w) TCPs and compared these to TOCP in chickens, the most sensitive species to this type of neurotoxicity. The mixed isomer TCPs in aviation lubricants produced no effects at an oral dose of 30 mg.kg^{-1} whereas TOCP produced OPIDN at a dose of 7.5 mg.kg^{-1} , indicating that the mixed isomers of TCP containing less than 1% TOCP are at least four times less toxic than TOCP itself. In contrast, Freudenthal *et al* [14] showed that oil containing 3% TCP was able to induce a delayed neuropathy in chickens. Clearly, oils from different sources exhibit different neurotoxic potentials and further research is necessary to determine the contribution of the meta and para isomers to the OPIDN.

3.5.3 Centers [15] proposed the formation of the neurotoxic organophosphate trimethylolpropane phosphate (TMPP) from TMP esters and TCP esters at temperatures between 350°C and 700°C . Though TMPP has been found in the atmospheres of warships during simulated shipboard fires [16] it was not found in any of the analyses carried out by Marshman, though co-chromatography of this compound with other identified constituents is possible. Moreover, the neurotoxicity of TMPP is of a different type to TCP esters. TMPP is an irreversible inhibitor of the g-aminobutyric acid (GABA) inhibitory pathways and produces tonic/clonic convulsions, such symptoms have not been reported in cabin air quality incidents.

3.6 Gases

- 3.6.1 The possibility that toxic gases such as carbon monoxide and oxides of nitrogen can be produced during the pyrolysis of aviation lubricants cannot be excluded. Some carbon monoxide was detected in the pyrolysis products reported by Marshman but the concentrations detected do not exceed those where toxic effects are observed. The highest concentration of carbon monoxide found during pyrolysis experiments was 3.5 ppm (or 4.025 mg.m⁻³) generated from 2g of oil in a 1m³ chamber, (i.e. 2.0125 mg/m³/g of lubricant). The long-term exposure limit for carbon monoxide is 35 mg.m⁻³.
- 3.6.2 Oxides of nitrogen (NO_x) are produced when the amine anti-oxidants in the oil perform their function and are oxidised to protect the other constituents of the oil. NO_x compounds are released when N-phenyl-1-naphthylamine is heated to decomposition [6] but less than 1 ppm was found in all of the pyrolysed oil mists tested by Marshman [4]. Though many different oxides of nitrogen can be formed they all react rapidly in air to form nitrogen dioxide (NO₂) which is the most toxic and has been assigned a long-term exposure limit of 5.7 mg.m⁻³. Assuming the experimental concentration of NO_x in Marshman's experiments to be 1 ppm and that this is in the form of NO₂, this is equivalent to 1.8 mg.m⁻³ in a 1 m³ container produced from 2g of oil.
- 3.6.3 The carbon dioxide concentration produced by pyrolysis of 2g of oil at 350-450°C was 0.05 ppm (0.057 mg.m⁻³ in a 1 m³ vessel).

3.7 Modification of the Toxic Effects of Pyrolysis Products by Altitude

Tests of the toxicity of the compounds discussed in this report have not been performed under conditions of reduced oxygen tension similar to those maintained in aircraft. Any consideration of the effects of altitude on toxicity must, therefore, be theoretical and open to experimental testing. However, certain statements can be made about the expected effects of reduced oxygen tension on toxicity. None of the chemicals reviewed have known toxic mechanisms which involve the oxygen transporting systems of the body such as haemoglobin or myoglobin, or oxygen utilisation mechanisms such as oxidative phosphorylation. There is no toxicology information indicating that general symptoms of irritation would be exacerbated by low oxygen tension.

4 Conclusions

- 4.1 A general assessment of the toxic potential of the components and thermal degradation products of aviation lubricating fluid, as collected by Marshman, has been carried out and no single component or set of components can be identified which at conceivable concentrations would definitely cause the symptoms reported in cabin air quality incidents.
- 4.2 There is no single symptom or set of symptoms which is characteristic of cabin air quality incidents.
- 4.3 The major constituents of aircraft lubricating fluid, i.e. high molecular weight esters, are recorded as having very low toxicity. It is concluded therefore that these components do not pose a risk even at high lubricant leak rates into the cabin air supply.
- 4.4 The occurrence of symptoms is not necessarily related to the presence of an odour in the cabin.
- 4.5 The symptoms of irritation could be induced by short chain organic acids formed during pyrolysis of aircraft lubricants.

- 4.6 Based on a review of the readily available literature, we do not believe that either of the meta and para isomers of tricresyl phosphate identified following pyrolysis can be associated with neurotoxic effects.
- 4.7 There is no rational basis for drawing conclusions about the toxicity of the contaminants reviewed under conditions of reduced pO₂ as in the cabins of pressurised aircraft.

5 Recommendations from DSTL

- 5.1 Further review and investigation of the toxicity of the meta and para isomers of tricresyl phosphate should be conducted to eliminate the potential neurotoxic effects of these compounds.
- 5.2 As a consequence of the non-identification of toxicological hazards from the pyrolysis of oil, it is recommended that sampling and analysis of the atmosphere on an aircraft during flight should be undertaken to determine contaminants in the cabin. Furthermore, it is recommended that other sources of chemical contamination should be investigated, e.g. the residue in the ECS equipment and ducts after prolonged use and cleaning materials used in the cabins themselves.
- 5.3 The short chain organic acids identified as constituents of pyrolysed oil are known to be non-specific irritants that may or may not have a specific odour. Further studies are necessary to define the longer term accumulative toxicity of these materials, particularly in relation to the symptom complexes that have been identified in cabin staff.
- 5.4 The effect of hypoxic conditions on the toxicity of oil pyrolysis products should be investigated.

6 References

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7 Tables

Table 1 Symptoms Reported on BAe 146 Flights in the Presence or Absence of Odour [3,8,9]

Reference to Smells	No Reference to Smells
Slight headache, headache, severe headache Light headed Heavy head Dizzy, dizziness	Headache, Huge head Light headed Heavy head, pressure in head Dizzy, giddy
Hard to concentrate Lethargic, lethargy	Difficult to concentrate, disorientated Fatigue, faint Intoxicated Loss of motor co-ordination
Dry eyes, irritated eyes, stinging eyes	Dry eyes, irritated eyes, stinging eyes, Burning eye, sore eyes, puffy eyes, blurred vision.
Nasal irritation, itchy nose, irritation in nose Sneezing	Pain in nose, irritating in nose, burning nose, sinus symptoms, tingling nose
Irritation in throat, sore throat Coughing	Irritation in throat, burning throat, dry throat, dusty throat
Chemical taste, metallic taste, oily after taste	Chemical taste, metallic taste, dusty taste, unusual taste
Tight chest Lack of air, breathless	Tight chest, pressure in chest Breathless, shortness of breath, laboured breathing Shallow breathing Respiratory difficulties, breathing difficulties Mild hypoxia
Nausea, vomiting	Nausea, queasy, vomiting
Tingling fingers and hands Stuffiness, hot and cold and shivery Shaky	Trembling hands, tingling Sweating, clammy and sweaty Slept badly all night

Table 2 Symptoms Reported from Three Open Literature Sources from Balouet & Winder [2]

Reference	Rayman [8]	Tashkin [9]	Van Netten [3]
Number of Cases/Reports	89	248	112
Watery eyes			6
Eye irritation	31	74%	
Burning eyes			27
Blurred vision			1
Loss of visual acuity	10	13%	
Runny nose		43%	
Sinus congestion	31	54%	6
Dry painful nose		57%	
Nose bleed		17%	
Burning throat			48
Throat irritation		64%	
Gagging and coughing	2		3
Cough dry		69	
Cough wet		6%	
Cough blood		2%	
Shortness of breath		73%	
Difficulty in breathing		68%	
Pain on deep breathing	6	81%	
Chest pains	6		7
Increased heart rate		2%	
Breathing problems requiring oxygen			2
Loss of voice		35%	
Headache	22	52%	29
Dizziness/loss of balance	42		7
Light-headedness	42		6
Feeling faint		54%	
Actually faint/loss of consciousness	4	4%	
Trouble thinking or counting	23	39%	
Disorientation	23		17
Behaviour modified	23	20%	
Feeling "spaced out"		36%	
Tingling of nose and lips	8		3
Numbness			2
Muscle cramp		29%	
Nausea	23	23%	9
Abdominal spasms/vomiting	23		
Change in urine		3%	

Table 3 Summary of Toxic Effects of Contaminants of Pyrolysed Aviation Lubricant

Compound	LD ₅₀ [6] mg.kg ⁻¹	Toxic Effects (vapour)	Odour Threshold	Exposure Limit	Hazard Rating [6]
Octanoic Acid	10,080	Severe irritation of eyes and throat and can cause eye and lung injury. Cannot be tolerated even at low concentrations [5]	0.008 ppm [5]		2
Decanoic Acid	>10,000	Severe irritation of eyes and throat and can cause eye and lung injury. Cannot be tolerated even at low concentrations [5]			3
N-Phenyl-1-naphthylamine	1625	No acute toxic effects listed. Suspect mutagen and carcinogen - tumorigenic in lung, thorax,			2
4,4'-dioctyldipheylamine	8000	When heated to decomposition it emits toxic fumes of NO _x .			1
Tricresyl phosphate (mixed isomers)	5190 3000[5]	Can irritate the eyes on contact, can irritate the nose and throat, can induce nausea, vomiting, diarrhoea, stomach pain and loss of appetite.		0.1 mg.m ⁻³	2
Tri-m-cresylphosphate Tri-p-cresylphosphate		Vapours may irritate eyes but only at high concentrations. Effect on workers producing tritolyphosphates is characterised by perivascular form of neuritis, decreased activity of plasma cholinesterase and chronic gastritis with deficient secretion, toxic encephalopathy, hypothalamic syndrome, polyneuritis. None of the usual toxic effects of cresols or phenols is described in clinical poisonings. Does not produce typical syndrome associated with cholinesterase inhibition as do phosphate esters like parathion, meta and para isomers are relatively inactive.			2

LD₅₀ - The dose causing 50% lethality in a group of rats when given orally.

Hazard Rating Key:

- 1 LD₅₀ of 4,000-40,000 mg.kg⁻¹ or an LC₅₀ of 500-5000 ppm or that the materials is combustible or has some reactivity hazard.
- 2 LD₅₀ of 400-4,000 mg.kg⁻¹ or an LC₅₀ of 100-500 ppm or that the materials are flammable or reactive.
- 3 LD₅₀ of below 400 mg.kg⁻¹ or an LC₅₀ of below 100 ppm or that the materials are highly flammable, or highly reactive.

8 Figures

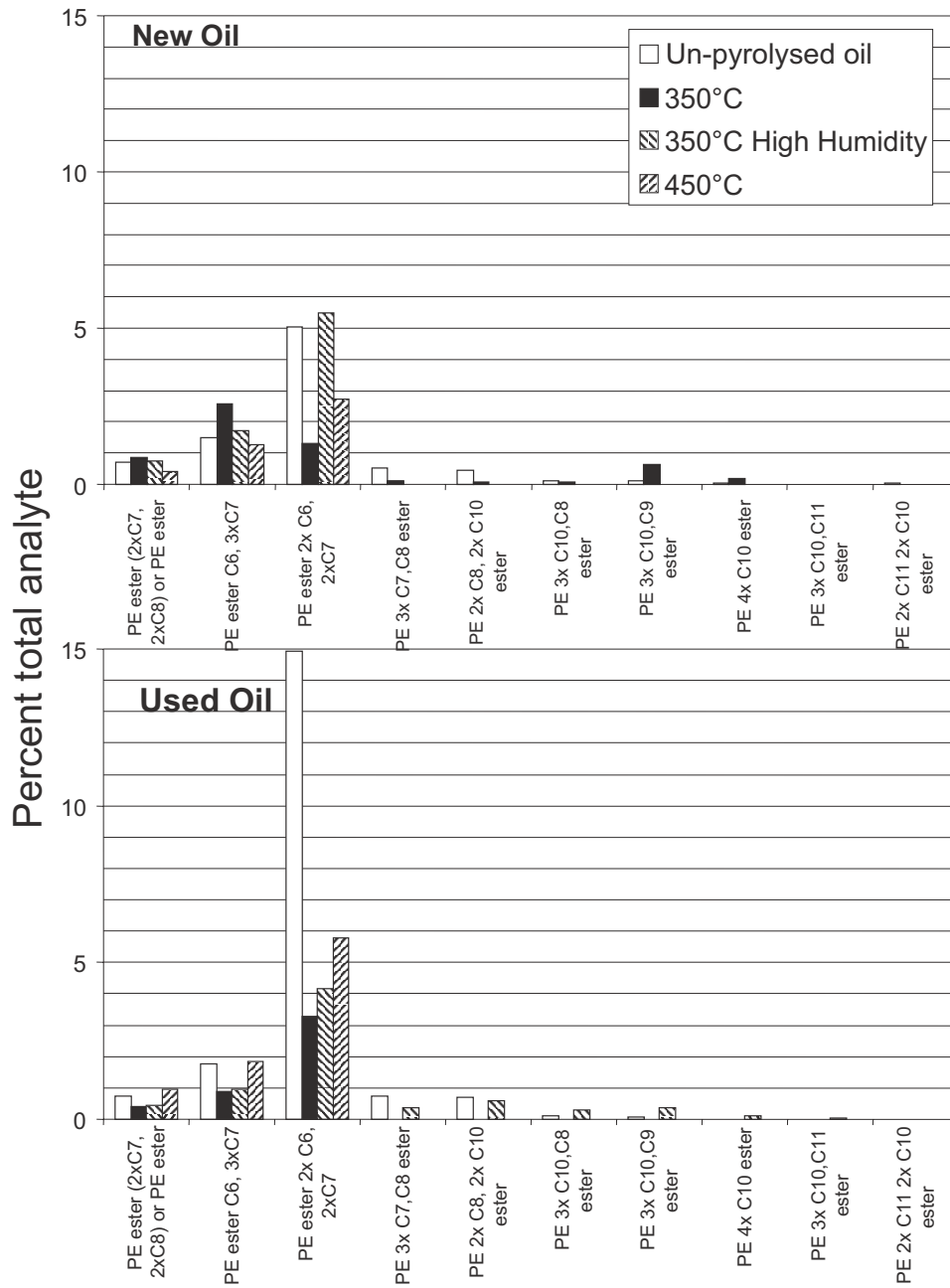


Figure 1 Pentaerythritol (PE) esters identified by GC-MS in pyrolysis products of new and used oils. Details of methods of pyrolysis and analysis are given in Marshman (2001) (Data used is the property of BAE Systems)

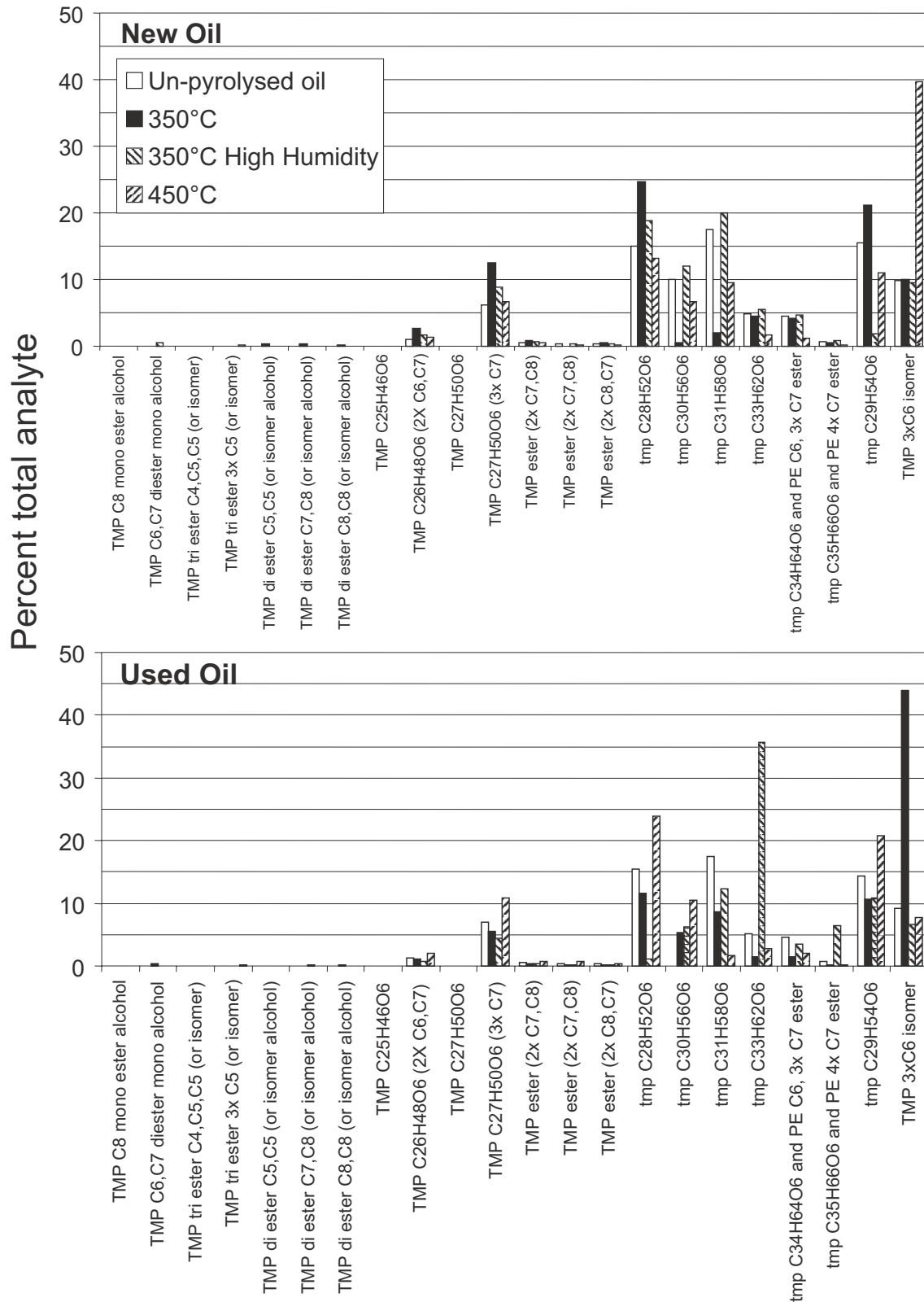


Figure 2 Trimethylpropane (TMP) esters identified by GC-MS in pyrolysis products of new and used oils. Details of methods of pyrolysis and analysis are given in Marshman (2001) (Data used is the property of BAE Systems)

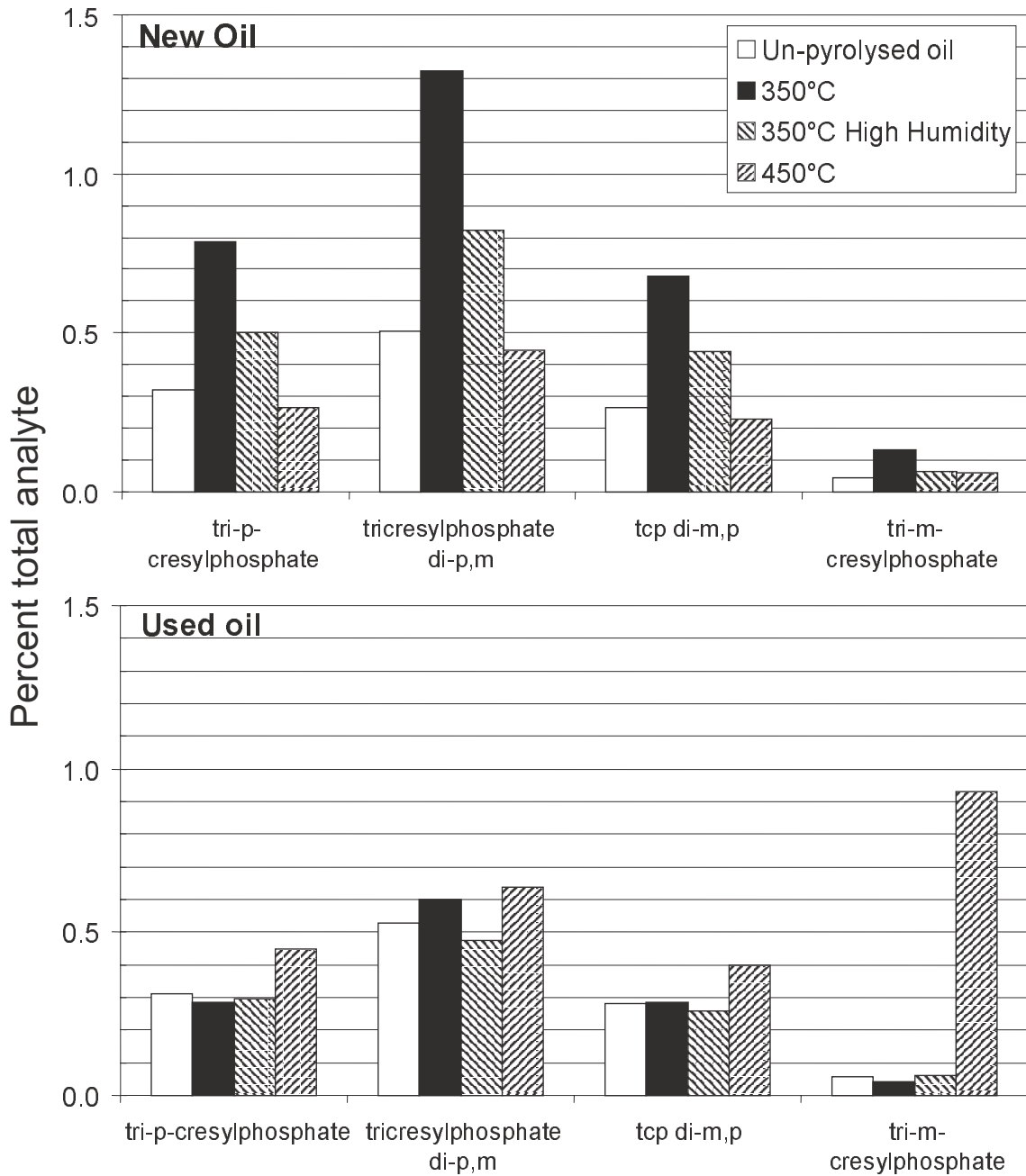


Figure 3 Tricresyl phosphate (TCP) esters identified by GC-MS in pyrolysis products of new and used oils. Details of methods of pyrolysis and analysis are given in Marshman (2001) (Data used is the property of BAE Systems)

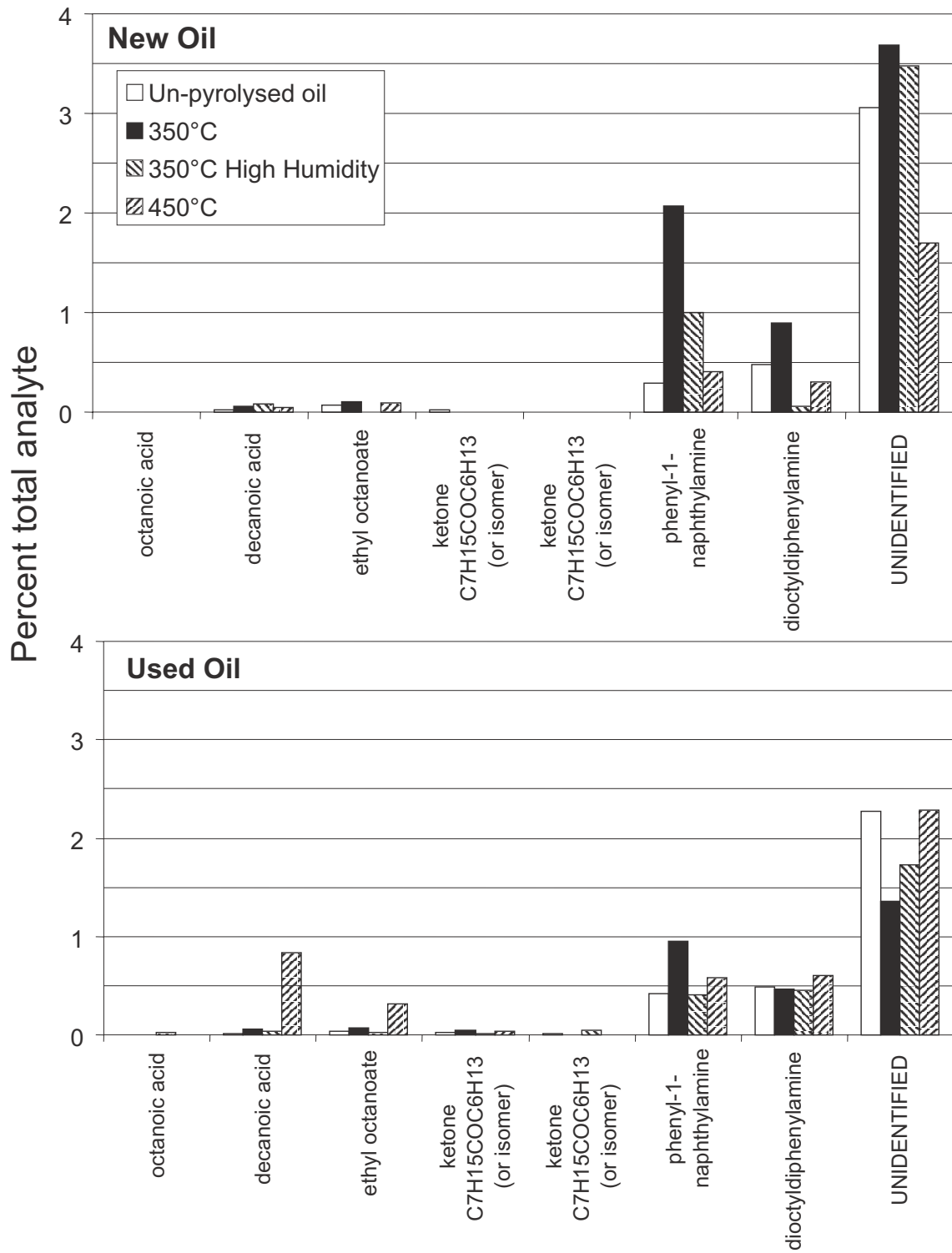


Figure 4 Organic acid, ketone and amine contaminants identified by GC-MS in pyrolysis products of new and used oils. Details of methods of pyrolysis and analysis are given in Marshman (2001) (Data used is the property of BAE Systems)

Chapter 2 Analysis of Aircraft Air-conditioning Duct Contaminants (UC)

1 Introduction

In recent years a variety of symptoms have been reported among flight and cabin crew of civil airlines, some of which have been associated with unpleasant odours circulated by the cabin air supply. A few of the symptoms were partially incapacitating but of short duration, it was suggested by a number of authors that these symptoms could have resulted from the leakage of oil into the engine bleed air of certain aircraft, particularly the BAe 146. This led BAE and the Civil Aviation Authority (CAA) to commission an analysis of the pyrolysis products of aviation lubricants by the Defence Evaluation and Research Agency (DERA) [1] and an assessment of their toxicity by the Defence Science and Technology Laboratory (Dstl) [2].

Subsequent to these studies the CAA supplied Dstl with three pieces of ducting taken from BAe 146 aircraft air conditioning systems; one brand new duct, one from an aircraft with a history of odours but no reported crew symptoms, and one from an aircraft with a history of odours and reported crew symptoms. This report describes a series of experiments to determine if any material could be found in the ducts which was not present in the pyrolysed oil and if this material could evaporate into the airflow of the air conditioning system when humid air was passed through the duct.

The analyses described in this report were carried out in a United Kingdom Accreditation Service (UKAS) accredited laboratory using approved methods and the full analytical report is included in Appendix A.

2 Supplied Materials

Three BAe 146 environmental control system ducts were supplied by the CAA for analysis by Dstl:

- Duct 1 - An unused duct supplied brand new from BAE Systems
- Duct 2 - A used duct removed from an aircraft with a history of cabin odours but no reported crew symptoms, the duct had accumulated 26,061 flight hours
- Duct 3 - A used duct with a history of cabin odour events some associated with symptoms in crew, the duct had accumulated 25,315 flight hours [3].

The used ducts had been installed downstream of the environmental control system air-conditioning packs and were contaminated by a layer of black material consistent with carbonaceous deposits from burned fuels and lubricants. The ducting was removed from the aircraft some weeks before analysis could be carried out and although bagged and sealed in plastic, the possibility that volatile materials present during operation may have evaporated during the intervening period cannot be discounted. Upon receipt by Dstl the used ducting had a slightly oily odour reminiscent of burnt oil, or the volatile components of diesel fuel. Further descriptions of the ducts are given in the analysis report at Appendix A.

This report describes the results of analyses of the chemicals extracted from the carbonaceous deposits on the inside of the ducts and the insulation material of the ducts. Chemicals in these deposits could have been absorbed onto the carbon

particles in the airflow prior to deposition or directly from the air flowing through the ducts after deposition.

3 Methodology

The detailed methods used to analyse the ducting are given in Appendix A, these were chosen to detect the widest range of chemical entities possible.

The following tests were carried out:

- a) **Electron Microscopy:** This gives an image of the surface of the duct at high magnification enabling some conclusions to be drawn concerning the type of particles present. The electron microscope can also give an atomic absorption spectrum of the identified particles. This will identify the elements present but not their molecular form (e.g. it will identify sodium and chlorine, but not sodium chloride).
- b) **Solvent Extraction:** For this process a solvent is used to remove all organic material, whether this material is capable of evaporating from the surface of the duct into an airflow or not. The solvent extracts containing possible contaminants were analysed by gas chromatography (GC) which separates the various chemicals in the mixture. This analysis was combined with either a flame photometric detector (FPD), which detects phosphorus containing compounds only, or a mass spectrometer (MS). The mass spectrometer gives information on the molecular structure of each chemical in the gas chromatogram. Combining the length of time that any chemical is retained on the GC (retention time; *tr*) and its molecular weight is a very powerful method of identifying the chemicals in any mixture. In this study, only the FPD detector gave the amount of chemical present, the MS was set to give qualitative information on the identity of the chemical, not the amount present. These are the most reliable and sensitive analytical methods currently available for the separation and identification of unknown mixtures of chemicals.
- c) **Thermal Desorption-Gas Chromatography-Mass Spectrometry - of Nitrogen Gas Extraction:** For this process a portion of ducting was heated in a flow of nitrogen gas in order to analyse only those components which were capable of evaporating from the surface into the airflow of the air conditioning system. Two temperatures were used in experiments to measure these volatile compounds: 70°C and 350°C. For the 70°C tests, portions of ducting were heated to 70°C in a chamber under a flow of nitrogen gas. The nitrogen was then passed through a sorbent tube which absorbed volatile chemicals for analysis. For the 350°C tests, samples of the particulate materials lining the ducting were heated to 350°C in a thermal desorption tube in order to force all volatile and semi-volatile chemicals off the particles and into the gas flow. For all tests the sorbent tubes and samples of nitrogen gas containing possible contaminants were analysed by gas chromatography (GC), using flame photometric detection (FPD) and mass spectrometry (MS).
- d) **Thermal Desorption-Gas Chromatography-Mass Spectrometry - Hot Humid Air Extraction:** For this process portions of ducting were sealed in a manifold in a climatic chamber. Air in the temperature range 27°C to 100°C and humidity range of 25% to 100% was passed over the duct. The exhaust stream was sampled and analysed using thermal desorption gas chromatography mass spectrometry (TD-GC-MS). Temperature and humidity conditions were chosen to represent normal and abnormal operating conditions of aircraft environmental control systems. Details of the temperature and humidity concentrations are contained in Appendix A Part 2.

- e) **Odour Characterisation:** After chemical analysis had been carried out the ducts were packaged in plastic bags and stored in a cardboard carton. After 15 weeks, the authors compared the odour of the used ducting with that of pure samples of various chemicals detected in the extracts of the ducts. A qualitative identification of the odour in the ducting was made.

4 Results

The detailed results are contained in Appendix A.

4.1 Electron Microscopy (EM)

The inner surface of duct 1 contained only carbon, chlorine, calcium and copper and reflected the composition of the materials used in construction of the duct. The inner surface of ducts 2 and 3 gave large peaks for aluminium and silicon and smaller peaks for sulphur, phosphorus, iron, potassium, titanium, chromium and magnesium in addition to the carbon, chlorine, calcium and copper found in duct 1. The speciation of these additional elements is unknown but they are likely to exist as the native element or non-volatile chemical compounds. All of these elements are present in both new and used aviation lubricants as detailed in reference [4]. They are also found in ambient air. The higher concentration of these elements in the lining of used ducts than in oil indicates either a concentration on the duct lining over a period of time or an additional source of contamination. The detailed results from the EM are detailed in Appendix A paragraph 2.

This supports the thesis of synthetic lubricating oil as the source of exposed duct contamination.

4.2 Solvent Extractions

The GC-FPD analysis of the solvent extracts found tricresyl phosphate isomers (TCP), including the ortho isomer which were quantitated in the used duct extracts. The $\mu\text{g/g}$ amounts of the ortho-isomer are unlikely to exhibit toxicological effects.

The GC-MS analysis of the solvent extracts of both used duct samples showed similar results. The compounds identified, in addition to TCP, were oxygenates likely to be derived from synthetic ester turbine oil during pyrolysis. Extracts of unused duct did not contain any compounds found in extracts of used ducts, with the exception of materials used in the construction of the ducting.

A detailed list of the chemicals found in the solvent extracts from each piece of ducting is given in the analytical report (Appendix A paragraph 3). All the chemicals found were consistent with pyrolysis products of aviation lubricant and its additives. The small molecules found by solvent extract are tabulated in Table 1.

4.3 Thermal Desorption-Gas Chromatography-Mass Spectrometry-Nitrogen Gas Extraction

- 4.3.1 **70°C Thermal Desorption:** No oxygenated compounds were found in the headspace of used or unused duct material. This implies that no compounds above a carbon chain length of 5 volatilise from the ducts at 70°C within the 0.5ppb limit of detection.

- 4.3.2 **350°C Thermal Desorption of Particulate Material:** Compounds identified in duct solvent extracts of ducts 2 and 3 were also identified in thermally desorbed particulate material by GC-MS analysis. In addition the thermal desorption detected furfural in the particulate material. Furfural was not found in the solvent extracts of either duct or in the native oil. One possible reason for this is the conditions employed for analysis of

the solvent extracts may have resulted in the furfural signal, if present, not being detected. Therefore the presence of furfural in the solvent extracts is possible. The unequivocal identification of furfural would require further work. The detection of compounds by 350°C thermal desorption shows that compounds may be removed from the surface of the duct at elevated temperatures.

The chemicals which were evaporated from the particulate material lining the used ducts under conditions of thermal desorption (350°C) are listed in Tables 8 & 9 of the analysis report in Appendix A. All the chemicals found were consistent with pyrolysis products of aviation lubricant and its additives. The small molecules found are tabulated in Table 1.

4.4 **Thermal Desorption-Gas Chromatography-Mass Spectrometry - Hot Humid Air Extraction**

Pieces of duct were subjected to varying temperature and humidity conditions. No volatile materials were detected in the air stream above the limit of detection of 0.5ppb. This supports the data obtained when samples were extracted using nitrogen gas, in that no compounds were desorbed from the ducting even at temperatures and humidities similar to those likely to be found in an aircraft ECS within the 0.5ppb limit of detection.

4.5 **Odour Characterisation**

After the analysis had been completed the ducting was packed in plastic (not sealed) and returned to the cardboard carton in which it was received. After 15 weeks, the authors sampled the contents of the plastic packing by smell and then compared the odour qualitatively to that of several of the low molecular weight organic acids. In the opinion of both authors the duct material smelt strongly of pentanoic acid, but may have had other organic components present in the headspace. There was little odour of hexanoic or heptanoic acids, but these may have been present at low levels.

5 **Toxicological Interpretation**

5.1 **Definition of Toxic Effects**

A toxic effect is defined as any effect on the organism which is deleterious to health. The effect does not have to be life threatening, any effect which is outside of the normal physiology for the organism can be described as toxic. Thus, irritation of the skin, eyes or respiratory tract, nausea and vomiting, dizziness or collapse are all types of toxic effect. Certain effects are sufficiently benign to be regarded as essentially non-toxic, bad odours may be one example of this (see below for further discussion).

5.2 **Toxicity and Odour**

The relationship between toxicity and odour is not a simple one. Though odours can be very useful in determining the presence of a particular gas or vapour in the environment, the variable relationship of odour threshold and the minimum concentration which will produce toxic effects renders odour an unreliable indicator of toxicity. An odour can be very pungent and warn of the presence of the compound well below toxic concentrations (e.g. pyridines or hydrogen sulphide) or there may be no odour at all (e.g. carbon monoxide). Similarly, the presence of an odour alone is not necessarily indicative of a toxic effect (e.g. perfume odorants).

5.3 **Comments on Compounds Listed in Table 1**

The chemicals present in the solvent and nitrogen gas extracts of the ducting were present in the pyrolysed oil and their toxicology has been previously reviewed [1, 2].

In Chapter 1 it was determined that the pentaerythritol and trimethylpropane esters are not toxic [5-7], which may be due to their large molecular size, and no significant inherent toxicity of these molecules has been reported in the literature. The smaller, more volatile, molecules are most likely to be the cause of any toxic effects and odours in the cabin air. From all the compounds detailed in Appendix A the smaller molecules found have been tabulated in Table 1 plus one of the higher molecular weight compounds with known toxicological effects. Discussion of the toxicology of compounds in Table 1 now follows.

In assessing the possible effects of the Table 1 chemicals in the cabin air environment it would be necessary to know the quantity of contaminant people would be exposed to. Other than for tricresyl phosphate (TCP), the current study can give no estimate of the possible concentrations of these compounds in cabin air, which makes it impossible to conclude if they are responsible for the symptoms observed. The subsequent review (other than for TCP) is limited to the inherent toxicities of the compounds and their presence in the lining of the ECS ducting should not be interpreted as evidence of causality for any event occurring in the cabin.

Tricresyl phosphate (TCP) was found in the solvent extracts of the duct (Test 2 detailed earlier in the report). The TCP content of the unused oil and material lining the supplied ducts was quantified by GC-FPD to establish the TCP content in $\mu\text{g/g}$ of oil or duct (see Appendix A Table 1). Meta and para isomers of tricresyl phosphate, in addition to the triortho isomer (which is only just detectable in the original oil), were found in the contaminant lining the used ducts in concentrations higher than the parent oil. This increase in TCP concentration implies the duct has absorbed oil, and hence TCP over a period of time and retained the TCP in preference to the other oil constituents. However, comparable concentrations were not found when the ducts were extracted using nitrogen gas (70°C), supporting the conclusion that some tricresyl phosphate would be absorbed by the ducts. Due to its involatile nature, it is unlikely that TCP will be released back into the air stream. This is supported by the absence of TCP in air sampled during the temperature and humidity trial.

In the previous studies of pyrolysed oil carried out at DERA Pyestock [1] no tri-orthocresylphosphate (TOCP) was detected because the GC-MS method used was very much less sensitive than the GC-FPD method used in this study. Given the established toxicity of TOCP and the "worst case scenario" (i.e. assuming all of the TCP present is as toxic as TOCP) an "average" 70kg man could eat approximately 7000 kg of pyrolysed oil per day for 74 days and still be free of the organophosphate induced delayed neuropathy (OPIDN) associated with TOCP (calculation detailed at Appendix C). A 1g.m^{-3} aerosol of oil is a heavy, visible mist, if inhaled at 15 L.min^{-1} (the volume of air inhaled by the average man at rest) for 24 hours would give a total inhaled dose of 22g. An individual could inhale 300 times this amount and still not inhale a dosage that would cause OPIDN. Though oral toxicity estimates would not normally be used to estimate inhalation toxicity, the doses here are so large that (without an indication of a direct effect on the lungs) it is inconceivable that the TOCP in pyrolysed oil or in the ECS duct lining could cause OPIDN in aircraft crew or passengers.

Very little toxicological data was available for the other compounds listed in Table 1 with the exception of furfural and 4-methylphenol (a.k.a. p-cresol). The descriptions of the toxic effects listed are the best estimates from limited data and should be interpreted as such. Almost no information could be located on the toxicity of 2-ethylacrolein, but what is available indicates that it is not as irritant as non-substituted acrolein.

In order for a chemical to have an occupational exposure limit set (TWA or IDLH in Table 1) by regulatory authorities, it must be used industrially and be of known toxic hazard. Chemicals for which there is no exposure limit set may still be toxic but not be encountered in the workplace, or be sufficiently toxic, to warrant regulation beyond the principle of control to the lowest possible exposure. Where occupational exposure limits have been set they are a guide to what best scientific knowledge indicates is a level of exposure where toxic effects will not be manifest. Other than TCP, which has been discussed above, two of the chemicals identified in this study have occupational exposure standards set, furfural and 4-methylphenol. No study to date has produced sufficient information on the concentrations of these two chemicals in pyrolysed oil or on the duct linings to enable an estimate of the likely exposure in a cabin air environment.

The organic acid, octanoic acid, (this was also identified in references [1] and [2]) is a possible irritant chemical. The irritancy associated with octanoic acid is also associated with other acids of the series, in this case pentanoic, hexanoic, heptanoic, nonanoic, and decanoic acids. Pentadecanoic acid and hexadecanoic acid are less irritant though their toxicology has not been fully investigated. All these acids are expected breakdown products of the pentaerythritol and trimethylolpropane esters which make up the lubricant.

Symptoms of exposure to an irritant by inhalation are initially itching eyes (usually by direct action on the eye), lachrymation (running nose and tearing), itching and soreness to the nose and throat. As the exposure time or concentration increases coughing and shortness of breath associated with constriction of the airway becomes evident and this can lead to dizziness and collapse. Exposure to very high concentrations can cause all the above, and nausea and vomiting in extreme cases. It is an important note that the results of the present study give no indication of the likely concentrations of any of the compounds measured in the cabin air of effected aircraft.

There were no chemicals present in the duct associated with symptom reports (duct 3) which were not present in the duct associated with odours but no symptoms (duct 2). 2,4,4-trimethyl-1-pentene and octanal were present in the duct with no symptom reports but were not present in the duct with symptom reports.

5.4 **Comments on Trimethylolpropane Phosphate (TMPP)**

Suggestions made in previous publications of the possible involvement of trimethylolpropane phosphate (TMPP) [8, 9] and diacetylbenzene [10-13] in aviation lubricant pyrolysis products, prompted specific scrutiny of the analytical results for these chemicals. Neither TMPP nor diacetylbenzene were found (above the limit of detection, 0.5 ppb) in any of the analyses from used or unused ducts under any conditions used in these tests.

6 **Chemicals Responsible for Odour in the Ducts**

The odour associated with the ducts 15 weeks after the analysis was very similar to that of pentanoic acid, and the reported acrid, or sweaty, odour is a good description of the odour of this compound. However, pentanoic acid was only detected in the solvent extracts of the ducts, not in the air flow over the ducts during experiments to replicate the conditions of humidity (70°C, 100%RH). This is because the sorption tube used to sample the air flowing over the duct samples only absorbed chemicals with a carbon chain length of 6 or greater, and pentanoic acid has a chain length of 5. Pentanoic acid could therefore have been present in the air of the thermal desorption test and the hot humid test and not been captured by the sampling method.

The odour of the ducts does however raise the following questions:

- a) Are there other chemicals in the lining of the ducts that could also be responsible for the odour?

The descriptions of the odours reported in cabin air "rancid and sweaty" implicate the low molecular weight organic acids. Of these the most likely candidate, based upon the odour of the pure material, is pentanoic acid which was found to be very similar to the odour in used ECS ducting. The presence of other low molecular weight organic acids such as butyric acid and hexanoic acid in pyrolysed oil and in the duct air, which could contribute to the odour, cannot be completely excluded on the basis of analyses carried out to date.

- b) Could odorant chemicals be present above their odour threshold but below the limit of detection of the analytical methods used in this study?

Essentially no, since the limit of detection in this study was 0.5 ppb, all the chemicals, for which an odour threshold is available, would have been detected analytically at concentrations too low to be detected by their odour.

- c) Could there be any chemicals present at concentrations which might cause intoxication below the limit of detection which could be of concern?

Dstl know of no chemical which could conceivably be present in cabin air from aviation lubricant which could produce the reported symptoms at a concentration of less than 0.5 ppb ($\sim 0.5 \mu\text{g}\cdot\text{m}^{-3}$). Any chemical producing toxic effects at these concentrations would be extremely toxic and it is unlikely that its toxicity would not have been characterized in other studies.

7 Further Discussion of Odour

It is important to note that it is not possible to conclude with certainty if any of the chemicals detected would be present at concentrations in the duct air of an operating ECS system at above their odour threshold.

The GC-MS analysis method used in this study for all chemicals other than the TCP esters was qualitative and cannot support an estimate of the concentration of any chemical. For the TCP esters, knowledge of the concentration of the chemicals in the duct lining without knowledge of the partitioning of the chemical from the duct lining into the air similarly confounds estimation of cabin air concentrations.

In conclusion, the identification of pentanoic acid as the chemical responsible for the odour of the ducting is based completely on the similarity of its odour with that of the used ducting and has not been confirmed analytically. The presence of other low molecular weight organic acids such as butyric acid and hexanoic acid in pyrolysed oil and in the duct air, which could contribute to the odour, cannot be completely excluded on the basis of analyses carried out to date.

There are chemicals (not found in these ducts) which smell so unpleasant that the odour in itself will cause a violent reaction, usually dizziness, nausea, vomiting and possible transient loss of consciousness (fainting). It is, however, unlikely that such an agent alone is responsible for the symptoms reported in cabin air quality incidents, since personnel would consistently report the odour before symptoms and there is little correlation between odour and symptom reporting.

8 Conclusions

- 8.1 The two pieces of used ducting were contaminated with a carbonaceous material containing chemicals entirely consistent with the pyrolysis products of synthetic aircraft lubricating oil.
- 8.2 The unused duct contained no detectable toxic compounds. The used ducts were similar in chemical composition. Both ducts contained compounds consistent with synthetic-ester turbine oil contamination.
- 8.3 No evidence of the volatilisation of the compounds identified on the surface of the ducting up to 100°C and 100% relative humidity above a limit of detection of 0.5 ppb could be found. Moreover, tests carried out under conditions of temperature and humidity similar to those found in an operating ECS failed to liberate any of the chemicals found in solvent extracts or by aggressive thermal desorption.
- 8.4 Some of the chemicals identified are irritants of the respiratory tract and could induce some of the symptoms reported in cabin air quality incidents. However, in the absence of any information about the concentrations of these chemicals, it is not possible to draw any conclusion about the causative agent or the cabin air quality incidents.
- 8.5 Furfural and 4-methyl-phenol both have concentrations defined, above which they are considered immediately damaging to life and health, the reason for these compounds having a limit set is because there is regular human exposure to them. Furfural for example is a common food additive. The fact that a limit exists or does not exist should not be construed as an indication of the relative toxicity of the chemical.
- 8.6 The odour of the contaminated ducting is very similar to that of pentanoic (a.k.a. valeric) acid, found in the extracts of the used ducting. Pentanoic acid is an irritant chemical and could produce the acute symptoms reported in cabin air incidents, if present at high enough concentrations. Insufficient information on concentrations present in cabin air is currently available to support any conclusion as to whether pentanoic, or a similar organic acid, is responsible for the reported symptoms.
- 8.7 In addition to compounds reported in the previous study [2], some other compounds were found in the used ducts (e.g.. ethylacrolein, TOCP). This study used a more sensitive technique to measure phosphorous containing compounds and demonstrated concentrations of TOCP in the duct linings which were previously below the LOD. Moreover, absorption and retention of chemicals from pyrolysed aviation lubricant in the carbonaceous deposit lining the ECS duct would concentrate chemicals above the LOD, resulting in the detection of previously undetected chemicals. Toxicological review of the previously unrecorded chemicals, however, revealed that they were unlikely to cause the symptoms reported.

9 Recommendations from DSTL

Further research to establish an irritant threshold for pentanoic acid in inspired air is required to determine if it may be responsible for the acute effects reported in cabin air quality incidents.

The concentrations of low molecular weight organic acids (propanoic, butanoic and pentanoic acids) in the cabin air of aircraft during flight or simulated oil leakage should be determined.

Table 1 Potential Effects of Chemicals if Encountered in Sufficient Quantity. (Summary of some Physico-chemical and Toxicological Properties of the Volatile and Semi-volatile Compounds Determined by Solvent Extraction and Thermal Desorption).

Name	Present in duct	M.Wt.	Present in previous study?	CAS No	Exposure limits	Odour threshold (ppb) [15]	Possible effects by inhalation listed in Materials Hazards Datasheets
2-ethylacrolein	2,3		N	922-63-4	None-listed	NL	Mild irritant to eyes and respiratory tract
2,4,4-trimethyl-1-pentene	2	112.22	N	107-39-1	None-listed	NL	Causes eye irritation. Respiratory tract irritation. The toxicological properties of this compound have not been fully investigated. May cause narcotic effects in high concentration. Vapours may cause dizziness and suffocation.
Furfural	2,3	96.1	N	98-01-1	TWA 5ppm (20 mg.m ⁻³) IDLH 100 ppm (400 mg.m ⁻³)	3000-23000	May cause irreversible eye injury, irritation and possible burns. Harmful if inhaled. May cause allergic respiratory reaction. Vapours may cause dizziness or suffocation. Causes irritation of the mucous membrane and upper respiratory tract.
Heptanal	2,3	114.19	N	111-71-7	None-listed	3	May cause eye irritation. May cause respiratory tract irritation. Vapours may cause dizziness or suffocation.
Pentanoic acid	2,3	186.25	N	2082-59-9	None-listed	3000	Causes eye burns, may cause chemical conjunctivitis and corneal damage. Cause chemical burns to the respiratory tract. The toxicological properties of this chemical have not been fully investigated. May cause systemic effects.
Octanal	2	128.21	N	124-13-0	None-listed	0.7	Causes irritation to the eyes, chemical conjunctivitis and corneal damage. Causes irritation to the respiratory tract. Vapours may cause dizziness or suffocation. May cause burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting. Can produce delayed pulmonary oedema.
Hexanoic acid	2,3	116.16	N	142-62-1	None-listed	3000	Causes eye burns. Causes chemical burns to the respiratory tract, effects may be delayed.

Table 1 Potential Effects of Chemicals if Encountered in Sufficient Quantity. (Summary of some Physico-chemical and Toxicological Properties of the Volatile and Semi-volatile Compounds Determined by Solvent Extraction and Thermal Desorption).

4-methyl-phenol	2,3	108.2	N	106-44-5	TWA 2.3ppm (10 mg.m ⁻³) IDLH 250ppm (1107.5 mg.m ⁻³)	NL	Irritant to eyes,
Heptanoic acid	2,3	130.19	N	111-14-8	None-listed	3000	Causes eye burns, may cause conjunctivitis and corneal damage. Causes chemical burns to the respiratory tract. Aspiration may lead to pulmonary oedema.
Octanoic acid	2,3	144.21	Y	124-07-2	None-listed	3000	Causes eye burns. Dust is irritant to the respiratory tract. Causes chemical burns to the respiratory tract. Aspiration may cause respiratory swelling and pneumonitis. Causes irritation of mucous membrane.
Nonanoic acid	2,3	158.24	N	112-05-0	None-listed	3000	Causes eye burns. Causes chemical burns to the respiratory tract. The toxicological properties of this substance have not been fully investigated.
Decanoic acid	2,3	172.72	Y	334-48-5	None-listed	10000	Causes eye irritation, may cause chemical conjunctivitis. May cause respiratory tract irritation.
Pentadecanoic acid	2,3	242.4	N	1002-84-2	None listed	NL	May cause eye irritation. May cause respiratory tract irritation. The toxicological properties of this substance have not been fully investigated
Hexadecanoic acid	2,3	116.16	N	57-10-3	None-listed	NL	May cause mild eye irritation. This material is not volatile therefore only possible to breath as a solid aerosol.
Tricresyl phosphate (mixed isomers)	2,3	Not Available	N	Not Available	0.1 mg.m ³	NL	Vapours may irritate eyes but only at high concentrations. Causes organo phosphate induced delayed neuropathy

Name

Chemical name of compound identified.

Duct

In which duct or ducts the chemical was identified.

M. Wt.

Molecular Weight (g.mol⁻¹).

Present in previous study	Whether the chemical was detected in previous studies of aviation lubricant pyrolysis products carried out by DERA and Dstl.
CAS No	Chemical Abstracts Registry number.
Exposure limits	Quoted where an occupational exposure limit has been determined. TWA – Time weighted Average – the dose to which a worker can be exposed 8 hours per day, 5 days per week without ill effect. DLH – Immediately dangerous to life or health, the concentration which will not impede escape for 15 minutes. None-listed – There is no occupational limit listed in any of the following databases ACGIH [16], NIOSH [17], OSHA [18] or EH-40 [19].
Odour threshold	The concentration at which the odour of the chemical can be detected by the human nose.
Adverse Effects	This list is an extract from the Material Safety Data Sheets published by chemical manufacturers relating to eye effects and inhalation.
NL	No odour threshold listed.

The toxicological effects listed in Table 1 are abstracted from the descriptions of toxic effects given in materials safety data sheets (MSDS) published by the chemicals industry. As such, they are drawn from a wide base of published and unpublished material but are often made up of key phrases (e.g. "may cause irritation"). There is no indication from this source of data of the concentrations that cause these effects. Moreover, the data which supports these descriptions of toxic effects have not been reviewed in detail for this Paper.

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Appendix A to Chapter 2

Analytical Report No. 0206846 Ducting Analysis

Glossary

ASE	Accelerated Solvent Extraction
CCD	Central Composite Design
EDXA	Energy Dispersive X-ray Analysis
EI	Electron Impact Ionization
EM	Electron Microscopy
FPD	Flame Photometric Detector
GC	Gas Chromatography
MS	Mass Spectrometry
TCP	Tricresyl Phosphate

Part 1: Characterisation of Analytes by GC-MS, GC-FPD, ATD-GC-MS and EM

1 General Comments on Duct Morphology

Three BAe 146 environmental control system ducts were supplied for analysis by CAA. An unused duct (duct 1), a used duct removed from an aircraft with history of cabin odours (duct 2), and a used duct with a history of cabin odour events (duct 3). The used ducts had been installed downstream of the environmental control system air-conditioning packs and had approximately 25000 flying hours of service time.

1.1 Duct 1 (Unused Duct)

Duct 1 was noticeably lighter in weight than ducts 2 and 3. The interior surface of the duct was free from particulate material. The exterior surface was uniform in colour with no visible staining of the outer layer (Figure 1). There was no significant odour associated with this duct.

1.2 Ducts 2 and 3 (Used Ducts)

These ducts were heavier than duct 1. The interior surface of the ducts was coated with a film of black particulate material which could be dislodged easily. The particulate material gave a translucent stain when placed on a piece of white paper suggesting the presence of oil. The exterior surfaces of the ducts were stained with a 'tidemark' of a dark brown colour. On cutting the duct open, the lagging was found to be saturated with a green/yellow liquid which could be mobilised by applying gentle pressure to the duct (Figure 2). Both ducts had an associated acrid odour.

2 Electron Microscopy

Samples for examination and analysis were made by cutting small pieces from the inner surface of the ducts and scrapings from the inner surface of ducts 2 and 3. The samples were mounted onto standard specimen stubs and analysed by energy dispersive X-ray analysis (EDXA) using an Hitachi S2700 scanning electron microscope fitted with a Link Systems thin window detector. The specimens were then coated with 40nm gold using an Anatech sputter coater and examined and photographed in an Hitachi S800 scanning electron microscope. All micrographs were taken at the same magnification for ease of comparison. Micrographs have been compiled in Annex A.

EDXA provides information on the elements present in the sample from boron upwards in the periodic table. This technique gives no indication of the speciation of the element, i.e. the form of the element. Samples are prepared under vacuum therefore elements like chlorine and sulphur, which are volatile, will be present as compounds and not the native element. Metal such as aluminium and copper may be present as the native metal or as chemical compounds.

2.1 Duct 1

The inner surface of the duct consists of a woven fabric. Micrograph 186801 shows a portion of the weave showing several extruded flattened fibres twisted together and then woven. The individual fibres are approximately 20 µm in diameter. The spectrum from the fibres shows a large carbon peak and smaller peaks for chlorine and calcium.

The outer surface of the duct consists of a fleece of small non-woven fibres. There are droplets along the length of some fibres and there are also areas where there is an adhesive gluing fibres together. The spectrum from the inner surface gives similar

peaks to that from the outer surface but with the addition of a small amount of silicon, sulphur and copper.

The unused duct has an inner surface of a woven fabric and an outer surface of a non-woven fabric the structure of which can be seen in micrographs 186801 and 186901. On analysis the only elements present in the material are carbon, chlorine, calcium, silicon sulphur and copper.

2.2 **Duct 2**

The inner surface of the duct material is covered with a mass of black material so that only a few of the fibres from the woven fabric are visible.

The outer surface is not as clogged as the inner surface but there are areas where the fibres are covered with material and glued together. Some of the material from the inner surface was scraped off and micrograph 187201 shows the structure of the scrapings. The scrapings were analysed by EDXA and the spectrum shows large peaks for aluminium and silicon and smaller peaks for calcium, phosphorus, sulphur, iron, carbon, potassium, titanium, chromium, chlorine and magnesium. The spectrum from the inner surface of the duct is similar to that obtained from the scrapings.

2.3 **Duct 3**

The micrographs and spectra from this duct are very similar to those from duct 2. As in duct 2 the inner surface is covered in a thick black layer so that few of the fibres from the woven fabric can be seen. The outer surface has areas where the non-woven fabric fibres are glued together. Energy dispersive X-ray analysis gives the same elements present as in duct 2 for both the inner surface and the scrapings. The peaks for several of the elements present on this duct are larger than those seen on duct 2.

2.4 **Summary of Electron Microscopy Analysis**

In conclusion, in ducts 2 and 3 the inner woven surface is clogged with a mass of black material and this can also be seen to a smaller extent on the non-woven outer surface. Analysis the inner material and scrapings from the inside of the ducts give large peaks for aluminium and silicon and smaller peaks for sulphur, calcium, phosphorus, iron, carbon, calcium, potassium, titanium, chromium, copper, chlorine and magnesium. The inner surface of duct 1 contained only carbon, chlorine and calcium and copper and will therefore reflect the composition of the materials used in construction of the duct.

The used ducts show enhanced levels of aluminium, silicon, sulphur, phosphorus, iron, potassium, titanium and chromium compared to the unused duct suggesting contamination by a source or sources of these elements. The speciation of these elements is unknown but they are likely to exist as the native element or non-volatile chemical compounds. Possible sources of these elements in the used ducts are ambient air and oil leakage.

3 Solvent Extraction of Ducting

Solvent extraction involves agitating the sample with an organic solvent. Compounds in the sample which are soluble in the organic solvent are dissolved and can be analysed by GC. This allows the organic compound composition of the sample to be determined.

Pre-weighed pieces of ducting were extracted with 5 ml of solvent (dichloromethane, methanol or hexane) and shaken vigorously for 30 mins. The solvent was filtered

through a 0.45 μm filter and diluted for analysis by GC-MS and GC-FPD. ASE was also used to extract samples with 25 ml dichloromethane under increased temperature and pressure. Oil samples were diluted to a concentration of 2 mg/ml prior to analysis by GC-MS or GC-FPD.

3.1 **GC-FPD**

Gas chromatography (GC) involves volatilising sample components into a flow of inert carrier gas. The components then come into contact with an analytical column coated with a stationary phase. The degree of interaction of the sample components and the stationary phase determines the degree of retention of the components on the column and gives rise to characteristic retention times.

There are numerous detectors available for GC analysis. The flame photometric detector (FPD) can be configured to specifically detect phosphorous or sulphur. In this study GC-FPD was used to screen samples for potentially toxic organophosphorous compounds.

Figure 3 shows that duct 1 gave only a phosphorous signal for the internal standard (triphenyl phosphate) by FPD. Extracts of ducts 2 and 3 gave four strong phosphorous signals by FPD (Figures 4 and 5), indicative of four phosphorous containing compounds. The retention time of a compound is a result of its structure and volatility. Comparison of samples with reference standards gives a match for retention time and therefore aid in identification of an unknown compound. Mass spectra were obtained for three of these compounds in duct 2 and 3 extracts and compounds identified as isomers of TCP as shown in Table 1. The ortho, meta and para isomers were quantified by calibrating the GC-FPD system with pure standards of each isomer.

Reference to Table 1 indicates that similar amounts of each isomer are extracted by each of the solvents employed. Similar concentrations are also obtained by shaking the duct sample in solvent (mild extraction technique) and by use of ASE (aggressive extraction technique). This suggests that TCP isomers are soluble in solvents spanning a broad range of polarities under relatively mild conditions. Thus TCP isomers are likely to be readily dissolved from the walls of the duct when in contact with a suitable organic solvent or solvating medium.

Table 1 also indicates that the mass of each TCP isomer (μg) per g of oil or ducting sample varies greatly. The levels of TCP isomers are far greater in samples of ducting than in unused and used oil which suggests the duct material is acting as a removal and concentration structure for this compound. Thus the duct can remove TCP and other engine oil related compounds, but these compounds are potentially available to re-dissolve in the air stream.

In order for TCP to be redissolved in the air stream, air containing a significant organic component (aerosolised liquid or vapours) would have to be present due to the low solubility of TCP in water, i.e. TCP may not dissolve to any great extent in moist or dry air. From this observation and the actual low quantities of o-TCP present in duct extracts, no significant toxicological effect would be observed in flight crew.

3.2 **GC-MS**

Unlike FPD, mass spectrometric detection (MS) is used to identify molecules containing a variety of elements. The chromatographic principles are the same as in the FPD, but the MS functions by ionising sample molecules. This is accomplished by collision of high energy electrons with the sample molecules causing the molecules to fragment into charged particles or ions. The resulting fragmentation pattern of a

compound is akin to a fingerprint and hence can be used to determine the structure of the molecule. Comparison with databases of fragmentation patterns is also useful.

Extracts were analysed on 60 and 30m columns following a ten-fold dilution. EI spectra were recorded and compared against databases at QinetiQ, Pyestock. The extract of duct 1 was found to contain few compounds, which were identified as synthetic esters. Extracts of ducts 2 and 3 contained numerous compounds. The identity of these compounds was tentatively established by comparing spectra for each of the peaks on the chromatograms against the QinetiQ FLC custom libraries. Tables 2-6 list the compounds found in each extract. Table 7 details the compounds found in diluted Exxon turbine oil and oil samples analysed previously by QinetiQ, Pyestock before and after pyrolysis trials. The compounds listed are common to all oils analysed.

Figures 6 and 7 allow comparison of unused Exxon turbine oil and a dichloromethane extract of duct 3. It is evident that the samples contain many of the same compounds. Figure 7 suggests that the solvent extract contains more lower molecular weight compounds than the Exxon oil. This could be due to decomposition of the oil. This is supported by the presence of alkanolic acids (carboxylic acids) in the extracts which are the primary degradation products of synthetic esters. Carboxylic acids can exhibit irritant effects in individuals. The levels found in duct extracts are unlikely to cause irritation.

3.3 **Headspace-GC-MS**

Headspace analysis is used to investigate the release of highly volatile compounds from a sample. The sample is heated to a moderate temperature (~70°C) and the released compounds analysed by GC-MS.

Pieces of duct were placed inside a headspace tube and heated to 70°C under a flow of nitrogen. The evolved vapour was transferred to a GC-MS system and compounds identified by comparison with databases.

Only long chain alkanes were found in the headspace of each of the duct samples indicating that heavier turbine oil derived components were not purged from the exposed ducting under these conditions. Long chain alkanes are ubiquitous compounds found in almost all organic based materials. They have little or no known toxicity to humans, therefore their presence in cabin air samples is of no consequence in a toxicity study.

3.4 **Thermal Desorption GC-MS**

Thermal desorption involves heating a sample to elevated temperatures in a stream of inert carrier gas. Volatile and semi-volatile components will be removed from the sample and are analysed by GC-MS.

Particulate material from ducts 2 and 3 was thermally desorbed at 350°C and vapours analysed by GC-MS. Two groups of compounds were easily identified (Figure 8). A group composed of alkanolic acids, aldehydes and ketones was observed with retention times between 10 and 15 minutes and a group of TMP/pentaerythritol esters between 20 and 30 minutes. The identification of the individual TMP/pentaerythritol esters was not possible since these spectra were not compared to the QinetiQ databases. The chemical composition of the desorbed vapour is detailed in Tables 8 and 9. This indicates that the particulate material is comprised of a mixture of decomposed and non-decomposed turbine lubricating oil.

As indicated previously, alkanolic acids and ketones may have an irritant effect on humans. There is little known about the toxicity of TMP/pentaerythritol esters.

Part 2: Characterisation of Analytes Desorbed from Ducting under Varying Temperature, Humidity and Time of Airflow

Pieces of ducting (2x2 cm) were sealed in a PTFE manifold in a climatic chamber. Air of varying relative humidity was delivered via stainless steel tubing to the assembly while the chamber was maintained at a set temperature. A portion of the exhaust stream was sampled onto a tube containing Tenax TA allowing adsorption of released vapour phase components. This polymeric material will generally trap molecules composed of six carbon atoms and higher but some polar analytes and molecules of less than six carbon atoms may pass through the tube without adsorption. The flow rate of the sampling pump was varied to ensure the same air volume was sampled during each experiment (20 litres). A drying trap was employed to minimise the amount of water reaching the sampling tube. The experimental matrix is shown in Table 10.

The experimental strategy used CCD which allows the interaction of the variables to be elucidated using peak areas as response measurements. This approach required only 20 experiments which is considerably fewer than would be required to investigate the system using a sequential approach. These 20 experiments were performed for ducts 1, 2 and 3.

No compounds were found above the instrumental noise for the set of experiments applied to duct 1. Ducts 2 and 3 yielded more compounds compared to duct 1, but no oil-related compounds, only long chain alkanes (not reported). Therefore it is reasonable to conclude that no oil components were volatilised from the ducting under the conditions employed in this study. The limit of detection for this method was estimated to be 0.5 µg/m³.

Table 1 Identity and Quantity of Phosphorous Containing Compounds in Solvent Extracts of Ducts 2, 3 and Oil Samples

Sample	Dstl Laboratory Sample Number	Concentration of TCP (µg/g Oil or Duct)		
		Ortho-isomer	Meta-isomer	Para-isomer
Exxon turbine oil		0.002	0.138	0.044
Pre-test oil from Pyestock trial		0.001	0.137	0.044
Post test oil from Pyestock trial		0.001	0.145	0.044
Engine oil from aircraft		0.002	0.149	0.047
Duct 1, hexane extract	0206846r01	<LOD	<LOD	<LOD
Duct 1, dichloromethane extract	0206846r02	<LOD	<LOD	<LOD
Duct 1, methanol extract	0206846r03	<LOD	<LOD	<LOD
Duct 2, hexane extract	0206847r01	0.6	28.1	0.8
Duct 2, dichloromethane extract	0206847r02	0.8	39.4	1.4
Duct 2, methanol extract	0206847r03	0.5	23.1	1.1
Duct 3, hexane extract	0206848r01	0.9	68.1	3.5
Duct 3, dichloromethane extract	0206848r02	0.6	55.8	7.1
Duct 3, methanol extract	0206848r03	0.6	44.7	3.1
Duct 1, ASE/dichloromethane extract	0206846r04	<LOD	<LOD	<LOD
Duct 2, ASE/dichloromethane extract	0206847r04	0.9	35.8	2.5
Duct 3, ASE/dichloromethane extract	0206848r04	1.0	67.4	8.1

<LOD concentration less than 0.001 µg/g duct

Table 2 Compounds Identified in 6846r04 (Hexane Extract of Duct 1)

Retention Time (mins)	Peak ID
13.560	799 TMP ester
13.840	799 TMP ester
14.052	799 TMP ester
46.862	999 TMP ester

Table 3 Compounds Identified in 6846r06 (Methanol Extract of Duct 1)

Retention Time (mins)	Peak ID
13.855	799 TMP ester
13.948	799 TMP ester
14.081	799 TMP ester

Table 4 Compounds Identified in 6846r07 (Dichloromethane ASE Extract of Duct 1)

Retention Time (mins)	Peak ID
13.535	799 TMP ester
13.748	799 TMP ester
14.040	799 TMP ester

TMP = trimethylolpropane

Penta = pentaerythritol

The numbers preceding the base ester name indicate the acid chain lengths attached to the central alcohol.

Due to the similarity of many of the EI spectra for the esters it is impossible to be totally certain of the exact chain length make up of the finished ester.

No ester or other peaks were found in the dichloromethane extract of this duct

Table 5 Compounds Identified in 6847r04-6847r07 (Solvent Extracts of Duct 2)¹

Retention Time (mins)	Peak ID	Retention Time (mins)	Peak ID
9.87	pentanoic acid	32.09	4566 Penta ester
11.43	heptanoic acid	32.40	4448 Penta ester
12.13	octanoic acid	33.955	4444 Penta ester
13.4	decanoic acid	34.34	4469 Penta ester
15.46	isopropyl myristate	34.73	4444 Penta ester
16.63	isopropyl palmitate	35.204	667 TMP ester
17.54	556 TMP ester	36.36	4466 Penta ester
18.27	666 TMP ester	36.879	4468 Penta ester
22.057	556 TMP ester	37.98	4444 Penta ester
22.75	556 TMP ester	39.618	677 TMP ester
22.91	4444 Penta ester	39.897	4448 Penta ester
23.665	667 TMP ester	42.476	4469 Penta ester
23.94	4444 Penta ester	43.074	4448 Penta ester
25.261	4444 Penta ester	44.749	779 TMP ester
25.580	779 TMP ester	45.148	669 TMP ester
26.297	666 TMP ester	46.61	4466 Penta ester
26.590	4445 Penta ester	50.931	4468 Penta ester
28.079	4469 Penta ester	51.822	679 TMP ester
28.32	m-tricresyl phosphate	54.76	4666 Penta ester
28.624	556 TMP ester	55.730	4467 Penta ester
29.31	m,m,p-tricresyl phosphate ²	59.599	779 TMP ester
29.807	4446 Penta ester	66.79	4666 Penta ester
30.32	p,p,m-tricresyl phosphate ²	68.067	4488 Penta ester
30.937	799 TMP ester	69.623	699 TMP ester
31.45	p-tricresyl phosphate	73.84	5668 Penta ester
31.535	667 TMP ester	75.19	4488 Penta ester
31.788	4446 Penta ester		

1. hexane, methanol, dichloromethane and dichloromethane ASE extracts had the same composition
2. identity of isomer unconfirmed

TMP = trimethylolpropane

Penta = pentaerythritol

The 4444 penta ester was also present in 6847r07

Table 6 Compounds Identified in 6848r04-6847r08 (Solvent Extracts of Duct 3)¹

Retention Time (mins)	Peak ID	Retention Time (mins)	Peak ID
9.87	pentanoic acid	28.092	4469 Penta ester
11.43	heptanoic acid	28.32	m-tricresyl phosphate
12.13	octanoic acid	28.637	556 TMP ester
13.4	decanoic acid	29.31	m,m,p-tricresyl phosphate ²
14.09	799 TMP ester	29.847	4446 Penta ester
14.39	799 TMP ester	30.32	p,p,m-tricresyl phosphate ²
15.46	isopropyl myristate	30.977	799 TMP ester
16.63	isopropyl palmitate	31.45	p-tricresyl phosphate
17.138	4444 Penta ester	31.562	667 TMP ester
19.01	4444 Penta ester	31.801	4446 Penta ester
19.61	4499 Penta ester	33.955	4446 Penta ester
21.14	4449 Penta ester	35.231	667 TMP ester
21.38	4444 Penta ester	36.401	4466 Penta ester
21.990	4449 Penta ester	38.009	4447 Penta ester
22.070	666 TMP ester	39.658	677 TMP ester
22.91	4444 Penta ester	39.870	556 TMP ester
22.921	4444 Penta ester	42.436	4469 Penta ester
23.678	667 TMP ester	44.816	677 TMP ester
23.971	4444 Penta ester	45.228	669 TMP ester
24.09	4449 Penta ester	51.808	679 TMP ester
25.274	4449 Penta ester	59.652	779 TMP ester
25.593	677 TMP ester	69.622	999 TMP ester
26.603	4444 Penta ester		

1. hexane, methanol, dichloromethane and dichloromethane ASE extracts had the same composition
2. identity of isomer unconfirmed

Table 7 Compounds Identified in Samples of Oil (Common to all Oil Samples Tested from Previous Research by Qinetiq, Pyestock)

Retention Time (mins)	Peak ID
19.722	phenyl alpha naphthylamine
23.617	667 TMP ester
25.532	677 TMP ester
28.32	m-tricresyl phosphate
28.563	556 TMP ester
29.31	m,m,p-tricresyl phosphate ¹
30.32	p,p,m-tricresyl phosphate ¹
30.863	779 TMP ester
31.434	666 TMP ester
33.867	dioctyl diphenylamine
35.037	667 TMP ester
37.882	4444 Penta ester
39.411	677 TMP ester
39.676	556 TMP ester
44.595	677 TMP ester
44.941	669 TMP ester
51.548	679 TMP ester
59.365	779 TMP ester
69.375	699 TMP ester

1. identity of isomer unconfirmed

Table 8 Compounds Identified in Particulate Material of Duct 2 (from Thermal Desorption Experiment), excluding TMP and Pentaerythritol Esters (6847r08)

Retention Time (mins)	Peak ID
3.76	2-ethylacrolein
4.62	2,4,4-trimethyl-1-pentene
7.40	furfural
8.52	heptanal
9.23	pentanoic acid
9.82	octanal
9.97	hexanoic acid
10.67	4-methyl-phenol
10.82	heptanoic acid
11.64	octanoic acid
12.45	nonanoic acid
13.17	decanoic acid
19.14	pentadecanoic acid
20.18	hexadecanoic acid
24.04	m-tricresyl phosphate
24.21	m,m,p-itricresyl phosphate
24.38	p,p,m-tricresyl phosphate
24.57	p-tricresyl phosphate

Table 9 Compounds Identified in Particulate Material of Duct 3 (from Thermal Desorption Experiment), excluding TMP and Pentaerythritol Esters (6848r08)

Retention Time (mins)	Peak ID
3.78	2-ethylacrolein
7.42	furfural
8.52	heptanal
9.16	pentanoic acid
10.01	hexanoic acid
10.73	4-methylphenol
11.00	heptanoic acid
11.83	octanoic acid
12.45	nonanoic acid
13.20	decanoic acid
19.15	pentadecanoic acid
20.16	hexadecanoic acid
24.03	m-tricresyl phosphate
24.20	m,m,p-tricresyl phosphate
24.37	p,p,m-tricresyl phosphate
24.57	p-tricresyl phosphate

Table 10 Experimental Strategy for Desorption of Analytes from Ducting under Varying Environmental Conditions

Run Order	Temperature (°C)	Humidity (Relative %)	Time of Airflow (mins)
1	55	50	45
2	55	50	45
3	27	19	36
4	27	81	54
5	83	81	36
6	83	19	54
7	27	81	36
8	55	50	45
9	83	81	54
10	83	19	36
11	55	50	45
12	27	19	54
13	100	50	45
14	55	100	45
15	10	50	45
16	55	50	45
17	55	50	45
18	55	50	60
19	55	50	30
20	55	0	45



Figure 1 Section of Duct 1



Figure 2 Section of Duct 2

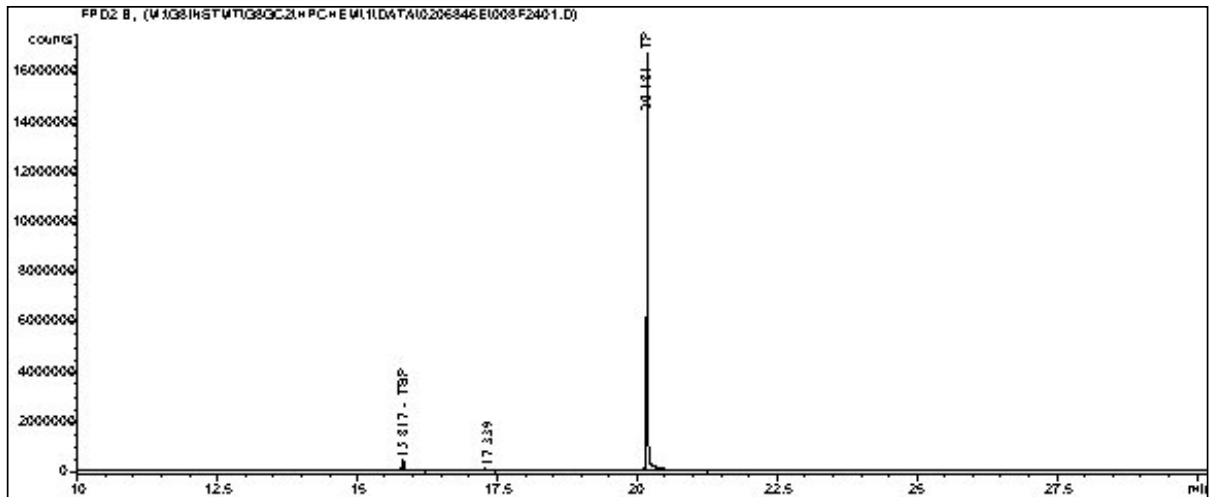


Figure 3 FPD Chromatogram of Dichloromethane Extract of Duct 1

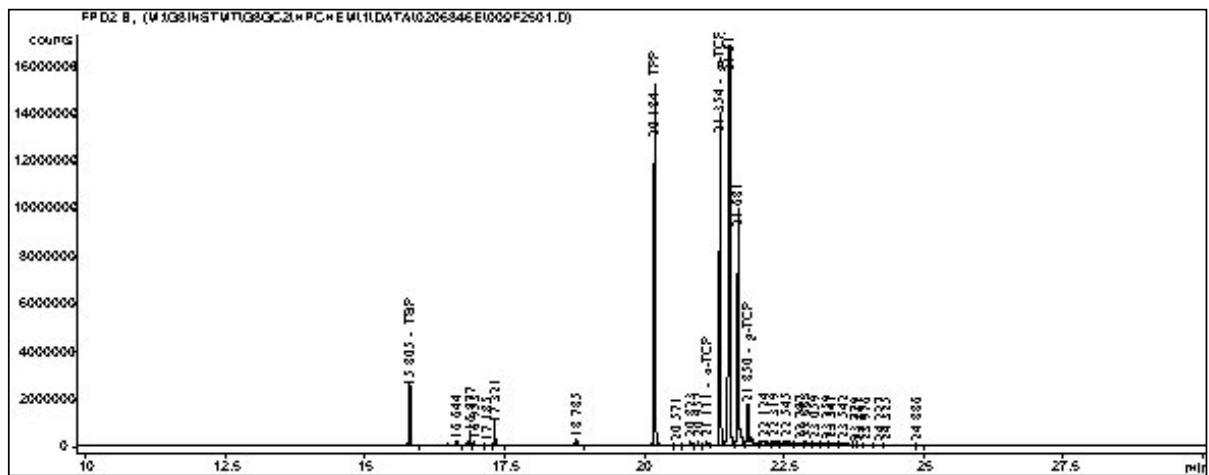


Figure 4 FPD Chromatogram of Dichloromethane Extract of Duct 2

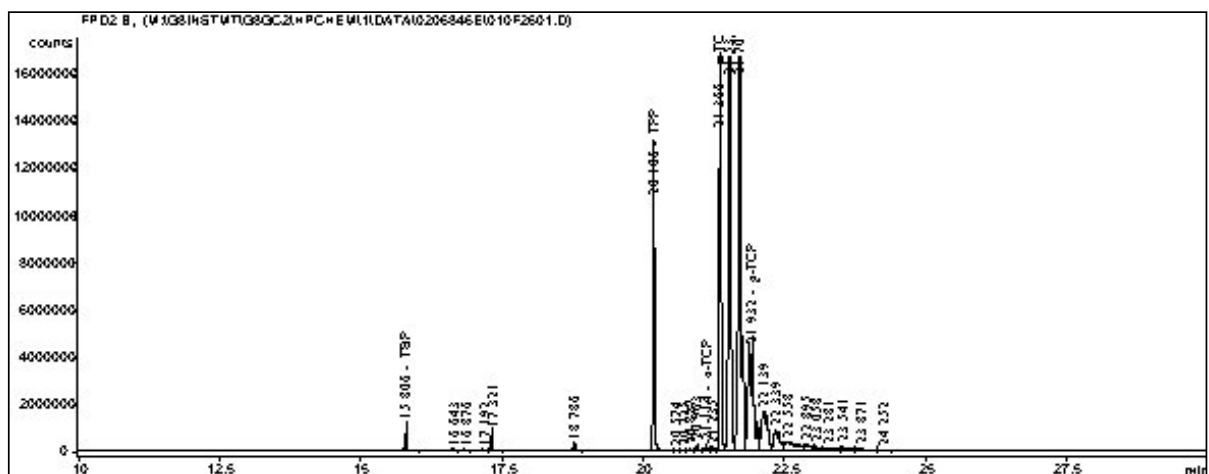


Figure 5 FPD Chromatogram of Dichloromethane Extract of Duct 3

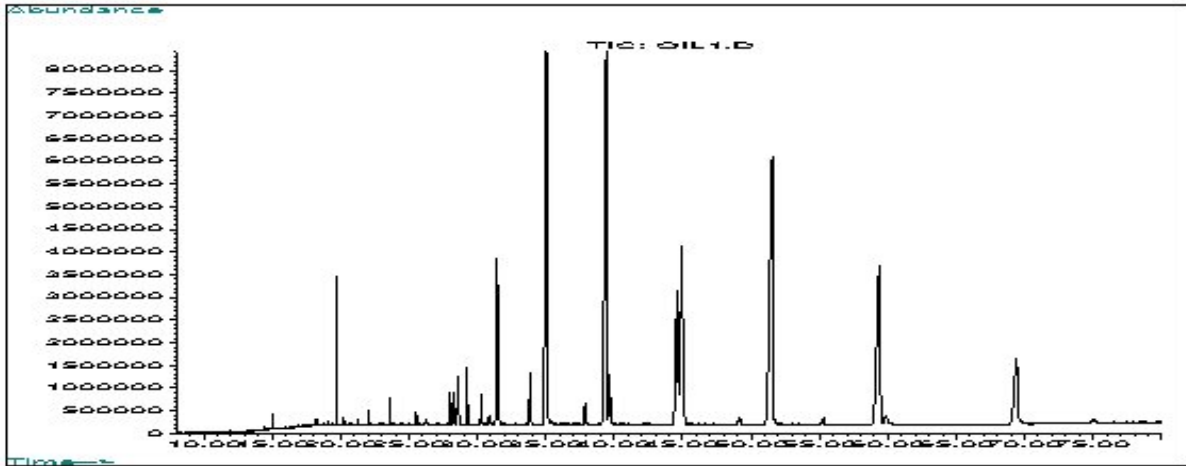


Figure 6 GC-MS Chromatogram of Unused Exxon Oil (2mg/ml)

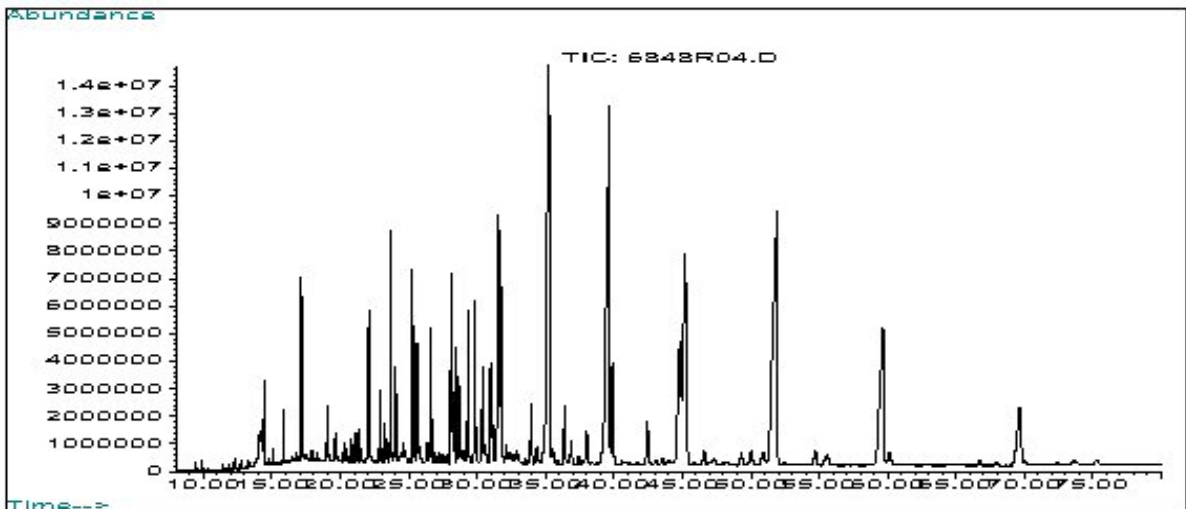


Figure 7 GC-MS Chromatogram of Dichloromethane Extract of Duct 3

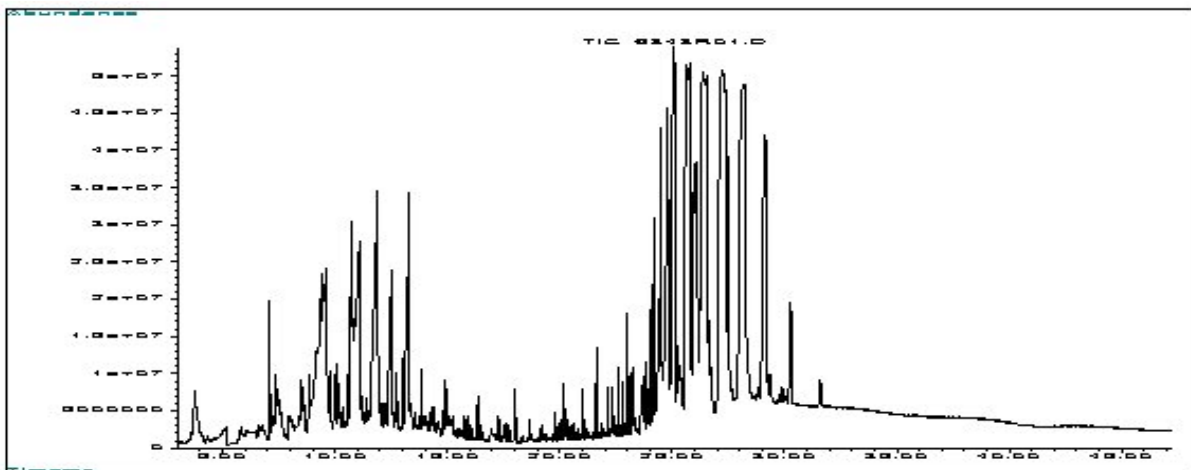


Figure 8 GC-MS Chromatogram of Thermal Desorption of Particulate Material

Appendix B to Chapter 2 Electron Microscopy Data

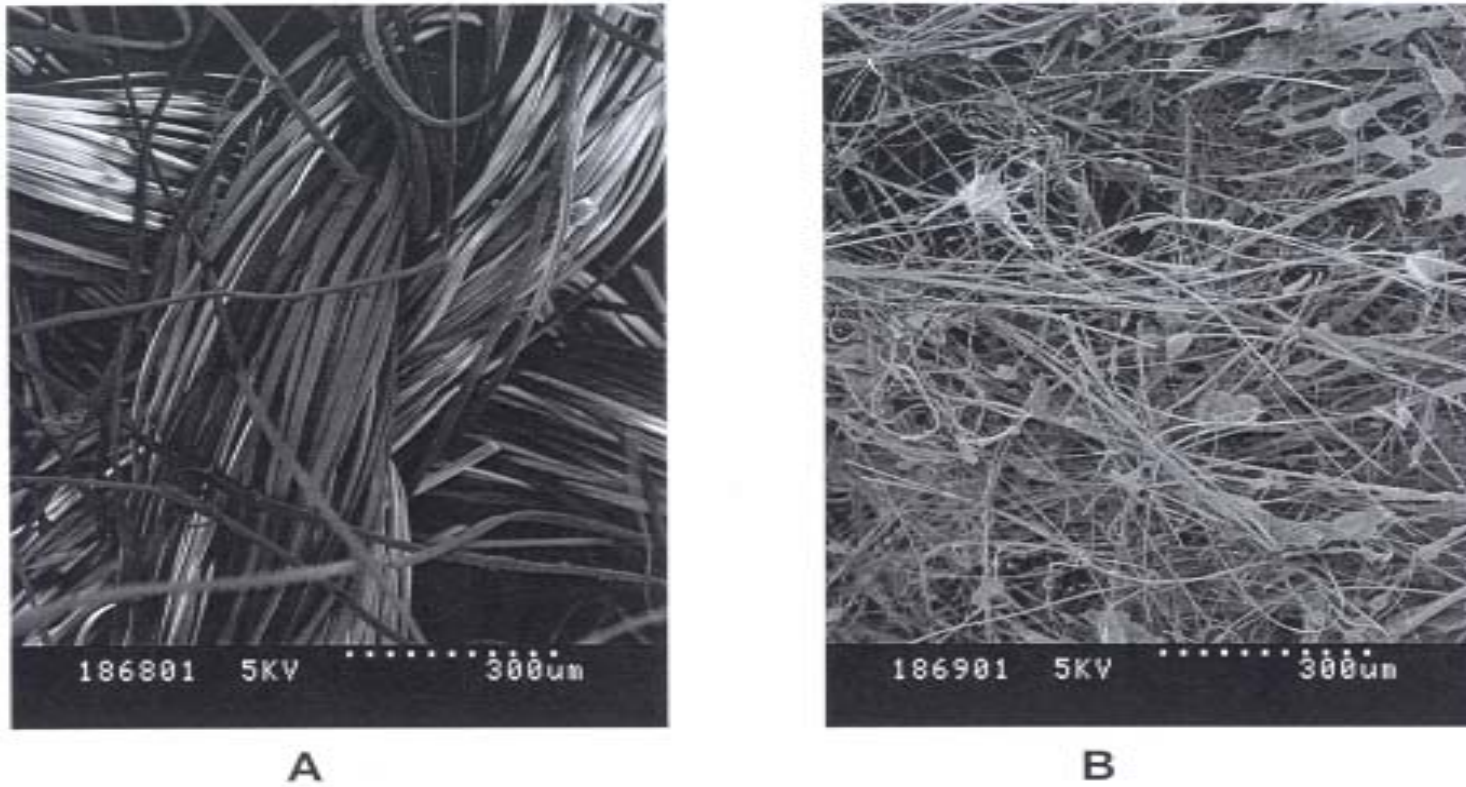


Figure 1 Electron micrographs of the lining of a portion of unused ducting (duct 1).

A - Showing several extruded flattened fibres twisted together and then woven.

B - Outer surface of non-woven fabric.

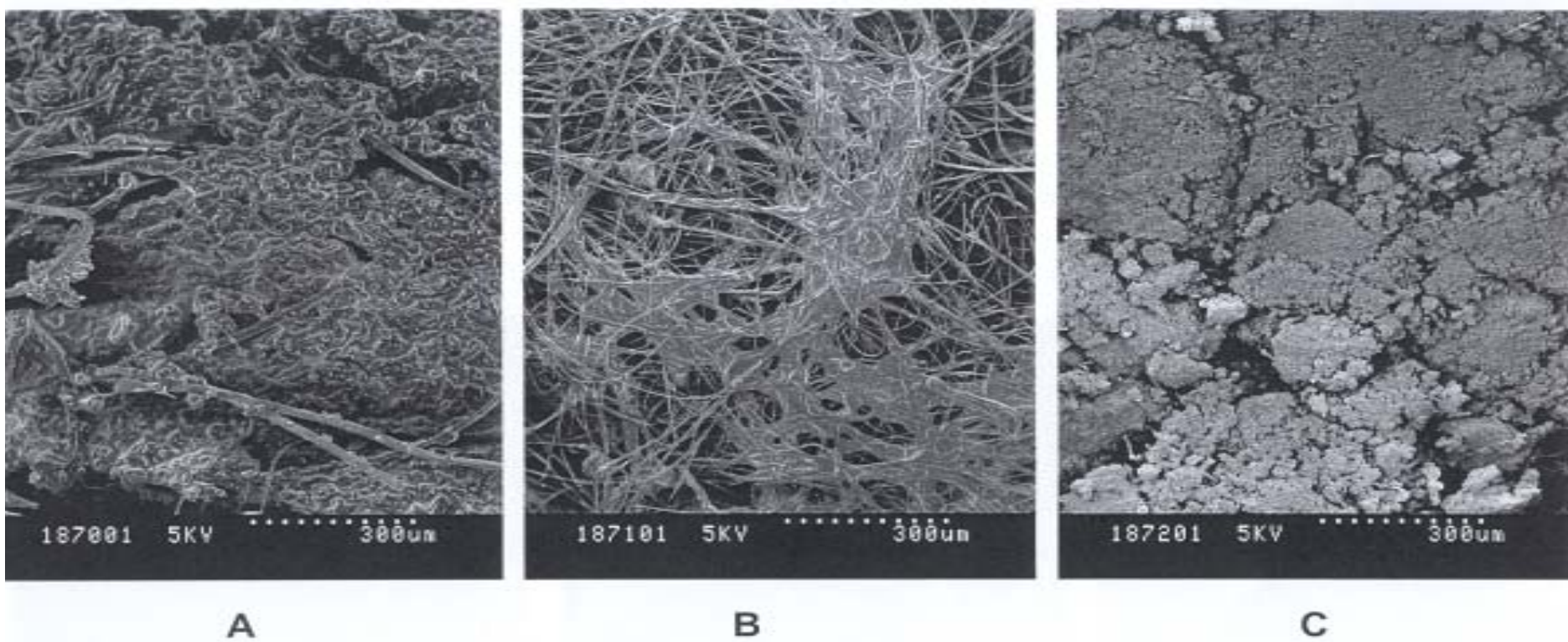


Figure 2 Electron micrographs of the lining of a portion of used ducting taken from an aircraft upon which symptoms of illness had not been reported (duct 2).

A - Inner woven fabric.

B - Outer non-woven fabric.

C - Scrapings of the black deposit on the surface of the ducts.

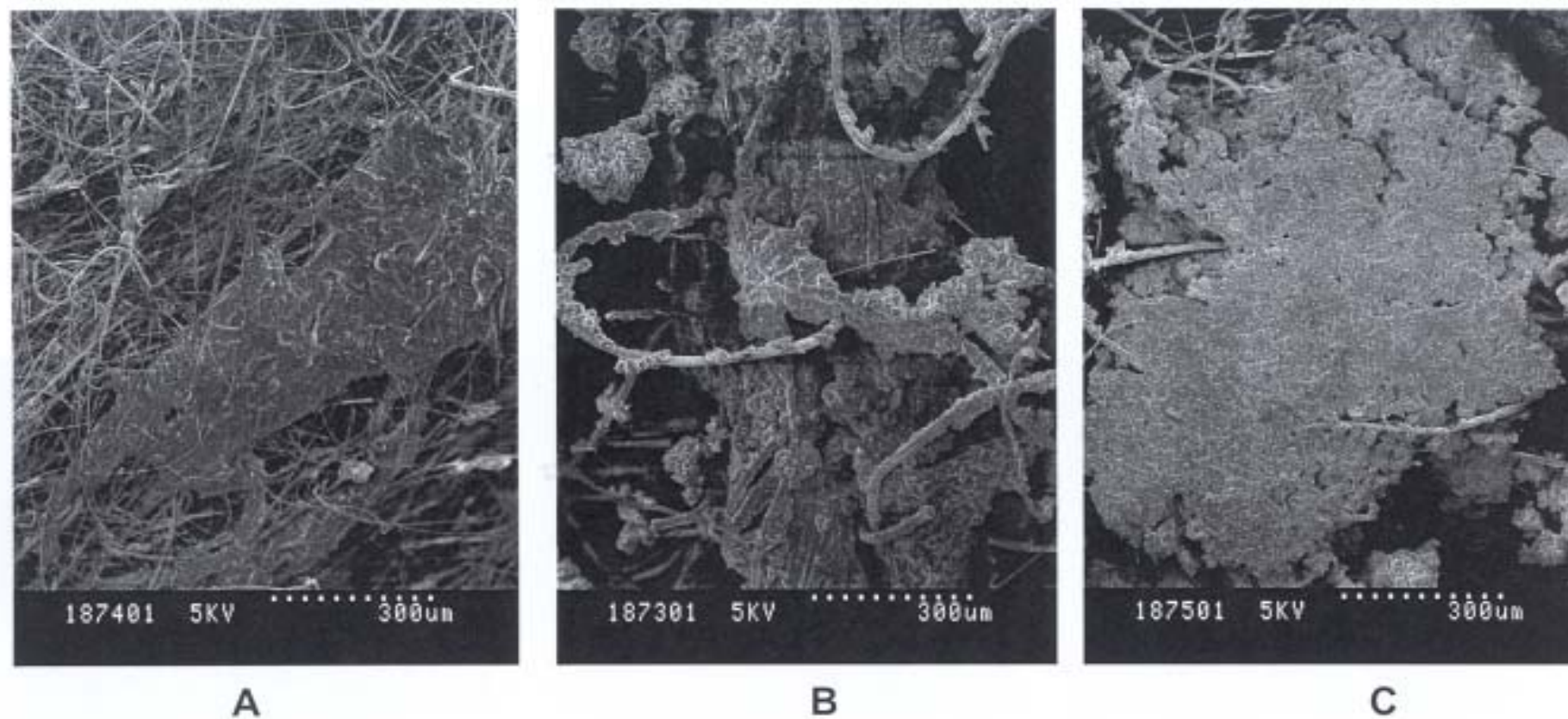


Figure 3 Electron micrographs of the lining of a portion of used ducting taken from an aircraft upon which symptoms of illness had been reported (duct 3).

A - Inner woven fabric.

B - Outer non-woven fabric.

C - Scrapings of the black deposit on the surface of the ducts.

Appendix C to Chapter 2

Calculation of Dosage of Oil required to produce Organosphosphate Induced Delayed Neuropathy (OPIDN) from Tri-Orthocresylphosphate Content

Studies of the chronic toxicity of TOCP have shown that the most sensitive species known (chickens) can be fed $20 \text{ mg.kg}^{-1}(\text{body weight; BW}).\text{day}^{-1}$ without showing signs of OPIDN. Signs of toxicity were observed at $60 \text{ mg.kg}^{-1}(\text{BW}).\text{day}^{-1}$.

Given the TCP content of the pyrolysed oil supplied to Dstl by QQ Pyestock and used in the previous analysis of oil pyrolysate as $0.19 \text{ } \mu\text{g.g}^{-1}$ oil (table1, Appendix A)

Assuming all the TCP has the same toxicity as TOCP (over estimating the toxicity by 100 times).

TCP content of oil

$$0.19 \text{ } \mu\text{g.g}^{-1} \equiv 0.19 \text{ mg.kg}^{-1} \text{ oil} \equiv 0.19 \times 10^{-3} \text{ g.Kg}^{-1} \text{ (oil)}$$

dosage without OPIDN

$$20 \text{ mg.Kg}^{-1}.\text{day}^{-1} \equiv 20 \times 10^{-3} \text{ g.Kg}^{-1} \text{ (BW)}. \text{day}^{-1}$$

Therefore, oral dosage of oil without OPIDN effect is given by

$$20 \times 10^{-3} \text{ g.Kg}^{-1}(\text{oil}).\text{day}^{-1} / 0.19 \times 10^{-3} \text{ g.Kg}^{-1}(\text{BW}).\text{day}^{-1} = 105 \text{ Kg(oil).Kg}^{-1}(\text{BW}).\text{day}^{-1}$$

Assuming a 70 kg body weight for the average human subject. The total dosage that would not induce OPIDN would be $105 \times 70 = 7350 \text{ Kg.day}^{-1}$.

An average man would therefore be able to ingest 7 metric tonnes of pyrolysed oil per day for 74 days without effect.