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MELBOURNE, VICTORIA

REPORT
MRL-R-1116

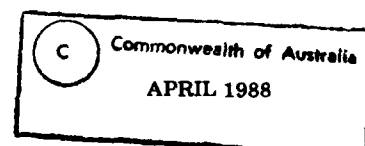
CONTAMINATION OF ENVIRONMENTAL CONTROL SYSTEMS
IN HERCULES AIRCRAFT

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A.G. Kelso, J.M. Charlesworth
and G.G. McVea

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MATERIALS RESEARCH LABORATORY**

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**CONTAMINATION OF ENVIRONMENTAL CONTROL
SYSTEMS IN HERCULES AIRCRAFT**

**A.G. Kelso, J.M. Charlesworth
and G.G. McVea**

ABSTRACT

The assistance of MRL was requested by RAAF in determining the origins of contamination of turboprop bleed air used for environmental control in several Hercules C-130 transportation aircraft. Air sampling in the interior of affected planes was performed in-flight and on the ground, together with laboratory sampling of vapour from all of the suspected contaminating fluids. Gas chromatographic (GC) and GC/mass spectrometric (MS) analysis of collected samples confirmed that aviation turbine fuel (avtur) leakage produces a continuous background of hydrocarbon vapour around 0.1 to 0.5 ppm in affected aircraft. Positive indications of turbine oil vapours were found in filter bags taken from the air-duct system of suspect aircraft. Some traces of organophosphorous compounds, particularly the tricresyl phosphate additive in the oil, were found in the air filter bags. However at present there is no evidence to support a hypothesis that neurotoxic bicyclopophosphorous compounds derived from the oil additive are present.

It is strongly recommended that in addition to normal maintenance of turbine oil seals and fuel nozzles, the use of charcoal cloth filters in the air ducting system be investigated as a means of absorbing the noxious odours.

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CONTAMINATION OF ENVIRONMENTAL CONTROL
SYSTEMS IN HERCULES AIRCRAFT

1. INTRODUCTION

1.1 Description of the Problems Encountered with the Environmental Control Systems in Turboprop Aircraft

Aircraft powered by turboprop engines have been in service with the RAAF for over 25 years. One of the oldest of these is the Hercules C-130 transport, which is equipped with four Allison T-56 turboprop engines, providing both the motive power and bleed air for climate control in cabin and cargo areas.

It is acknowledged that the use of turbine bleed air for pressurization and airconditioning is unsatisfactory in passenger aircraft due to the possibility of contaminated air filling the interior. The RAAF has reported many instances of strongly odorous vapours entering the airconditioning system of several of the C-130 aircraft, the incidence of which has escalated considerably in the last 12 months (Figure 1). This has given rise to concern for the long term health of flight-crews and, in the short term, operational safety problems which may result from incapacitation of pilots and crew.

In June 1987, the assistance of MRL was requested by RAAF (1) in determining the origins of the air contamination in several of the most severely affected C-130 aircraft. The problem was reported to have reached the stage where operational restrictions were being imposed on aircraft in order to limit the extent to which flight crews were exposed to fumes.

Extensive technical investigations by RAAF (2) had failed to locate the cause of the problems or to identify the chemical nature of the fumes; however it was considered highly probable that at least one of the fluids used within the engine was involved. These fluids are:-

1. synthetic lubricating oil, to MIL-L-23699C, NATO 0-156
2. hydraulic oil, to MIL-H-5606E, NATO H515
3. avtur fuel, to DEF (AUST) 5240A, NATO F34

It is possible that any of these materials, or their degradation products, could infiltrate the air bleed system and eventually taint the respirable air in the bulk of the aircraft interior. A suspicion was also held that the incidence of objectionable fuming was associated with a change in supply of aircraft turbine oil, from Mobil Jet Oil 2 to Exxon 2380. Enquiries and investigations were made in relation to the compatibility of the two oils, however results gave no reason to believe that the supply change of itself had initiated the problem.

Other investigations had been concerned with the disassembly of the suspect engines to examine for possible fluid leakage areas, and the testing of suspected faulty seals (3). Faults were found in some of the engines, which could have allowed, for example, leakage of turbine oil past O-ring seals in the compressor extension shaft housing or past compressor labyrinth seals, or leakage of avtur. However, because of the comparatively few confirmed faults, and the generally inconsistent correlation between ground test-cell and in-flight assessments, the results of these investigations have been inconclusive.

1.2 Air-Bleed System in Non-Passenger Military Aircraft

Figure 2 shows a schematic outline of the main features of the C-130 turboprop engine. The air for the cabin airconditioning system is bled from a valve located in the region between the compression and combustion zones. Discussions with RAAF engineering staff indicated that the possible sources of contamination of this air include leakage of fuel (avtur) from the fuel atomization nozzles, leakage of turbine oil past the labyrinth seals adjacent to the compressor shaft bearing and/or leakage of lubricating oil past the O-ring adjacent to the extension shaft bearing.

A further possible, but improbable, source of contamination is leakage of hydraulic fluid along the extension shaft from the turbine driven accessory gearbox.

1.3 Reported Toxic Effects Of Oil Vapours In Civilian Aircraft

In the USA in 1981 it was reported that several unexplained crashes of civilian turboprop aircraft may have been due to pilot disablement resulting from the inhalation of toxic fumes (4-6). It was postulated that these fumes originated in the turboprop power plant and could be introduced into the cabin with the bleed air taken from the turbine compressor for the purpose of pressurizing the aircraft.

Both engines from one of the crashed aircraft were recovered and a composite operational engine assembled from the parts, and later tested. Samples of compressor bleed air from the engine were collected and chemically analysed. From this work, and other studies, it was alleged that a broken carbon seal would allow lubricating oil to enter the compressor section. This oil-contaminated bleed air could

then enter the cabin, and any toxic substances present would have the potential to incapacitate both pilot and passengers.

The U.S. National Transportation Safety Board (NTSB) examined the accident statistics for turboprop aircraft and concluded that the frequency and nature of the accidents justified further tests on the quality of the bleed air. In these tests (7) Garrett Turboprop TPE-331 engines were operated on test stands under various conditions, including the deliberate introduction of Exxon 2380 oil directly into the engine air-intake. Samples of the bleed air from the compressor were collected and analysed with on-line techniques, and also by three independent participating laboratories supplied with collected samples. Results of the on-line analyses gave no indication that harmful concentrations of any of the oxides of carbon or nitrogen were present in the bleed air. Combined GC-MS analysis of the collected samples showed that a number of other identifiable gases were present in concentrations which would, in all probability, not alter the perception or behaviour of the pilot. However, the possibility that unidentified substances of high toxicity were present could not be eliminated. Further, the direct oil-injection experiments revealed that an aerosol of oil was generated in the bleed air which was removed upstream by glass-wool filters placed in front of the analytical and sampling devices. In the case of an unfiltered stream of air, it was suggested that toxic effects may result from the inhalation of this oil mist.

Crane et al (4) also measured the effects following acute exposure to the thermal decomposition products of Exxon 2380, and similar lubricants, using experimental animals. A brief discussion of this work, and the continuing concern about the possible formation of a neurotoxic substance, trimethylolpropane phosphate (TMP-P), as expressed by a meeting of the Air Standardization Committee (8) and studied by Kelman et al (9) and Wyman et al (10), is presented in Appendix I.

2. SCOPE OF THE INVESTIGATION

2.1 Aims

At the outset of work, the primary goal was to identify the chemical composition of the odorous vapours in the environmental control system of RAAF Hercules C-130 aircraft. The determination of concentrations, and any possible physiological effects of vapours was a potential secondary goal. By identifying the nature of the pollutants it was hoped that the source of the problem could be traced, and methods or procedures recommended for the minimization of the problem.

The approach adopted was to sample the air entering the aircraft cargo/cabin compartments from the bleed air ducts, while the engines were operating in a variety of situations, and to analyse these samples for any traces of contamination.

A method of "fingerprinting" potential pollutants and then cross-checking these with the aircraft air-sampling results was employed. This was achieved by

laboratory-scale sampling, and then analysis, of vapours and pyrolysis products from the decomposition/evaporation of the aircraft fluids suspected of leaking into the system.

2.2 Limitations

Because of limits on flying-time in aircraft with some of the most severely affected engines, the scope of this investigation was restricted in terms of development and optimization of techniques for the collection and analysis of polluting odours.

The method chosen for the analysis of vapours was gas chromatography, using flame ionization detection (FID), for total organics and thermionic specific detection (TSD), for selective detection of phosphorous and/or nitrogen compounds. Gas chromatography combined with mass spectrometry (GC/MS) was used for more positive identification of components wherever possible.

An approximate estimate of the minimum detectable level for a single component present in the sampled air can be calculated using the maximum sensitivity, for practical purposes, of the FID. This limit is generally recognised to be at least 10^{-9} g sec⁻¹ (11) which, for a peak-width at the baseline of 5 seconds (ie a typical response), gives a minimum detectable level of 5×10^{-9} g. The pumping rate was fixed at 500 mL min⁻¹ for 30 min (see Experimental section) and the adsorbed material from each of the collection tubes was normally concentrated to approximately 1 mL. Using an unsplit injection technique with a 2 μ L aliquot from the concentrated tube washings allows a minimum detectable level for a single component in the sampled air of 0.02 mg/m³.

3. EXPERIMENTAL

3.1 Test Location and Aircraft Selection

Air-sampling was conducted over a 4-day period from 17 Aug to 20 Aug 1987 at RAAF Base, Richmond NSW. Atmospheres in four aircraft were tested, in one case on the ground with engines running, and in all other cases in flight. The standard sampling configuration was a battery of five collection tubes within the cargo compartment fixed to the wall below and between the two main duct outlets, and individual tubes inside these ducts. A summary of the conditions and aircraft sampled is given in Table 1.

3.2 Test Program

3.2.1 Methodology of Sampling

The standard method for collection of atmospheric organic vapours is the aspiration of air at a known rate through a tube which contains a particulate substrate capable of quantitatively adsorbing the polluting vapours (12). A frequently used alternative approach is to use "passive" monitoring whereby no artificial pumping of vapours is required and the adsorbent is simply exposed to the ambient atmosphere for an appropriate period of time.

The aspirated approach was considered to be the most suitable method for the present work because a large throughput of air could be achieved during fuming engine operations, thus allowing trace levels of pollutants to be analysed. Passive monitoring is known to be subject to the effects of individual diffusion characteristics of absorbing molecules and requires long periods of exposure when small quantities of contaminants are to be detected. A limited amount of work was performed with activated charcoal 3M-brand passive monitors, however the main emphasis was directed towards aspirated sampling.

The vacuum pumps used in this study were of two types

- A. A small, highly portable battery-powered pump capable of sampling at a maximum rate of 1.5 L min^{-1} for 6 h. A maximum of two sample tubes was used simultaneously with this pump.
- B. A large medical-grade pump operating from the 110 V power supply available on the aircraft, and capable of sampling at 25 L min^{-1} . This was fitted with a manifold consisting of multiple ports for up to ten sample tubes.

Glass sample collection tubes 6 x 0.6 cm ID were prepared containing approximately 0.06 g of Porapak Q adsorbent in a 1 cm plug retained by silanized glass wool. The tubes were treated before use by washing with 3 x 1 mL portions of chromatography-grade hexane. The washings were confirmed free of impurities by GC analysis. A standard restrictor was placed between the sample tubes and the vacuum pump to allow for a calibrated flow of approximately 500 mL min^{-1} through each tube.

Several tests were carried out on the synthetic fibre air-filter bags from within the ducting system of a candidate C-130 aircraft. These were cut into strips and ultrasonically extracted with 1L hexane, then concentrated to approximately 10 mL with a rotary evaporator.

3.2.2 Sample Analysis

Solutions were obtained by washing the sample tubes with hexane, then concentrating to 1 mL or less. GC analyses were performed on a Varian 3700 GC using a 25 m x 0.33 mm ID fused silica column, with methyl silicone bonded liquid phase (BP 1-0.5), and flame ionization detection. Temperatures of injection and detection

zones was 300°C, and the column temperature was held at 50°C for 1.5 min, then programmed at 5°C min⁻¹ to 280°C. The solvent effect produced by 2 µl Grob splitless injection of sample solutions, with 1.5 min delay time, was used to enhance sample response.

3.2.3 Laboratory Sampling of Vapours

Initial studies were performed to measure the composition of vapours from the head-space above all of the suspect fluids. Avtur vapours were sampled at 25°C, vapours from both turbine oils were sampled at 100°C and 200°C, and hydraulic fluid vapours were sampled at 100°C. The Exxon turbine oil was subjected to bomb pyrolysis at 450°C and the liquid decomposition products analysed by GC and GC/MS.

3.2.4 Oil Foaming Study

Foaming characteristics of lubricating oils were measured in order to add to the information supplied by Materials Testing Laboratories (1). The standard ASTM method (13) was employed and tests were performed on both the turbine oils, and a 1:1 mixture of each, at 100°C, 150°C and 200°C.

4. RESULTS AND DISCUSSION

GC analysis of each batch of sampling tubes demonstrated a reproducible response and a well defined chromatographic pattern of behaviour. Every sample collected under acceptable engine performance conditions (ie. no noticeable objectionable odour) showed no significant level of organic contaminant, using the standard extraction/analysis scheme.

In each case where bleed air from an agreed "dirty" engine was sampled, the resulting chromatographic analysis revealed the presence of avtur (Figure 3). In two cases where bleed air from previously suspect engines was sampled (aircraft 005 and 177), the opinions of all personnel present during the sampling were that the air was acceptable. In one of these cases, aircraft 005, it was later confirmed that a suspect engine had recently been replaced. No other contaminant was apparent in the chromatographic analysis of any sample tube.

In all comparisons of "cargo compartment" and "inside duct" collections, sampling the ambient air in the cargo compartment appeared to provide more efficient collection of contaminated air.

Following further concentration of 1 mL sample tube extracts to around 50 µL, a hydrocarbon pattern indicative of avtur could be seen in the chromatogram of

the acceptable bleed air samples. However, the overall avtur response from these samples was invariably of the order of 2-3% that from objectionable bleed air samples. Comparison of the total response of the avtur pattern from collected samples with that from a hexane solution containing a known concentration (0.1%) of avtur, indicated that the concentration of residual avtur vapour in the sampling area during suspect engine operation is of the order 0.1 to 0.5 ppm.

The results of GC analysis, with FID detection, of the hexane extract from an air-duct filter bag are shown in Figure 4, together with chromatograms of the Exxon 2380 and Mobil jet oil vapours sampled at 200°C. It is evident that the family of peaks occurring at the longer retention times in the GC trace from the filter bag extract may represent a combination of the two families of peaks at the longer retention times in the GC traces of the two turbine oil vapour samples.

The poorly shaped peaks occurring in the first half of chromatograms from the oil vapour samples, more prominently in the Exxon sample, were identified by GC/MS as carboxylic acids in the range butyric to pelargonic. The presence of these acids also in the filter bag extracts from two aircraft, 003 and 171, was confirmed by similar GC/MS examination, even though they are not present in sufficient concentration to appear in the FID chromatogram. A comparison of the single-ion mass spectra obtained from collected vapour from Exxon 2380 and from a filter bag extract is shown in Figure 5. This is consistent with previously obtained data pertaining to the composition of the oils, as measured by ¹H NMR analysis in this laboratory (14). Exxon 2380 is a complex mixture of monobasic acids reacted with polyfunctional alcohols. The molar ratio of alcohols is 0.65 trimethylolpropane : 0.25 pentaerythritol : 0.10 dipentaerythritol. The acids are valeric, heptylic, caprylic, capric, pelargonic, caproic, isovaleric and butyric.

The total number of species which are possible under these circumstances can be calculated using the following formula (15)

$$N = \frac{(n + r - 1)!}{r! (n - 1)!} \quad (1)$$

where N represents the possible number of ester species when a polyol containing r hydroxy groups is esterified with n different acids.

For example, in the case of Exxon 2380

$$N = \frac{(8 + 3 - 1)!}{3! (8 - 1)!} + \frac{(8 + 4 - 1)!}{4! (8 - 1)!} + \frac{(8 + 6 - 1)!}{6! (8 - 1)!} \\ = 2166$$

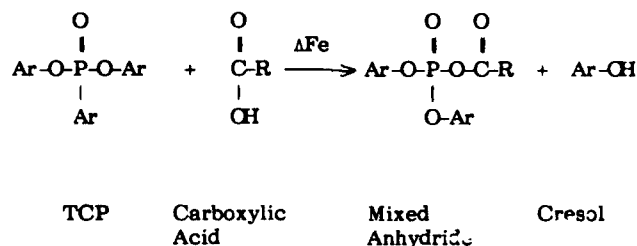
Because of their high molecular weight many of these 2166 species will not be present at a significant level in the vapour in equilibrium with the oil at 200°C. This is confirmed by the GC analysis of the vapours, which indicates that only the lowest molecular weight esters are detected. The toxicity of the esters and unreacted acids are, in all probability, not high (16).

The low boiling species other than acids indicated in Figure 4 are alkanes, predominantly C9-C15. These are thought to occur as a result of residual hydrocarbon-type washing solvent which has been used to clean the filter bags as part of the C-130 airconditioning maintenance program.

Further confirmation of traces of turbine lubricating oil in the filter bag extract is provided by phosphorus/nitrogen specific detection GC analysis. Figure 6 illustrates some examples of the separation of N/P compounds from the oil vapour samples, and the filter extracts. The similarity in pattern again suggests that the filter bag has absorbed a significant amount of turbine oil from the bleed air entering the ducting system. Identification of all of the compounds in these chromatograms has yet to be achieved, however one certain source is the antiwear additive tricresyl phosphate (TCP), which is reported to be present at levels around 3-5% in these turbine oils (10).

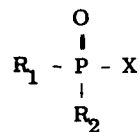
MIL-L-23699 specification lubrication oil is required to have not more than 1% of the ortho-tricresyl phosphate isomer. Tricresyl phosphate is prepared using commercial grade cresol, which is itself a mixture of the o, m and p isomers. From equation (1) it can be calculated that there are 10 possible isomers of tricresyl phosphate, only one of which contains all ortho-cresyl groups. Figure 7 illustrates the N/P detector GC analysis of a typical sample of commercial grade tricresyl phosphate. The prominent group of peaks in this chromatogram, and also those in Figure 6, are the isomeric forms of tricresyl phosphate, together with impurities. Measured toxicity data (OHSA time weighted average) for the ortho isomer indicates that the airborne concentration should not exceed 0.1 mg/m³. Since the N/P detector is at least as sensitive as the FID (11), the air sampling and analysis techniques used in the present study should have enabled these levels to have been detected if present. The absence of any phosphorus compounds in the cabin air samples implies that at the time of sampling the levels of tricresyl phosphate were not hazardous.

Tricresyl phosphate is known to undergo a transesterification reaction with organic acids and esters at 250°C or higher in the presence of ferrous metals (17). A typical example of such a reaction is the following



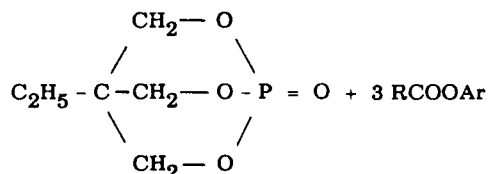
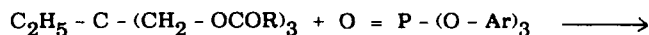
R = Alkyl, Ar = cresyl

It has been reported (18) that a wide variety of cholinesterase inhibitors occur with the general structure



where R_1 and R_2 are capable of many variations, including phenols, and the X group can be a carboxylate.

A similar reaction to the above is likely to lead to the formation of TMP-P
i.e:



As yet we have not been able to detect the presence of any reaction products of TCP in samples taken from aircraft. However, because of their high toxicity it is important to ensure that any such products do not contaminate the bleed-air system in sufficient quantities to cause behavioural changes.

Other experiments performed as part of the present study revealed no traces of hydraulic fluid in any of the samples and the oil-foaming experiment gave no indication that excessive foaming during engine operation would be responsible for overflow of oil into the compressor bleed air.

5. CONCLUSIONS

1. Avtur leakage, presumably from fuel nozzles, in reported dirty engines produces a continuous background of hydrocarbon vapour, around 0.1 - 0.5 ppm. In clean engines the level is very much lower ie. reduced by a factor of 50. This result correlates well with the subjective perception of odorous engines. These levels of avtur in the environmental control system are not thought to be hazardous.

2. No evidence of any vapour contaminant, other than avtur, from in-flight air samples was found using the methods of analysis and detection which were considered appropriate to this study.

3. A positive indication of turbine oil vapour (including tricresyl phosphate) was found in the air filter bags taken from the air duct system of suspect aircraft.

4. All results are consistent with previous assessments that leaking fuel nozzles are major contributors to avtur contamination of the turbine bleed air. Furthermore, defective O-ring seals in the compressor extension shaft housing and compressor labyrinth seals may cause some ingress of turbine oil vapour into the air-conditioning system.

5. Traces of the neurotoxic organophosphorous compound TMP-P, believed to be derived from the tricresylphosphate additive in the oil, have been found in laboratory pyrolysed oil samples. At present, there is no evidence to confirm that this compound is present in samples taken from the aircraft.

6. RECOMMENDATIONS

1. Previous studies on the airflow requirements for cabins in passenger transport aircraft have suggested the use of activated charcoal as an adsorbent for odours (19). Charcoal cloth, which is now readily available and widely used as an adsorbent for organic vapours may offer a relatively inexpensive and simple method for removal of the contaminant in the compressor bleed air (20,21). This fabric is flexible, both shock and vibration resistant, and has a rate of vapour adsorption which is reported to be five to twenty times greater than for the most effective nutshell charcoals. Although not in a position to provide details of the modifications required we believe that charcoal cloth could be included as an extra layer attached to the outer surface of the existing air-duct filter bags.

2. An alternative approach would be to instal engine-driven compressors to supply the environmental air for the cabin and cargo areas. This would require more extensive modification and cost, and regular maintenance.

3. More frequent replacement of seals, O-rings and fuel nozzles must also be considered as a possible remedy.

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APPENDIX I

In the animal exposure tests conducted by Crane et al (4) rats were exposed to the thermal decomposition products from synthetic and petroleum based lubricants and from a fire resistant hydraulic fluid. These flaming and non-flaming decomposition experiments were performed in the range 300° to 600°C using physiological end-points including time-to-death and time-to-incapacitation. Effects due to carbon monoxide (CO) production were allowed for by monitoring CO levels and then applying previous knowledge of the toxic effects of CO on rats. Significant differences in rat response times and in CO production were observed in the flaming and non-flaming modes, and also among the different oils tested.

In a second set of experiments, both rats and chickens were exposed to lubricant and light paraffin oil aerosols for 7 h then monitored for 35 days for any physiological evidence of toxicity. Thermal stability measurements revealed that with Exxon 2380, measurable CO evolution occurred at 360°C, accompanied by a dramatic increase in smoke density. As the temperature increased the animal response times became shorter and were found to be approximately inversely related to temperature. It was concluded that the major toxic component of the thermal decomposition products from Exxon 2380 is CO.

In the oil misting experiments it was found that particle sizes ranged from heavier droplets that settled out rapidly, and were therefore only briefly available for inhalation, to finer particles that remained longer in suspension. Because of this problem, the fraction of the total nebulized oil which was inhaled by the animals could not be measured.

In all cases none of the exposed animals was incapacitated during the exposure period and all behaved normally during postexposure observation. Commenting on these test results Crane et al (4) concluded that the nonflaming mode at 400°C is an adequate model for the thermal degradation of oil in a turboprop engine. Conversely, in a spillage situation such as may occur following an accident, materials can freely burn and the test results under flaming conditions become more appropriate.

From the information obtained in the nonflaming experiments it was shown that none of the tested aircraft fluids generated a quantity of any smoke component that was significantly more toxic to the rat than the CO which was produced. Any bleed air contaminant originating from lubricant decomposition in the engine would seem, from this result at least, to be no more toxic than the CO content, which in the Garrett/NTSB tests was reported to be insignificant.

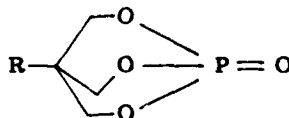
The work by Crane et al (4) does not appear to have ended the speculation and controversy regarding the effects of inducting turboprop bleed air into the aircraft cabin space. The following passage is an extract from a recent meeting of the Air Standardization Co-Ordination Committee (8).

"During 1985 it was brought to the attention of the US Navy Submarine Medical Research Laboratory (NSMRL) that if pyrolyzed under the right conditions, MIL-L-23699 type oils form trimethylolpropane phosphate (TMP-P), a higher neurotoxic substance. This conclusion was the result of experiments conducted by a private consultant working for the plaintiff in a legal action concerning the crash of an aircraft. The consultant theorized that an engine malfunction caused the pyrolysis of the oil and that the TMP-P which was formed was subsequently inducted into the bleed air system of the engine and ultimately into the cockpit of the aircraft.

Since the immediate assumption from this work was that any materials containing phosphorus and polyurethane-type materials could also produce TMP-P or related neurotoxins, all Navy Systems Commands were immediately tasked with identifying all such materials used by the Navy. Simultaneously NSMRL initiated a program to investigate the formation of TMP-P from MIL-L-23699, duplicating the original experiments conducted by the consultant, and from the other Navy materials identified as containing the proper precursors. After some initial difficulties, NSMRL personnel were able to pyrolyze a material which eluted through the GC at the same time as the standard for TMP-P; however, mass spec analysis conclusively showed that this substance was not TMP-P. Very limited toxicological studies conducted with this material were also negative. Additional tests are now being performed to evaluate the effects on products formed by changes in the method of pyrolysis."

It would appear from this report that the possibility of a toxic pyrolysis product cannot yet be conclusively rejected as a contributing factor to the current problems being experienced by RAAF.

The production of a bicyclopophosphate neurotoxic agent during pyrolysis of synthetic aircraft lubricant oil has in fact been observed in yields ranging from 100 µg/g to over 9000 µg/g oil (9). The process is reported to be a linear function of temperature over the range 400 to 645°C, with some trimethylolpropane phosphate production occurring within 2 minutes. As shown below, TMP-P is one of the most toxic of the bicyclopophosphate esters which have been tested, with sublethal effects including "progressive loss of behavioural and mental functions (such as) behaviour dependent escape responses".



R:	CH ₃	C ₂ H ₅	C ₃ H ₇	C ₄ H ₉	HOCH ₂
LD ₅₀ : (mg/kg) (i.P.)	32	1.0 (TMP-P)	0.18	1.5	> 500

In the most recent study (10), published during the course of the present investigation, it was demonstrated that the formation of TMP-P was dependent on the presence of both an organophosphorous additive, such as tricresyl phosphate, and trimethylolpropane ester base stock. After pyrolysis, lubricants composed of only a pentaerythritol base did not cause neurotoxicity in mice or rats following intraperitoneal injection, however injection of 1.2 mL of trimethylolpropane lubricant pyrolyzed in a sealed tube for 30 min at 430°C produced convulsions and death in 4 of 5 rats. No toxic bicyclophosphorous esters other than TMP-P could be detected in the oils, and MIL-L-23699 lubricants which had been used in engines under vigorous test conditions caused no neurotoxicity when intraperitoneally taken by rats.

TABLE 1

SUMMARY OF AIRCRAFT SAMPLING

Aircraft No.	Situation	Conditions
003	ON GROUND	Bleed air from suspect engine no. 3 was shut off, allowing bleed air from the other three engines to enter the cargo compartment. Samples collected during this period provided an example of acceptable environmental air. On replacing the collection tubes with a fresh set, suspect bleed air was sampled when bleed from no. 3 engine only was allowed to enter the cargo compartment.
003	IN FLIGHT	Cargo compartment air supply was sampled while bleed from no. 3 engine only was allowed to enter.
005	IN FLIGHT	"
177	IN FLIGHT	"
171	IN FLIGHT	Regulation of bleed air controls provided two sampling periods, allowing collection of samples from each of two suspect engines (no. 1 and no. 4).

FIGURE 1.
C-130 ENGINE OIL FUME INCIDENTS

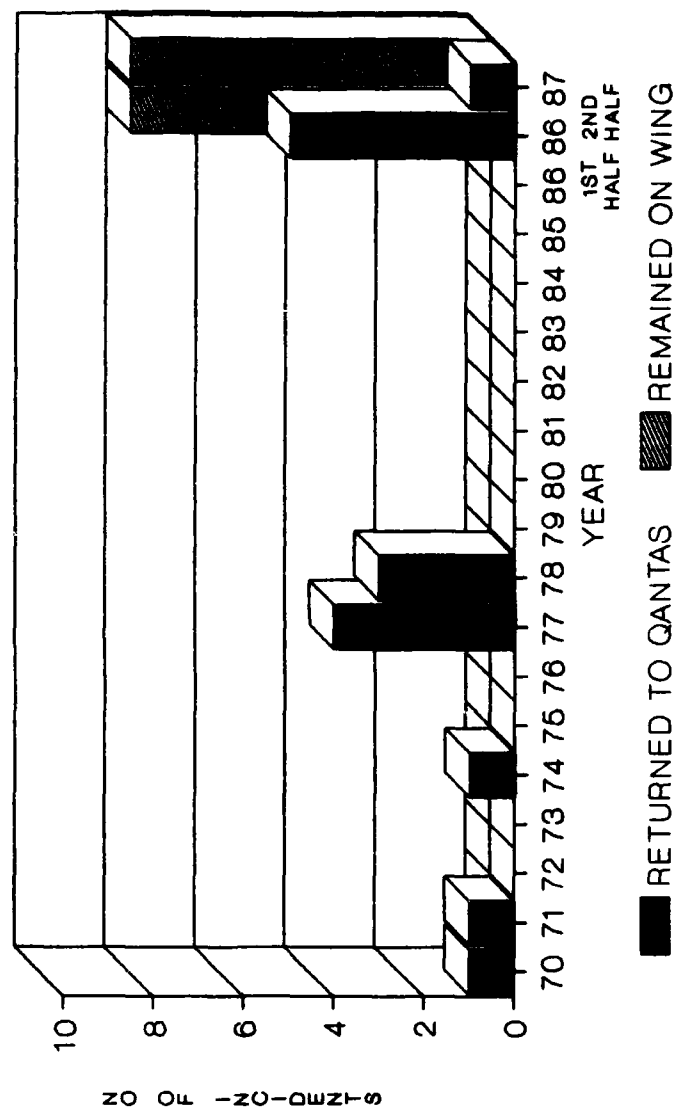


FIGURE 2
SCHEMATIC DIAGRAM OF TURBOPROP ENGINE

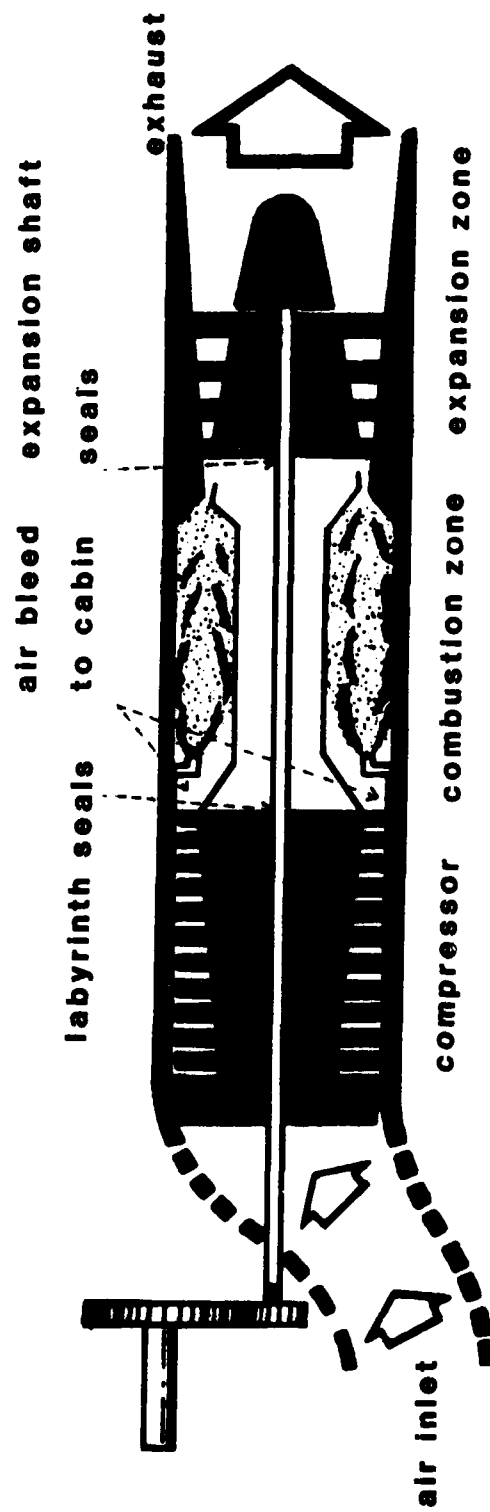


Figure 3
FID CHROMATOGRAMS

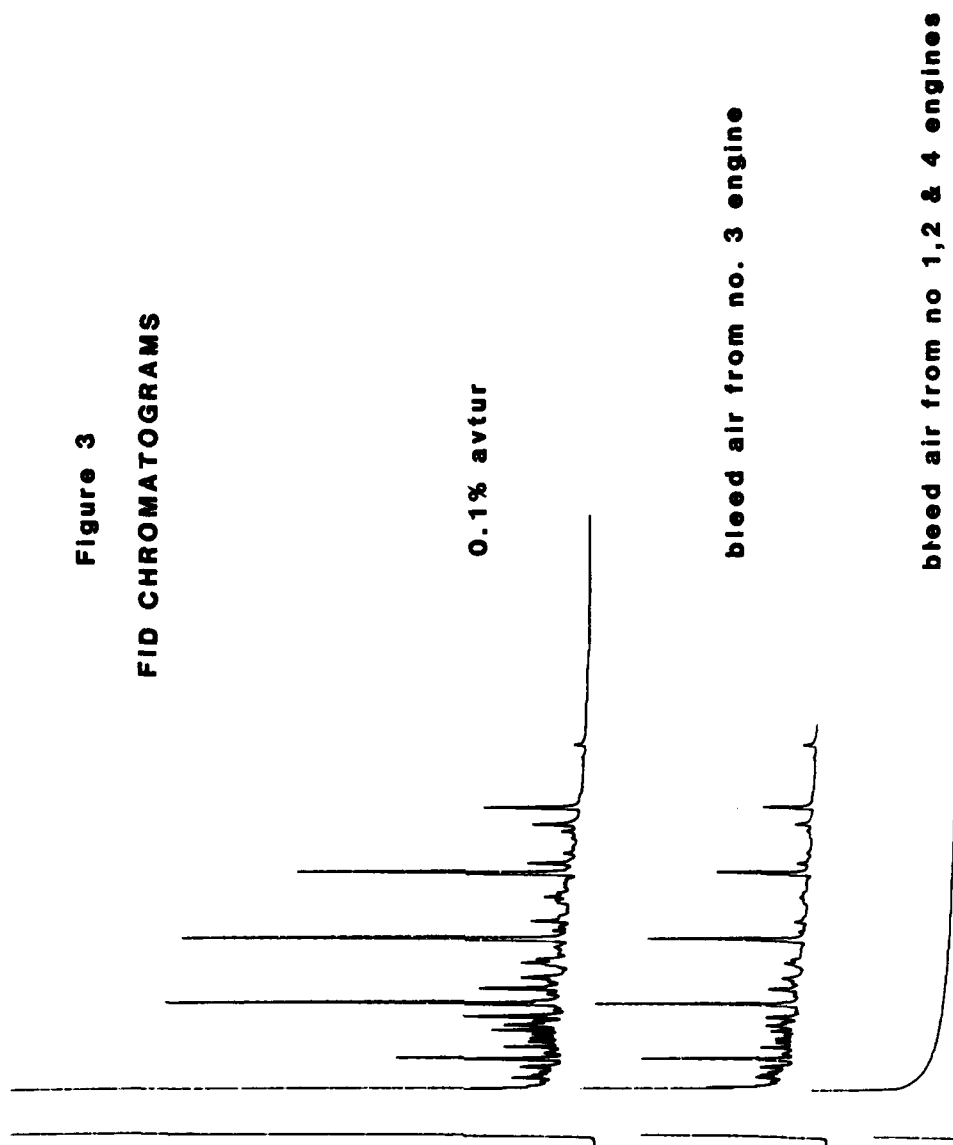


Figure 4. FID CHROMATOGRAMS

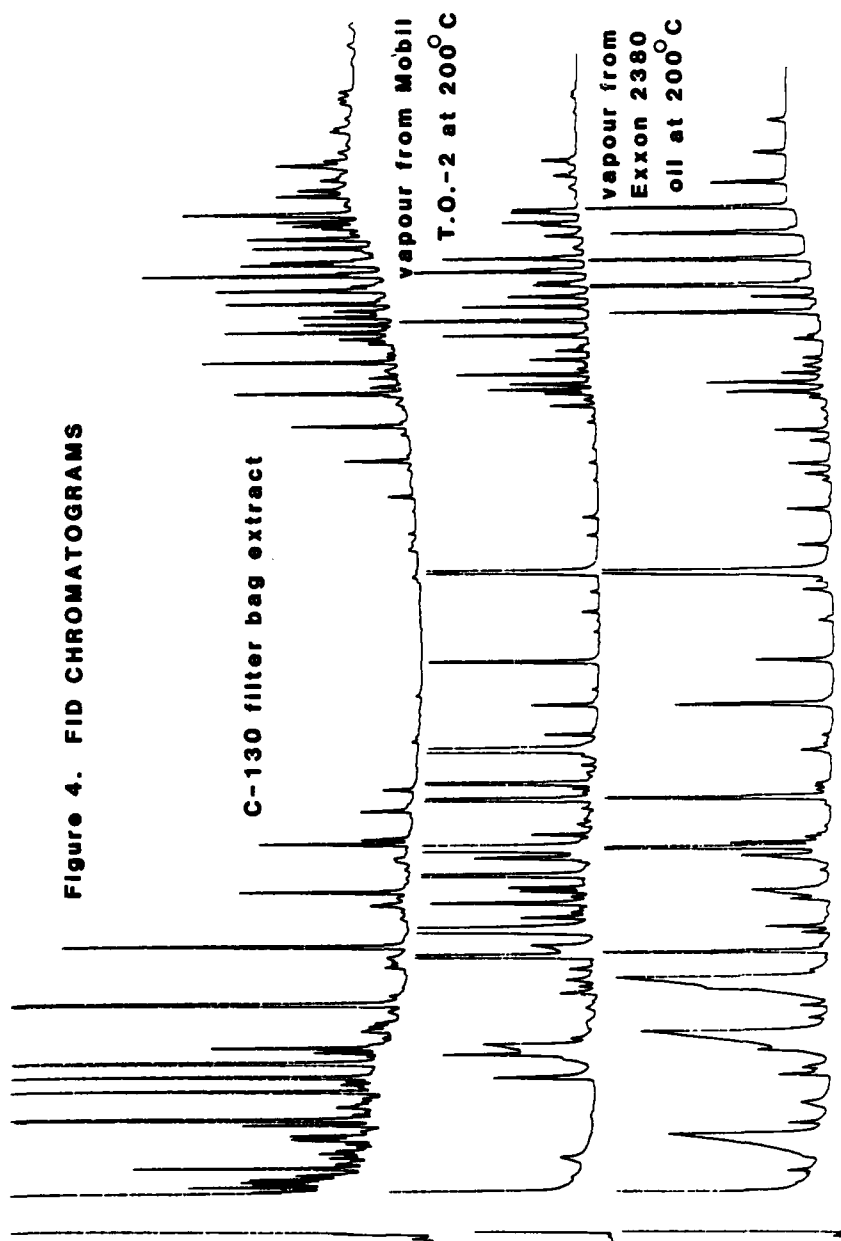


Figure 5. RECONSTRUCTED ION CHROMATOGRAMS

M/Z = 60

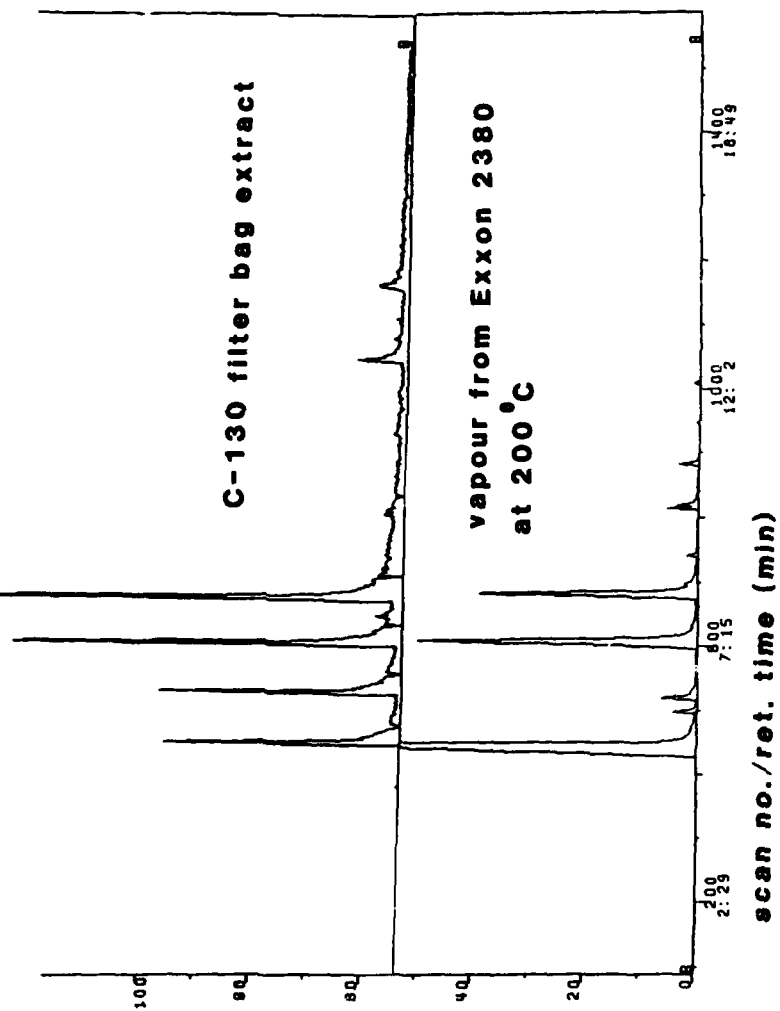


Figure 6.
N/P SPECIFIC DETECTION CHROMATOGRAMS

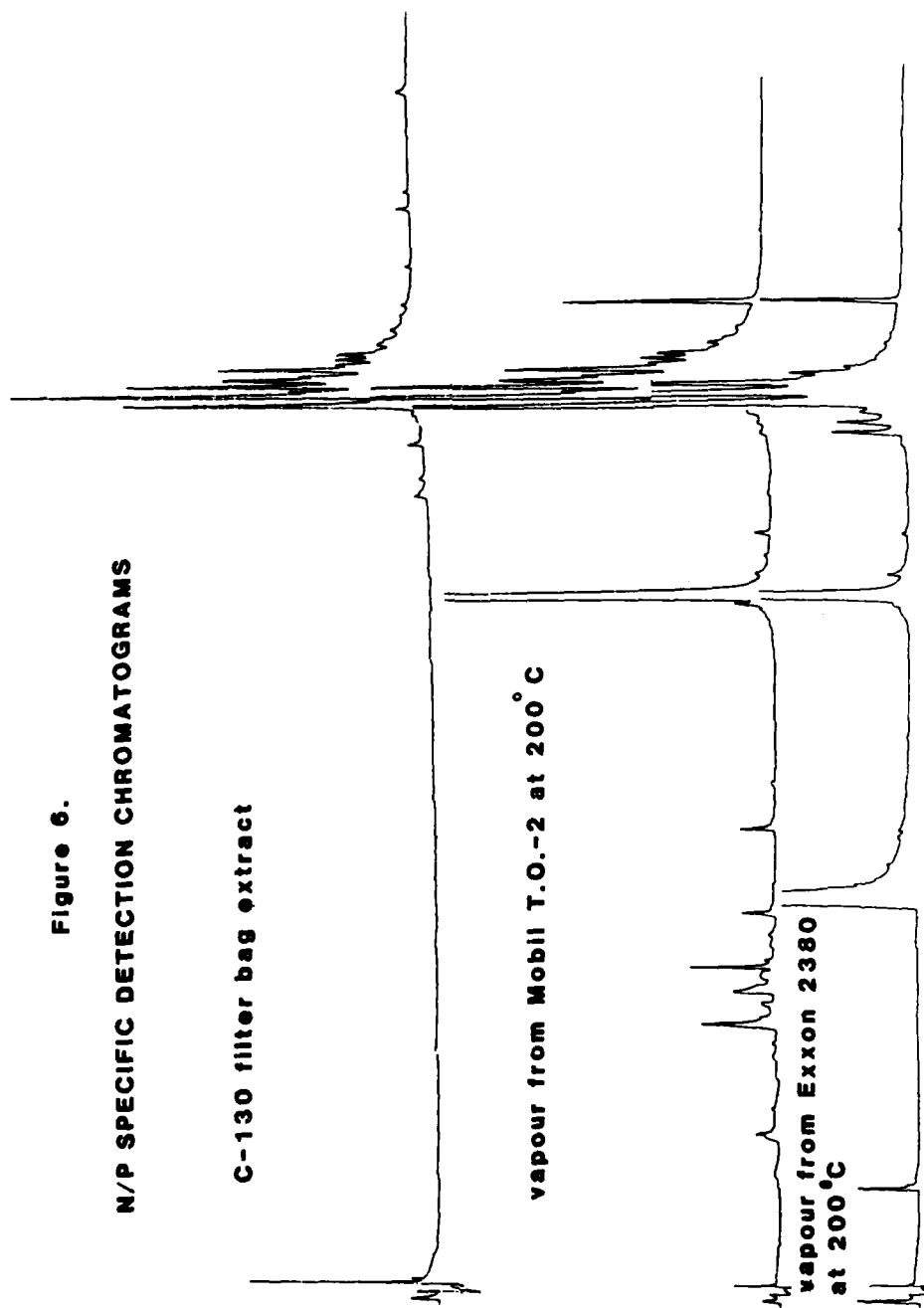


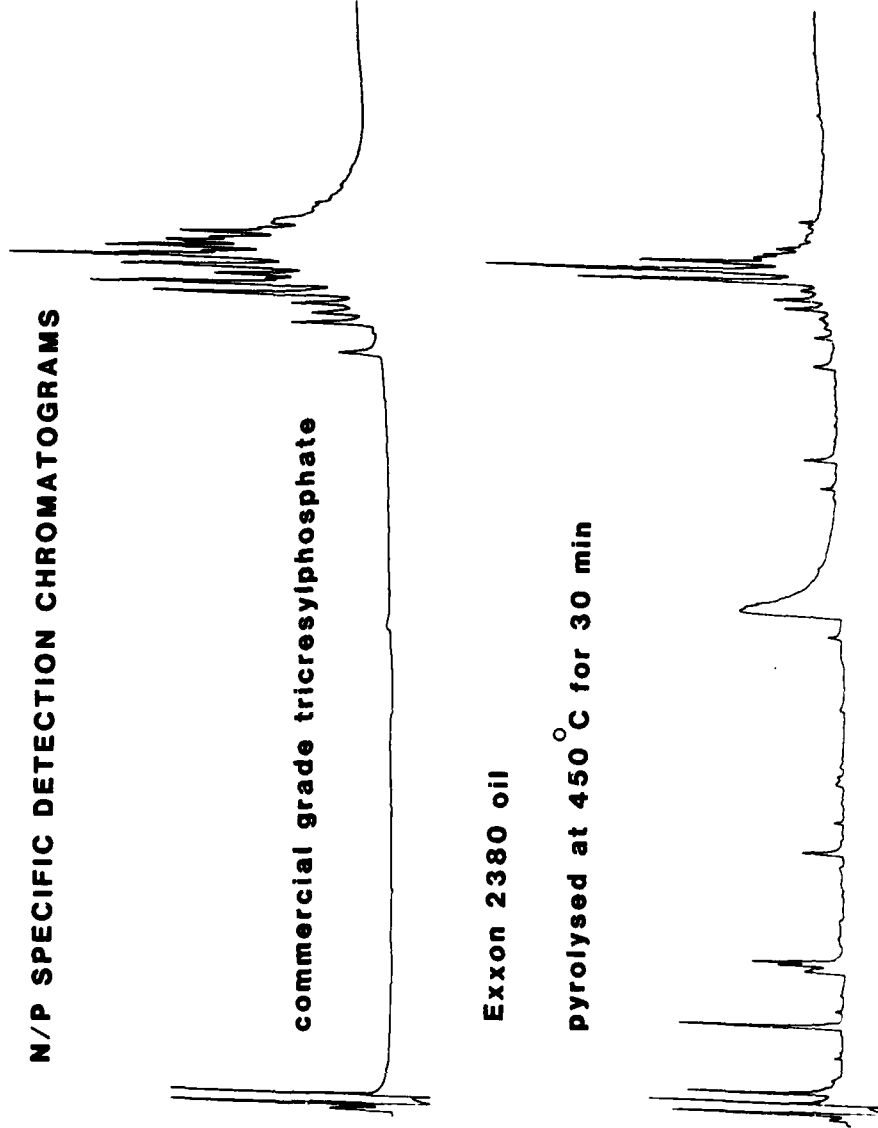
Figure 7.

N/P SPECIFIC DETECTION CHROMATOGRAMS

commercial grade tricresylphosphate

Exxon 2380 oil

pyrolysed at 450 °C for 30 min



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Contamination of environmental control systems in Hercules aircraft

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ABSTRACT

The assistance of MRL was requested by RAAF in determining the origins of contamination of turboprop bleed air used for environmental control in several Hercules C-130 transportation aircraft. Air sampling in the interior of affected planes was performed in-flight and on the ground, together with laboratory sampling of vapour from all of the suspected contaminating fluids. Gas chromatographic (GC) and GC/mass spectrometric (MS) analysis of collected samples confirmed that aviation turbine fuel (avtur) leakage produces a continuous background of hydrocarbon vapour around 0.1 to 0.5 ppm in affected aircraft. Positive indications of turbine oil vapours were found in filter bags taken from the air-duct system of suspect aircraft. Some traces of organophosphorous compounds, particularly the tricresyl phosphate additive in the oil, were found in the air filter bags. However at present there is no evidence to support a hypothesis that neurotoxic bicyclic phosphorous compounds derived from the oil additive are present.

It is strongly recommended that in addition to normal maintenance of turbine oil seals and fuel nozzles, the use of charcoal cloth filters in the air ducting system be investigated as a means of absorbing the noxious odours.

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