### **Cabin Air Sampling Study**

## **Functionality Test**

#### **Report prepared for the Department for Transport**

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January 2008

#### ABSTRACT

The Department for Transport (DFT), on behalf of the Government's Aviation Health Working Group (AHWG), commissioned Cranfield University to organise, manage and deliver a functionality test of a variety of air sampling devices capable of detecting a wide range of compounds in a cabin air environment. The functionality test was to be the preliminary stage of a major monitoring study of the cabin air environment, which the Department intends to conduct.

The results from the tests on both a BAe 146 and the B757 indicated that equipment and analytical techniques are available to monitor and provide data on contaminant chemicals in the cabin.

The functionality tests led to the identification of two techniques with independent methods for data collection and analysis which can be performed by independent laboratories and which can potentially be used for a future data collection investigation of cabin air quality. The techniques allow quantification of the concentration of the contaminants present so as to allow direct comparison between the sets of results. One method has been developed by BRE and is their intellectual property. The other technique involves a combination of the use of pumped TD tubes to collect air samples over predetermined phases of flight and the potential use of a PID (ppb) to indicate when a "fume event" has occurred. On the occurrence of a fume event, an additional TD sample should be taken, commencing within one minute of detection.

The techniques described can potentially be used for both background monitoring of cabin air in normal flight and for sudden "fume events". It is recommended that the Functionality Test is extended to finalise the methodology to be used for the collection of cabin air samples both during normal flight and immediately following a "fume event". It is suggested that the extended programme takes place early in 2008. This will enable samples to be collected and a preliminary data set established, during the winter weather, which is the time at which "fume events" have an increased probability of occurrence.

Finally, it is recommended that in any future major data collection study

- (i) the pilots and research scientists on the aircraft are required to complete a questionnaire.
- (ii) relevant information is obtained from the flight data recorder and aircraft maintenance reports for subsequent analysis.

The major data collection study will enable information to be gained on the substances which are released into the cabin air. Once this knowledge has been obtained, consideration should be given to a further study involving the collection of specimen samples from pilots following a "fume event". The aim would be to determine by laboratory testing, whether the substances released during a "fume event" and identified in the main data collection study, have been absorbed by the pilots.

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#### 1. BACKGROUND

The Department for Transport (DFT), on behalf of the Government's Aviation Health Working Group (AHWG), commissioned Cranfield University to organise, manage and deliver a functionality test of a variety of air sampling devices capable of detecting a wide range of compounds in a cabin air environment. The functionality test was to be the preliminary stage of a major monitoring study of the cabin air environment, which the Department intends to conduct.

The project flowed from the House of Lords Select Committee on Science and Technology report on "Air Travel and Health" in 2000. The Committee did not find evidence of harmful contaminants in cabin air but also said:

"We have seen no evidence that cabin air is monitored or sampled either routinely or even under abnormal or unusual conditions when passengers or crew feel that conditions are not right. We recommend airlines to carry out simple and inexpensive cabin air sampling programmes from time to time, and to make provision for spot-sample collection programmes from time to time, and to make provision for spot-sample collection in the case of unusual circumstances. This would be helpful for passengers and staff, and also benefit airlines themselves. We also suggest that this might form part of Government-sponsored research."

A government-sponsored research project has not been possible until now because of uncertainty over appropriate technology and methodology. But concerns have continued to be expressed, for example by the British Airline Pilots Association (BALPA), that the intermittent "fume events" on aircraft – in particular two types of aircraft – may have long-term health impacts. Hence the Government asked the independent Committee on Toxicity (COT) to review the evidence available and advise on further research required.

# 2. COT REVIEW OF THE CABIN AIR ENVIRONMENT, ILL-HEALTH IN AIRCRAFT CREWS AND THE POSSIBLE RELATIONSHIP TO SMOKE/FUME EVENTS IN AIRCRAFT.

In this report (Ref. 1) the COT advised that any research into cabin air sampling should involve the determination of the identity and concentration of chemical compounds and any particles that might be present in the cabin under normal conditions and during an oil/hydraulic fluid smoke/fume incident.

The COT also agreed that "there was considerable uncertainty regarding the identity of any VOCs, SVOCs and other pyrolysis products released into the cabin air during an oil or hydraulic fluid smoke/fume incident (paragraph 43 above and TOX/2007/10 Annex 1). Members considered that approaches to exposure measurement should cover the widest possible range of potential contaminants from oil/hydraulic fluid that could be analysed and should not focus on only a single chemical group. Also, the investigation should be undertaken on appropriate aircraft (e.g. B757s fitted with the RR535C engine identified by the COT as one possible aircraft to use) during flight." They also recommended the BAe 146 aircraft.

The COT provided preliminary estimates for the number of flights required for the main study. They suggested that for exposure monitoring per airframe/engine type more than 100 sectors would be required for background monitoring and up to 10,000 to 15,000 for sectors to assess exposures relating to oil/fume incidents, depending on the airframe and engine type, APU, air conditioning and engine services.

The COT proposed that the "time weighted solid phase microextract (SPME)" would be the most practical analytical sampling technique, given the large numbers of compounds to be detected, the cost of such devices and acceptability to commercial airlines. They recognised that SPME would not allow

monitoring of peak air concentrations during an oil/fume incident but would enable background information on the cabin air environment to be obtained. They also suggested the use of Photoionization Detectors (PIDs).

#### 3. METHODOLOGY FOR THE FUNCTIONALITY TEST

#### 3.1 Overall Test Design

The initial design for the functionality test was based on the recommendations from the COT. This proposal had been to collect cabin air samples from a BAe146 and Boeing 757 (fitted with a RR535 engine) on the ground with and without the engines running in order to assess the suitability of the equipment for use in a major investigation into cabin air quality. The sampling equipment to be assessed was to be SPMEs and PIDs.

Two potential roles for the equipment were considered:

- 1. Monitoring of overall VOC and SVOC concentration across all phases of a flight
- 2. Detection of anomalous elevations of VOC and SVOC concentrations ("fume events").

As actually carried out, however, the functionality test went beyond the COT recommendation in several aspects:

- 1. The inclusion of a second passive sampling technique using diffusive sampling onto thermal desorbtion (TD).
- 2. The use of an active sampling method, pumped sampling onto thermal desorbtion (TD) tubes (see 3.3.3), in order to allow the quantification as well as identification of VOC/SVOC contaminants of cabin air.
- 3. Since the increased concentrations of VOC/SVOCs in a "fume incident" were considered likely to be transient, consideration was also given to the feasibility of using a PID as a method for triggering other VOC/SVOC sampling methods (e.g. pumped TD), which might be expected to allow identification of specific VOC/SVOCs released during an incident.
- 4. Use of specialised air sampling equipment provided by the Building research Establishment (BRE).

#### 3.2 Scope

The work reported here represents an assessment of available methodologies for their potential use in an anticipated larger study. The results presented should not therefore be regarded as definitive measurements of aircraft cabin air quality.

We have assumed that in later studies sampling will be undertaken by a technically qualified investigator travelling in the aircraft. The scope of the functionality test included consideration of the likely workload of this individual against possible sampling designs. It is probable that only one technician will be allowed on any given flight, and this will inevitably place limitations on the type and frequency of samples that can be reliably obtained.

This study also examined the feasibility of carrying out sample analysis using a blinded experimental design, with separate organisations carrying out duplicate analyses. Potential issues here would revolve around sample labelling and transport, reporting, and the maintenance of confidentiality. No attempt has been made at this stage to reconcile at a detailed level the analytical procedures used by the participating laboratories.

#### 3.3 Equipment

#### 3.3.1 Solid Phase Microextract Fibres (SPME)

A Solid Phase Microextract Fibres (SPME) is a fibre which is coated with an adsorbent and mounted in a holder, which protects it until it is required. To take a sample, the fibre is extended and the VOCs in the environment adsorb onto it. Because this is a diffusive process, quantification is not possible. Although air-sampling fibre holders are available, SPME is more commonly found as a laboratory technique for headspace sampling. One significant disadvantage of SPME for air quality monitoring is the physical fragility of the fibres. Analysis is by gas chromatography-mass spectroscopy (GC-MS), with the SPME fibre holder being inserted into the heated sample port of the instrument.

#### 3.3.2 Photoionization detectors (PIDs)

Photoionization detectors (PIDs) are general-purpose, hand-held, battery-powered instruments which are capable of responding to a wide range of gases and vapours. The sample is drawn through a chamber where it is exposed to high-energy ultraviolet (UV) light. Ionization occurs when a molecule in the sample absorbs a UV photon which has an energy (measured in electron volts or eV) greater than the ionization potential of the molecule. The chamber also contains electrodes to which a potential charge is applied. Ionization results in a current between the electrodes which can be measured and used to estimate the concentration of species of interest in the sample.

#### 3.3.3 Thermal Desorbtion (TD)

Thermal Desorbtion (TD) is a sampling method which allows the volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) present in an air sample to be analysed without the need to retain a gaseous sample. Typically, appropriate adsorbents are placed in a stainless steel tube about 10cm long by 1cm diameter. Two adsorbents, a specialised polymer and an activated carbon black, have been used in the cabin air quality pilot study. The different properties of these two substances result in a method which responds to a very wide range of VOCs and SVOCs.

TD tubes can be used in passive or pumped mode. In passive mode, one end of the tube is left open to the air for a defined time and VOCs and SVOCs enter the tube by simple diffusion. This method is used in environmental exposure assessment when individuals wear a TD tube as workers in the nuclear industry might wear a radiation badge. In pumped mode, air is passed through the tube at a defined rate for a predetermined time, the VOCs and SVOCs in the sample are retained and the gaseous component exhausted. Because the total volume of the sample is known it is possible to estimate the concentration of each VOC or SVOC in the environment from which it was drawn. A further advantage of pumping is that the time for which the sorbents are exposed to the environment is relatively short and can be closely controlled. For these reasons, pumped TD is the method of choice for cabin air quality monitoring of VOCs and SVOCs.

Analysis of TD samples is by gas chromatography-mass spectroscopy (GC-MS). The TD tube is heated to >300°C, which causes the VOC/SVOCs to desorb, and flushed with carrier gas (usually helium) which carries the VOC/SVOCs to the instrument itself. The GC separates out the compounds which are thus presented in sequence to the MS. Individual compounds may be identified by comparison of the resulting mass spectra with commercially available spectrum libraries.

#### 3.3.4 Building Research Establishment Equipment

The Building Research Establishment (BRE) have extensive experience and their own equipment and techniques for air sampling and analysis. They were invited to take part in the cabin air sampling on the BAe 146 aircraft and the Boeing 757.

#### 4. TEST SAMPLING ON A BAe 146 AIRCRAFT.

#### 4.1 Data Collection

The first stage of the functionality test involved the collection of samples from the cabin air of a BAe 146 aircraft whilst parked in the hangar. Samples were taken with and without the Auxiliary Power Unit (APU) and Air conditioning packs (ECS) running.

As an additional check of the sampling techniques used, an "unknown" solvent (prepared by Cranfield University) was released at a pre-determined time in the BAe 146 cabin, whilst the engines were running. This enabled information to be gained about the capability of the various types of sampling equipment to provide information on the identity of a substance and its concentration.

The test conditions, during which samples were taken are summarised below:

- 1. Aircraft hangar background
- 2. Aircraft cabin background
- 3. Aircraft with APU and ECS packs on
- 4. Aircraft with APU and ECS packs on and "unknown" solvent release.

The devices were placed and operated by a scientist from Cranfield and an occupational hygienist from an independent commercial laboratory.

The samples collected using diffusive SPME fibres and diffuse and pumped TD tubes were collected and analysed by Analytical and Environmental Services (AES). The pumped samplers were set to a flow rate of 80ml/min and the samples were run for approximately 15 minutes for each test condition. The PID data was collected by AES and analysed by Cranfield University. BRE collected and analysed their samples independently. The scientists from these organisations were instructed by the project manager not to communicate with each other in the time between the test and submitting their report to the project manager. This they agreed and performed. The airline operator took no part in the data collection.

#### 4.2 Results

The full results from the analyses undertaken by BRE, AES and Cranfield University can be found in the separate reports from each of these organisations. These are located in the appendix of this report.

#### 4.2.1 Results from analysis of cabin air samples using SPMEs and Thermal Desorption

- The sampling for volatile and semi-volatile compounds using pumped thermal desorption tubes resulted in the detection of; Benzene, Toluene, Xylene, 1,2,4-Trimethyl benzene, C9-C15 Aliphatic hydrocarbons, C6-7 Aliphatic hydrocarbons, Dioctyl phthalate, C20-30 Aliphatic hydrocarbons, Tributylphosphate, 2,5-Diphenylbenzoquinone, Tertiary Butylphenol and Trimethylpentylphenol.
- Although the plane was in the confines of the hangar for this exercise, Tributylphosphate was present at all times within the cabin, even before switching on the APU. This indicates that residual amounts linger within the cabin. The results indicate that the kerosene range compounds (C9-C15) increased when the APU was switched on, as did the concentrations of the C20-C30 compounds which are associated with lubrication oils. This suggested that small amounts of unburned fuel (perhaps from within the exhaust fumes) and oil vapours were being taken into the air conditioning system. 2,5-Diphenylbenzoquinone also appeared in the sample when the APU was switched on.
- The unknown solvent introduced into the cabin was mainly toluene. Since this compound is readily identifiable by its smell, xylene was added at a concentration of approximately 10%. Toluene was correctly identified as the main solvent. Although not explicitly described in the relevant laboratory reports, all methods also detected xylene at concentrations well above

background. Moreover, pumped TD sampling recorded toluene and xylene in the correct proportions in cabin air (27.0 and 2.3 mg/m<sup>3</sup> respectively).

- The compounds determined were all at low concentrations less than 0.1mg/m<sup>3</sup> (apart from the test with the introduction of the unknown solvent), which is less than any of the workplace exposure levels for the compounds determined.
- Diffusive thermal desorption tubes were also trialled in the exercise. The tubes effectively picked up low levels of the BTEX and other hydrocarbons, but did not pick up the tributylphosphate. The levels could not be accurately quantified without suitable uptake rates for the determinants detected and the masses collected on the tube were very low, indicating that this methodology is less appropriate for this type of exercise.
- The sampling of volatile and semi-volatile compounds using SPME fibres also identified the presence of various hydrocarbons and also indicated that toluene was the unknown solvent that was introduced into the cabin. Conversion of the laboratory SPME results to atmospheric concentrations was not practicable as uptake rates have not been established. It should be noted that detection of other compounds in the samples may have been prevented by the presence of siloxanes and other silicon compounds in relatively large amounts. These artefacts originate in the adsorbent coating of the SPME fibre which "bleeds" them during analysis.
- The results indicated that the most appropriate technique for determining accurately the compounds present within the cabin was the pumped thermal desorption methodology. This is especially the case for compounds that may only be present for short periods of time, such as those released during any "fume event".

#### 4.2.2. Results from the PID

This test was designed to determine the ability of the PID to detect significant fume incidents by deliberately releasing an "unknown" VOC into the cabin. The results of the solvent release test are shown in the graph in the appendix. Peaks representing concentrations up to approximately 150ppm are clearly visible, with the whole incident occupying approximately 6 minutes. The MiniRAE was set to sample every 2 seconds, and at this resolution, wide variations in concentration within incident are also clearly visible.

In contrast, prior to solvent release the MiniRAE failed to register the presence of VOCs. However, the data recorded during the decay phase of the trial clearly demonstrate the instrument's ability to record concentrations below 1 ppm, suggesting that routine VOC concentrations in this environment are at or below the detection limit of this particular PID.

#### 4.2.3 BRE Results

Sampling was carried out using pumped adsorbent tubes. Subsequent analysis used thermal desorption technology coupled with GC/GCMS, and focussed primarily on the detection of engine oil, and the semi-volatile organic components of engine oil (Jet2) and hydraulic fluid (Hyjet4) used in the aircraft tested.

- Large concentrations of toluene and xylene were found in samples taken during Test 4 (when the chemical sample was deliberately released).
- Concentrations of Hyjet4 hydraulic fluid were similar for all of the samples taken within the aircraft cabin (Tests 2, 3 & 4), and up to seven times higher than that found as a background in the hangar (Test 1).
- Tri-butyl phosphate (typically found in hydraulic fluid and used as an additive in plastics) was found in all of the samples from the aircraft cabin (Tests 2, 3 & 4) at levels up to twenty times above background level (Test 1).
- Higher concentrations of Jet2 engine oil were found in the cabin during tests where the APU and ECS systems were running (Tests 3 & 4). These levels were up to seven times higher than background levels (Tests 1 & 2).

- Higher concentrations of total tri-cresyl phosphate (a component of engine oil) were found in the cabin during tests where the APU and ECS systems were running (Tests 3 & 4). These levels were up to fifty times higher than were found in Tests 1 & 2.
- The compounds determined were all at low concentrations in the range 0.02-50  $\mu$ g/m<sup>3</sup> (apart from the test with the introduction of the unknown solvent).
- As with the AES measurements (Section 4.2.1) these results indicate that the most appropriate technique for determining accurately the compounds present within the cabin is the pumped thermal desorption methodology. This is especially the case for compounds that may only be present for short periods of time, such as those released during any "fume event".
- Continuous monitoring showed a rise in the ultra-fine particle concentrations when the APU and ECS were operating. These particles may have come from the APU directly, or from re-ingestion of the APU exhaust into the aircraft.

#### 4.3 Summary

The results from the tests in the BAe 146 had provided valuable information on the performance of the sampling equipment on the ground. Rather than replicate the same procedures on the ground with a B757, it was decided for Stage 2 that more could be gained from collecting samples using the equipment in flight.

# 5. TEST SAMPLING ON A BOEING 757 FITTED WITH THE RR 535c ENGINE

#### 5.1 Data Collection

The sampling equipment was the same as for the BAe 146, with the following two minor exceptions. The PID device was changed from a device which would register one part per million, to one part per billion. Two SPME fibres were used to collect data from some of the test conditions in order that one could be analysed by AES and the other sent to another laboratory for an independent check on the analysis and findings.

The devices were placed and operated by a scientist from Cranfield and an occupational hygienist from an independent commercial laboratory. In addition to analysis by these two institutions of the samples they took, extra samples were sent to a further independent commercial laboratory.

A flight was planned which involved the test conditions during which samples were taken. These are summarised below:

- 1. Aircraft background
- 2. Aircraft background (APU and ECS on)
- 3. Taxi
- 4. Ascent/Climb
- 5. Cruise
- 6. Descent
- 7. Descent/Landing/Short Taxi
- 8. Stand (APU and ECS on)

All tests were conducted on the flight deck of the aircraft, with the door to the cargo bay closed. There were 3 scientists on the flight taking samples. One from BRE, one from AES and one from Cranfield.

#### 5.2 Results

The full results from the analyses undertaken by BRE, AES and Cranfield University can be found in the separate reports from each of these organisations. These are located in the Appendix of this report.

The results can be summarised as follows:

#### 5.2.1 "Fume Event"

The procedure for the flight and data collection went entirely as planned with one exception. This was that at the top of the climb phase, a "fume event" occurred. The event was of very short duration but was noticeable to all in the cockpit (crew and scientists) as a distinct oily type odour, which persisted for less than one minute before completely dissipating. Although the BRE sampling equipment indicated an increase in the number concentration for particles measured during this period, their mass concentration would have been extremely small. The result of this is that the pumped sample taken for analysis during this flight phase (i.e. over 18 mins) did not significantly affect the results from the climb phase of flight. (This will have implications for future test design – see section 6 of report). This means that although a "fume event" occurred on this flight, the samples taken cannot be regarded as an accurate measure of substances released during that event.

#### 5.2.2 Results from analysis of cabin air samples using SPME's and Thermal Desorption Tubes

The sampling for volatile and semi-volatile compounds using thermal desorption tubes at various stages of the test flight resulted in the detection of; Benzene, Toluene, Xylene, 1,2,4-Trimethyl benzene, Naphthalene, Heptanal, C9-C15 Aliphatic hydrocarbons, Phenlo, 3-Carene, Phenylethyne, C17 Aliphatic hydrocarbons, Ethyl hexyl phthalate, C20-C30 Aliphatic hydrocarbons and Hexadeconoic acid. The results of the sampling highlight that none of the detected compounds were present at concentrations in excess of 0.2 mg/m<sup>3</sup> (200  $\mu$ g/m<sup>3</sup>). For all samples, Toluene was the predominant analyte detected.

It should be noted that in all instances the detected concentrations from the sampling using thermal desorption tubes were significantly below the relevant HSE specified WEL where applicable. It should also be noted that wherever possible, WELs are set at a level at which there is no evidence of adverse effects on human health.

The sampling for volatile and semi-volatile compounds using SPME tubes at various stages of the test flight resulted in the detection of; Toluene, Heptanal, C9-C15 Aliphatic hydrocarbons, C15 Aromatic hydrocarbons, C17 Aliphatic hydrocarbons and C21 Aromatic hydrocarbons. It should be noted that it is not possible to quantify the results obtained using this sampling technique. It should also be noted that the presence of other compounds in the samples may have been masked by the large number of siloxanes and other silicon compounds produced as a result of the fibre bleed during sample injection.

#### 5.2.3. Results from the PID

Although the performance of the PID in this test was not satisfactory because of problems with the particular instrument which was used, it is believed to be a suitable method for detecting fume events in aircraft cabins. Its ability to respond quickly to a wide range of compounds will enable it to be used as a trigger for short duration pumped TD sampling should a fume incident occur. Using these two techniques will thus allow incidents to be firstly detected and then fully characterised. An instrument with parts per billion sensitivity will be required for monitoring of general background levels and for detecting "normal" variations in cabin air VOC concentrations. PIDs with the required performance will be evaluated as part of the methodological workup for further studies.

#### 5.2.4 Results from BRE Equipment

As with the BAE146 monitoring, sampling was carried out using pumped adsorbent tubes. Subsequent analysis used thermal desorption technology coupled with GC/GCMS, and focussed primarily on the detection of engine oil, and the semi-volatile organic components of engine oil (Jet2) and hydraulic fluid (Skydrol 500B4) used in the aircraft tested.

• The "bleed air contamination event" reported by those conducting the tests and the flight crew during the ascent phase (in particular the "thrust to climb" period) of the flight was coincident with a sharp, brief rise in ultra-fine particles.

- There was a higher concentration of Jet2 engine oil found within the sample taken during the stage of the flight in which the fume event occurred (Sample 4), compared with those found during other stages of the flight. Interestingly, some of the concentrations of Jet2 on the first feasibility study (on a BAe146 aircraft on the ground) were higher than this level, though no "bleed air contamination event" was noted by those present on that occasion.
- The concentration of total tri-cresyl phosphate found in Sample 4 was slightly higher than that found in other flight phases though a similar concentration was found in the background sample (Sample 1).
- Skydrol hydraulic fluid was found at similar levels in air samples from all stages of the flight, and at similar concentrations to those found for Hyjet hydraulic fluid during the first feasibility study.
- Tributyl phosphate, a major component of hydraulic fluids and also an additive in plastics, was found at concentrations somewhat below those found in the BAe146 in the first study when the APU and ECS were on.
- The compounds determined were all at low concentrations in the range 0.01-8  $\mu$ g/m<sup>3</sup>.
- As with the samples taken in the first feasibility study, these results indicate that the most appropriate technique for determining accurately the compounds present within the cabin is the pumped thermal desorption methodology. This is especially the case for compounds that may only be present for short periods of time, such as those released during a "fume event" like the one experienced during the monitoring.

#### 5.2.5. Independent analysis of samples.

The results from the analysis of the SPMEs and pumped samples sent to an independent laboratory highlighted the practical challenges associated with using one organisation to collect the samples and another to perform the analysis.

The results from the analysis performed by the independent company did confirm that the collection of data using pumped samples to be the most appropriate method. However, they were only able to provide an overall analysis of the substances found in the cabin, and not attribute these to the various phases of flight. Furthermore, it was not possible to reconcile the quantitative data from the two laboratories. This may be the result of genuine differences between the samples with which they were presented, but is more likely to represent differences in the analytical protocols used. Although the same basic method was employed, inconsistencies in such factors as analysis times, temperatures and flow rates may have affected the results. Unfortunately the information available in the respective reports does not allow this to be definitively assessed.

#### 5.3 Summary

Although a "fume event" occurred on this flight, the samples taken cannot be regarded as an accurate measure of substances released during that event. As discussed in the Conclusions below, measurements will need to be taken over a much shorter period in the next phase of the study.

#### 6. CONCLUSIONS

1. The results from the tests on both a BAe 146 and the B757 indicated that equipment and analytical techniques are available to monitor and provide data on contaminant chemicals in the cabin.

2. The functionality tests led to the identification of two techniques with independent methods for data collection and analysis which can be performed by independent laboratories and which can potentially be used for a future data collection investigation of cabin air quality. The techniques allow quantification of the concentration of the contaminants present so as to allow direct comparison between the sets of results. One method has been developed by BRE and is their intellectual property. The other

technique involves a combination of the use of pumped TD tubes to collect air samples over predetermined phases of flight and the potential use of a PID (ppb) to indicate when a "fume event" has occurred and to indicate that a pumped TD tube sample should be immediately collected within the following minute.

3. The techniques described can potentially be used for both background monitoring of cabin air in normal flight and for sudden "fume events". It is recommended that the Functionality Test is extended to finalise the methodology to be used for the collection of cabin air samples both during normal flight and immediately following a "fume event". It is suggested that the extended programme takes place early in 2008. This will enable samples to be collected and a preliminary data set established, during the winter weather, which is the time at which 'fume events' have an increased probability of occurrence.

- 4. Finally, it is recommended that in any future major data collection study
  - (i) the pilots and research scientists on the aircraft are required to complete a questionnaire
  - (ii) relevant information is obtained from the flight data recorder and aircraft maintenance reports for subsequent analysis.

5. The major data collection study will enable information to be gained on the substances which are released into the cabin air. Once this knowledge has been obtained, consideration should be given to a further study involving the collection of specimen samples from pilots following a "fume event". The aim would be to determine by laboratory testing, whether the substances released during a "fume event" and identified in the main data collection study, have been absorbed by the pilots. One approach would be to take samples of breath onto TD tubes which can then be analysed using protocols which are identical to those used for cabin air, allowing direct comparison.

6. We consider that we have defined a workable approach to the investigation of aircraft cabin air quality under both nominal conditions and during "fume events". However, some issues have become apparent which will need to be considered in carrying forward further work. These are outlined below:

- i) *Technician workload.* Several individuals were available to carry out sampling during the functionality test and it would not be possible for a single investigator to obtain samples as required using the equipment supplied. In particular it will be necessary to specify a suitable constant-flow pump for the TD work, which will require only one (or at the most, two) pumps to be carried and the TD tube replaced as needed.
- ii) *Duplicate analyses*. This exercise highlighted the difficulties of coordinating analyses across different laboratories. It is clear that in further studies sample handling, GC-MS protocols and reporting will need to be duplicated in fine detail.

#### 7. **RESPONSE TO REVIEWERS**

An earlier version of this report was assessed by four highly-qualified individuals, and we are grateful for their time and effort. We have made some changes to the body of the report in order to reflect some of their comments and concerns. Below we respond more specifically to points raised which we consider to be particularly important in conducting further work in this area. In this section, the relevant parts of the reviewers' comments are reproduced in italics. We are now in contact with Professor Spengler and Mr Vallarino to see if some of the parallel testing equipment they are developing in the USA can be incorporated into the next phase of the functionality testing. We are pleased that Professor Cherrie has been invited to be a member of the Steering Committee for the next phase of this work.

#### **Prof. John Spengler**

For the PIDs, the failure of the Phocheck device to respond during the actual test flight cast doubts on the usefulness of this instrument to detect combustion oil in the bleed air. The ground test of the MiniRAE showed that it would respond to toluene deliberately released at high concentrations. There is not convincing evidence to support the conclusion made in Appendix 8.3, "Cranfield Report on the Use of Photoionization Detectors". Under the section **Flight Test** the report states:

"This exercise produced no useful information, since the PID, although operated during all phases of the flight, failed to register anything above baseline."

*Thus, it is difficult to understand how several lines later, in the* **Conclusions** *section, the report can state:* 

"1. The PID is a suitable instrument for detecting fume incidents in aircraft cabins."

This unsupported conclusion is repeated and implied to be true in the main report.

We think it most likely that our difficulties were related to the particular instrument employed. The best approach to resolving this question will be to rehearse our sampling procedures on the ground prior to carrying out further work. We feel that the PID will prove a suitable instrument when it is performing to its advertised specification.

We do not agree that SPME and passive TDT sampling systems have limited value as fume incident detectors. Observations derived from the BRE sampling suggest that Jet2 engine oil and total tricresyl phosphate (TCP) were found in higher concentrations when APU/ECS were operating during the hangar study. Therefore, it might be possible to deploy passive samplers to integrate exposures on an aircraft over several flight segments as first level screening to identify specific aircraft for more detailed follow-up sampling. The failure of the diffusion techniques to provide reliable results in the constructed short-term test does determine their performance if used in an alternative sampling scheme.

This may be the case, but the reviewer is thereby suggesting a completely different approach and study design. Moreover, we feel that his suggested approach presupposes a level of knowledge regarding cabin air quality and the occurrence of fume events which does not, in our view, exist. Two assumptions in particular concern us: firstly that the only compounds of interest are tricresyl phosphates and secondly that particular aircraft are especially prone to fume events. Whilst there is significant anecdotal evidence to support these views, they cannot be regarded as proven. If either were to turn out to be incorrect, the scheme outlined by this reviewer would be at risk of producing a falsely negative outcome.

#### Jose Vallarino

Issues identified with sampling in the report and outlined below suggest that TD tubes require careful method development and qualified technicians to collect the sample to obtain maximum utility from the samples.

We strongly agree with this view and recommend that this approach be followed.

Incorrectly orienting some of the multi-sorbent thermal desorption tubes is a concern. Standard written protocols should be available to research technicians on the use and orientation of the multi-bed thermal desorption tubes. Only one laboratory identified this issue.

We are not sure that this actually occurred, and are puzzled as to how this laboratory reached this conclusion since it was not reported by the technicians on the test flight. However, we fully agree that

equipment should be utilised correctly and that methodologies should be developed to prevent incorrect orientation.

The PID was used as a detection tool for events, a condensation particle counter should be tested to see if it may detect smaller events and events of more limited duration than two minutes.

We agree and recommend that equipment for particle/aerosol counting be considered for future work. Another reviewer (**John Cherrie**) made a similar comment, pointing out that VOCs/SVOCs comprising a fume event might exist as aerosols rather than in the vapour phase.

#### 8. **REFERENCES**

1. CoT Report



#### CABIN AIR SAMPLING FEASIBILITY STUDY ON BEHALF OF THE DEPARTMENT FOR TRANSPORT, INITIAL FEASIBILITY ASSESSMENT USING A BAe146

REPORT AES-DfT-1 4355

6TH JUNE 2007

#### AES (ANALYTICAL & ENVIRONMENTAL SERVICES) NORTHUMBERLAND DOCK ROAD, WALLSEND, TYNE & WEAR NE28 0QD Tel: 0191 296 8500 Fax: 0191 2968560

AES (Analytical & Environmental Services) has produced this report within the terms of the contract with the client and taking account of the resources devoted to it by agreement with the client.

We disclaim any responsibility to the client and others in respect of any matters outside the scope of the above. This report is confidential to the client and we accept no responsibility of whatsoever nature to third parties to whom this report, or any part thereof, is made known. Any such party relies on the report at their own risk.

Report type: Air Monitoring Report issue: 25<sup>th</sup> September 2007 Report issue date:

File reference number:

Issuing office:

Newcastle-upon-Tyne

Final

AES-DfT-1 4355

Originator:

1 A

B Anstee

Section Manager – Air

September 2007

Checked & approved:

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Quality & Acoustics (North)

J Donalson Senior Scientist - Organics September 2007

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Appendix 2 Laboratory results for diffusive samplers

#### EXECUTIVE SUMMARY

- As part of the Department for Transport's feasibility study into sampling techniques for use in the assessment of aircraft cabin air quality, AES (Analytical & Environmental Services) have undertaken an initial feasibility exercise. This exercise was carried out during specified ground based operations of the Auxiliary Power Unit (APU) of a BAE 146 on June 6th 2007. The aim of the exercise was to initially assess the suitability of specified sampling techniques. Additionally, an unknown solvent was discharged into the cabin as a test of the laboratories ability to identify an unknown compound.
- The sampling for volatile and semi-volatile compounds using thermal desorption tubes resulted in the detection of; Benzene, Toluene, Xylene, 1 ,2,4-Trimethyl benzene, C9-C15 Aliphatic hydrocarbons, C6-7 Aliphatic hydrocarbons, Dioctyl phthalate, C20-C30 Aliphatic hydrocarbons, Tributylphosphate, 2,5-Diphenylbenzoquinone Tertiary Butylphenol and Trimethylpentylphenol.
- Tributylphosphate was present at all times within the cabin, even before switching on the APU. This indicates that residual amounts linger within the cabin. The results indicate that the kerosene range compounds (C9-C1 5) increase when the APU is switched on, as do the concentrations of the C20 C30 compounds which are associated with lubrication oils. This suggests that small amounts of unburned fuel (perhaps from within the exhaust fumes) and oil vapours are being taken into the air conditioning system it should be remembered that the plane was within the confines of the hangar for this exercise. 2,5-diphenylbenzoquinone also appears in the sample when the APU is switched on.
- Toluene was the unknown solvent introduced into the cabin. Other impurities of the Toluene test solvent were also determined.
- The compounds determined were all at low concentrations less than 0.1 mg/m<sup>3</sup> (apart from the test with the introduction of the unknown solvent), which is less than any of the workplace exposure levels for the compounds determined.
- Diffusive thermal desorption tubes were also trialed in the exercise. The tubes effectively picked up low levels of the BTEX and other hydrocarbons, but did not pick up the tributylphosphate. Tenax may have been a better sorbent to use in these tubes to capture the less volatile compounds. The levels cannot be accurately quantified without suitable uptake rates for the determinands detected and the masses collected on the tube were very low, indicating that this methodology is less appropriate for this study.
- The sampling for volatile and semi-volatile compounds using SPME tubes also identified the
  presence of various hydrocarbons and also indicated that toluene was the unknown solvent the
  was introduced into the cabin. Conversion of the laboratory SPME results to atmospheric
  concentrations was not practicable as uptake rates have not been established. It should also
  be noted that the presence of other compounds in the samples may have been masked by
  the large number of siloxanes and other silicon compounds produced as a result of the fibre
  bleed during sample injection.
- It is recommended that the most appropriate technique for determining accurately the compounds present within the cabin is the pumped thermal desorption methodology. This is especially the case for compounds that may only be present for short periods of time, such as those released during any 'fume' event.

#### 1. INTRODUCTION

- 1.1 As part of the Department for Transport's feasibility study into sampling techniques for use in the assessment of aircraft cabin air quality, AES (Analytical & Environmental Services) have undertaken an initial feasibility exercise. This exercise was carried out during specified ground based operations of the Auxiliary Power Unit (APU) of a BAE 146 on June 6th 2007. The aim of the exercise was to initially assess the suitability of specified sampling techniques. Additionally, an unknown solvent was discharged into the cabin as a test of the laboratories ability to identify an unknown compound. The exercise was performed by Ben Anstee and John Donalson of AES.
- 1 .2 This exercise is intended to allow each of the assessment techniques to be initially assessed within the cabin environment. Subsequent to this, it is proposed that in-flight measurements will be taken. Once a suitable methodology has been determined a more detailed assessment can be undertaken on a specified number of aircraft as a means of assessing cabin air quality with emphasis on 'fume events'.
- 1 .3 The exercise was carried out with the plane within the hangar, with the APU used to generate example cabin environments. This report and the sampling refer to prevailing conditions at the time of the survey and the findings should not be extrapolated to estimate potential exposures under other conditions.

#### 2. METHODOLOGY

- 2.1 Air sampling was undertaken under four different scenarios:
  - i) Hangar background
  - ii) Cabin background
  - iii) Cabin with APU on
  - iv) Cabin with APU on + unknown solvent
- 2.2 The plane used for the assessment was a BAE 146 aircraft.
- 2.3 Sampling was undertaken using pumped thermal desorption tubes, diffusive thermal desorption tubes and diffusive SPME fibres. The pumped samplers were set to a flow rate of 80ml/min and the samples were run for approximately 15 minutes for each scenario.
- 2.4 Other than the sample taken within the hangar, monitoring was carried out within the cockpit, with the samplers located on the top of the main instrument panel.
- 2.5 The diffusive samplers (Carbograph TD1 tubes and SPME fibres) were not exposed until they were in the assessment position. After the exposure period, the samplers were re-sealed for transportation to the laboratory.

#### 3. **RESULTS & CONCLUSIONS**

- 3.1 A full set of tabulated results from this monitoring survey calculated as concentration figures are included in Appendix 1 of this report. Additionally, the laboratory results of the diffusive thermal desorption tubes and SPME fibres are provided in Appendix 2.
- 3.2 The sampling for volatile and semi-volatile compounds using thermal desorption tubes resulted in the detection of; Benzene, Toluene, Xylene, 1,2,4-Trimethyl benzene, C9-C1 5 Aliphatic hydrocarbons, C6-7 Aliphatic hydrocarbons, Dioctyl phthalate, C20-C30 Aliphatic hydrocarbons, Tributylphosphate, 2,5-Diphenylbenzoquinone Tertiary Butylphenol and Trimethylpentylphenol.
- 3.3 Tributylphosphate was present at all times within the cabin, even before switching on the APU. This indicates that residual amounts linger within the cabin. The results indicate that the kerosene range compounds (C9-C1 5) increase when the APU is switched on, as do the concentrations of the C20 C30 compounds which are associated with lubrication oils. This suggests that small amounts of unburned fuel (perhaps from within the exhaust fumes) and oil vapours are being taken into the air conditioning system it should be remembered that the plane was within the confines of the hangar for this exercise. 2,5-diphenylbenzoquinone also appears in the sample when the APU is switched on.
- 3.4 Toluene was the unknown solvent introduced into the cabin. Other impurities of the Toluene test solvent were also determined.
- 3.5 The compounds determined were all at low concentrations less than 0.1 mg/m<sup>3</sup> (apart from the test with the introduction of the unknown solvent), which is less than any of the workplace exposure levels for the compounds determined.
- 3.6 Diffusive thermal desorption tubes were also trialed in the exercise. The tubes effectively picked up low levels of the BTEX and other hydrocarbons, but did not pick up the tributylphosphate. Tenax may have been a better sorbent to use in these tubes to capture the less volatile compounds. The levels cannot be accurately quantified without suitable uptake rates for the determinands detected and the masses collected on the tube were very low, indicating that this methodology is less appropriate for this study.
- 3.7 The sampling for volatile and semi-volatile compounds using SPME tubes also identified the presence of various hydrocarbons and also indicated that toluene was the unknown solvent the was introduced into the cabin. Conversion of the laboratory SPME results to atmospheric concentrations was not practicable as uptake rates have not been established. It should also be noted that the presence of other compounds in the samples may have been masked by the large number of siloxanes and other silicon compounds produced as a result of the fibre bleed during sample injection.
- 3.8 From the findings of this exercise, it is recommended that the most appropriate technique for determining accurately the compounds present within the cabin is the pumped thermal desorption methodology. This is especially the case for compounds that may only be present for short periods of time, such as those released during any 'fume' event.

Date: June 2007/ Version 1

**APPENDIX 1** 

**Results Tables** 

#### Hangar Background Date : 6th June 2007

Determinand	Vol Sampled (I)	Total analyte as target species (ng)	Blank (ng)	Concentration (mg/m3)
Benzene	1.52	9.2	4.7	0.0030
Toluene	1.52	23	6.2	0.011
Ethylbenzene	1.52	<3.0	0	<0.0020
m&p-xylene	1.52	3.7	0	0.0024
o-xylene	1.52	<3.0	0	<0.0020
Styrene	1.52	<3.0	0	<0.0020
1,2,4-Trimethylbenzene	1.52	<3.0	0	<0.0020
C6-C7 Aliphatic hydrocarbons	1.52	<3.0	0	<0.0020
C9-C15 Aliphatic hydrocarbons	1.52	29	0	0.019
Tributylphosphate	1.52	<3.0	0	<0.0020
2,5-Diphenylbenzoquinone	1.52	<3.0	0	<0.0020
Dioctyl phthalate	1.52	7.2	5.2	0.0013
Tertiary butylphenol	1.52	3.5	0	0.0023
Trimethylpentylphenol	1.52	<3.0	0	<0.0020
C20-C30+ Aliphatic hydrocarbons	1.52	<3.0	0	<0.0020

# Cabin Background Date : 6th June 2007

Determinand	Vol Sampled (I)	Total analyte as target species (ng)	Blank (ng)	Concentration (mg/m3)
Benzene	1.44	8.5	4.7	0.0026
Toluene	1.44	20	6.2	0.010
Ethylbenzene	1.44	<3.0	0	<0.0021
m&p-xylene	1.44	3.4	0	0.0024
o-xylene	1.44	<3.0	0	<0.0021
Styrene	1.44	<3.0	0	<0.0021
1,2,4-Trimethylbenzene	1.44	<3.0	0	<0.0021
C6-C7 Aliphatic hydrocarbons	1.44	8.6	0	0.006
C9-C15 Aliphatic hydrocarbons	1.44	25	0	0.017
Tributylphosphate	1.44	23	0	0.016
2,5-Diphenylbenzoquinone	1.44	<3.0	0	<0.0021
Dioctyl phthalate	1.44	7	5.2	0.0013
Tertiary butylphenol	1.44	<3.0	0	<0.0021
Trimethylpentylphenol	1.44	<3.0	0	<0.0021
C20-C30+ Aliphatic hydrocarbons	1.44	<3.0	0	<0.0021

#### Cabin Background - APU On Date : 6th June 2007

Determinand	Vol Sampled (I)	Total analyte as target species (ng)	Blank (ng)	Concentration (mg/m3)
Benzene	1.36	7.8	4.7	0.0023
Toluene	1.36	75	6.2	0.051
Ethylbenzene	1.36	<3.0	0	<0.0022
m&p-xylene	1.36	8	0	0.0059
o-xylene	1.36	<3.0	0	<0.0022
Styrene	1.36	<3.0	0	<0.0022
1 ,2,4-Trimethylbenzene	1.36	8.9	0	0.0065
C6-C7 Aliphatic hydrocarbons	1.36	17	0	0.013
C9-C15 Aliphatic hydrocarbons	1.36	90	0	0.066
Tributylphosphate	1.36	22	0	0.016
2,5-Diphenylbenzoquinone	1.36	13	0	0.010
Dioctyl phthalate	1.36	3.2	5.2	<lod< td=""></lod<>
Tertiary butylphenol	1.36	<3.0	0	<0.0022
Trimethylpentylphenol	1.36	3.2	0	0.0024
C20-C30+ Aliphatic hydrocarbons	1.36	14	0	0.010

#### Cabin Background - APU On + Solvent Date : 6th June 2007

Determinand	Vol Sampled (I)	Total analyte as target species (ng)	Blank (ng)	Concentration (mg/m3)
Benzene	1.20	22	4.7	0.014
Toluene	1.20	33000	6.2	27
Ethylbenzene	1.20	84	0	0.070
m&p-xylene	1.20	2700	0	2.3
o-xylene	1.20	41	0	0.034
Styrene	1.20	5.4	0	0.0045
1,2,4-Trimethylbenzene	1.20	4	0	0.0033
C6-C7 Aliphatic hydrocarbons	1.20	<3.0	0	<0.0025
C9-C15 Aliphatic hydrocarbons	1.20	43	0	0.036
Tributylphosphate	1.20	12	0	0.010
2,5-Diphenylbenzoquinone	1.20	10	0	0.0083
Dioctyl phthalate	1.20	3.3	5.2	<lod< td=""></lod<>
Tertiary butylphenol	1.20	3.8	0	0.0032
Trimethylpentylphenol	1.20	4.4	0	0.0037
C20-C30+ Aliphatic hydrocarbons	1.20	3.8	0	0.0032

Date: June 2007/ Version 1

**APPENDIX 2** 

Laboratory Results for Diffusive Samplers

SAMPLE: CABIN BACKGROUND DIF	FUSIVE THERMAL DESC	RPTION TUBE		
RECEIVED: 07/06/07 TIME:	SAMPLER:	LAB:HOWDON		
		LAB N <sup>0</sup> : 3225382		
DETERMINAND	METHOD	RESULTS		
MASS SPEC. IDENTIFICATION	030*	S7 588		
Analysis for Volatile Organic Compounds by ther components:	mal descrption GC/MS showed	the presence of the following major		
Benzene (<3 ng)	C9-C15 Aliphatic hydrod	carbons (<3 ng) <sup>⊤</sup>		
Toluene (<3 ng)	Tributylphosphate (<3 r	Tributylphosphate (<3 ng) <sup>T</sup>		
Ethylbenzene (<3 ng)	2,5-Diphenylbenzoquing	2,5-Diphenylbenzoquinone (<3 ng) <sup>T</sup>		
m&p-Xylene (<3 ng)	Dioctyl phthalate (<3 ng	Dioctyl phthalate (<3 ng) <sup>T</sup>		
o-Xylene (<3 ng)	tertiary Butylphenol (<3	tertiary Butylphenol (<3 ng) <sup>T</sup>		
Styrene (<3 ng)	Trimethylpentylphenol (	Trimethylpentylphenol (<3 ng) <sup>T</sup>		
1,2,4-Trimethylbenzene (<3 ng)	C20-C30+ Aliphatic hyd	C20-C30+ Aliphatic hydrocarbons (<3 ng) <sup>T</sup>		
C6-C7 Aliphatic hydrocarbons (<3 ng) <sup>T</sup>				
Compounds marked <sup>T</sup> are tentative identifications concentrations of these compounds are approxin an internal standard. Results relate only to the it	nations estimated from a previo			
Tests marked **" in this report are NOT inclu	uded in the UKAS accreditat	ion schedule for our laboratory		
Authorised by : John Donalson Senior S Under the authority of P Burton, Analytic	cientist Sig al Manager Dat	nature: e: 20/06/07		
DEPARTMENT FOR TRANSPORT fao : BEN ANSTEE	Analytical & Enviro Northumberland D	onmental Services Ltd. lock Road		

	RECEIVED: 07/06/07	TIME:	SAMPLER	: LAB:H		
				LAB N		
	DETERMINAND		METHOD	RESULTS		
	MASS SPEC. ID ENTIFICATIO	N	030*	87 589		
Analysis for components	Volatile Organic Compounds by t :	thermal desorption	GC/MS showed the presen	ce of the following major		
Benzene (<	3 ng)	C9-C15	Aliphatic hydrocarbons (<	ð ng) <sup>⊤</sup>		
Toluene (4.	5 ng)	Tributyl	Tributylphosphate (<3 ng)			
Ethylbenzen	e (<3 ng)	, ,	2,5-Diphenylbenzoquinone (<3 ng) <sup>T</sup>			
m&p-Xylene	(<3 ng)		Dioctyl phthalate (<3 ng) <sup>⊤</sup>			
o-Xylene (<	3 ng)	-	tertiary Butylphenol (<3 ng) <sup>™</sup>			
Styrene (<3	<b>u</b> ,		ylpen tylphen ol (<3 ng) <sup>⊤</sup>	_		
	hylbenzene (<3 ng) atic hydrocarbons (<3 ng) <sup>T</sup>	C20-C3	0+ Aliphatic hydrocarbons	(9.8 ng) <sup>+</sup>		
Compounds	marked <sup>T</sup> are tentative identificat ns of these compounds are appr	oximations estimate				
	tandard. Results relate only to th ed *** in this report are NOT in		AS accreditation schedu	le for our laboratory		
	d by : John Donalson Senio authority of P Burton, Analy		Signature: Date: 20/06/0	7 f. Dal		
DEPARTN fao : BEN AES	IENT FOR TRANSPORT ANSTEE	Norti Wall Tyne NE20	vtical & Environmental numberland Dock Road send & Wear 3 0QD (0191) 296 8500 Fax:	d		

<b>AES</b> ANALYTICAL REPO	RT			
SAMPLE: CABIN + APU + SOLVENT D	FFUSIVE THEF	RMAL DESORPTION TUBE		
RECEIVED: 07/06/07 TIME:	SAM	PLER: LAB:HOWDO		
		LAB N <sup>o</sup> : 3225	5384	
DETERMINAND	METHOD	RESULTS		
MASS SPEC. IDENTIFICATION	030*	\$7590		
Analysis for Volatile Organic Compounds by them components:	nal desorption GC/M	NS showed the presence of the following ma	jor	
Benzene (<3 ng)	C9-C15 Alipha	atic hydrocarbons (<3 ng) <sup>T</sup>		
Toluene (540 ng)	-	Tributylphosphate (<3 ng)		
Ethylbenzene (<3 ng)		enzoquinone (<3 ng) <sup>T</sup>		
m&p-Xylene (19 ng)		Dioctyl phthalate (<3 ng) <sup>T</sup>		
o-Xylene (<3 ng)	tertiary Butylpl	tertiary Butylphenol (<3 ng) <sup>T</sup>		
Styrene (<3 ng)	Trimethylpent	Trimethylpentylphenol (<3 ng)		
1,2,4-Trimethylbenzene (<3 ng)	C20-C30+ Alig	phatic hydrocarbons (3.9 ng) <sup>™</sup>		
C6-C7 Aliphatic hydrocarbons (<3 ng) <sup>T</sup>				
Compounds marked <sup>T</sup> are tentative identifications concentrations of these compounds are approxim an internal standard. Results relate only to the iter	ations estimated from	• •		
Tests marked **" in this report are NOT includ	led in the UKAS a	accreditation schedule for our laboratory	/	
Authorised by : John Donalson Senior Sc Under the authority of P Burton, Analytica		Signature: Date: 20/06/07	(	
DEPARTMENT FOR TRANSPORT fao : BEN ANSTEE AES	Northumb Wallsend Tyne & W NE28 0QI	lear		
ref S7590	I	Page 1 of 1		

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	RECEIVED: 07/06/07	FIME:	SAMPLE	R: LAB:I	
				LAB	
	DETERMINAND		METHOD	RESULTS	
	MASS SPEC. ID ENTIFICATION		030*	S7591	
Analysis for components	Volatile Organic Compounds by ther	mal desorption GC	/MS showed the prese	nce of the following major	
Benzene (<	:3 ng)	C9-C15A	phatic hydrocarbons (+	<3 ng) <sup>T</sup>	
Toluene (<	3 ng)	Tributylpho	Tributylphosphate (<3 ng) <sup>T</sup>		
Ethylbenzer		, ,	2,5-Diphenylbenzoquinone (<3 ng) <sup>T</sup>		
m&p-Xylene	,	2.1	Dioctyl phthalate (<3 ng) <sup>T</sup>		
o-Xylene (<	<b>e</b> ,	-	ylphenol (<3 ng) <sup>T</sup>		
Styrene (<3	<b>e</b> ,		en tylphen ol (<3 ng) <sup>T</sup>	( a ) T	
	thylbenzene (<3 ng) atic hydrocarbons (<3 ng) <sup>T</sup>	G20-G30+	Aliphatic hydrocarbons	(<3 ng)	
concentratio	a marked <sup>T</sup> are tentative identifications ons of these compounds are approxin standard. Results relate only to the it	nations estimated			
Tests mark	ked **" in this report are NOT inclu	uded in the UKA	S accreditation scheo	lule for our laboratory	
	d by : John Donalson Senior S authority of P Burton, Analytic		Signature: Date: 20/06	107 g. Dank	
DEPARTI fao : BEN AES	MENT FOR TRANSPORT ANSTEE				

<b>ARS</b> ANALYTICAL REPORT			
SAMPLE: BLANK SPME RECEIVED: 07/06/07 TIME	:	SAMPL	ER: LAB:ł
			LAB
DETERMINAND		METHOD	RESULTS
MASS SPEC. IDENTIFICATION		030*	S7 592
Analysis for Volatile Organic Compounds by thermal de components:	esorption GC	/MS showed the pres	ence of the following major
Benzene (<3 ng) Toluene (17 ng) Ethylbenzene (<3 ng) m&p-Xylene (<3 ng) o-Xylene (<3 ng)		3 ng) sthylben zen e (<3 ng) sphate (<3 ng) <sup>⊤</sup>	
The presence of other compounds in the sample may is a silicon compounds produced as a result of fibre bleed of Compounds marked <sup>T</sup> are tentative identifications base concentrations of these compounds are approximation Results relate only to the items tested.	during sampl d on searche	e injection. es of the NIST92 libra	ry of mass spectra. The
Tests marked **" in this report are NOT included in	in the UKAS	accreditation sche	edule for our laboratory
Authorised by : John Donalson Senior Scient Under the authority of P Burton, Analytical Ma		Signature: Date: 20/0	
DEPARTMENT FOR TRANSPORT fao : BEN ANSTEE AES	Northur Wallser Tyne & NE28 0	Wear QD	
ref S7592		ł	Page 1 of 1

	SAMPLE: HANGAR BACKGR		SAMPLI	ER:	LAB:H
					LAB N
	DETERMINAND		METHOD	RESULT	S
	MASS SPEC. IDENTIFICATION		030*	87593	
Analysis for components	rVolatile Organic Compounds by thermal d s:	lesorption GC/	/MS showed the pres	ence of the following	major
Benzene («	<3 ng)	Styrene (<			
Toluene (2			thylben zen e (<3 ng)		
-	ene (<3 ng) Tributylphosphate (<3 ng) <sup>T</sup>				
m&p-Xylene o-Xylene (<					
	ce of other compounds in the sample may	have been m	ackad by the large ru		
-	pounds produced as a result of fibre bleed			mber of siloxanes ar	nd other
silicon com Compounds concentrati		during sample ed on searche	e Injection. s of the NIST92 libra	ry of mass spectra.	The
silicon com Compounds concentratio Results rela	pounds produced as a result of fibre bleed s marked <sup>T</sup> are tentative identifications bas ons of these compounds are approximation	during sample ed on searche ns estim ated fr	e Injection. s of the NIST92 libra rom the response fac	ny of mass spectra. tor of an internal sta	The ndard.
silicon com Compounds concentrati Results rela Tests mari Authorise	pounds produced as a result of fibre bleed s marked <sup>T</sup> are tentative identifications bas ons of these compounds are approximation ate only to the items tested.	during sample ad on searche ns estimated fr in the UKAS tist	e Injection. s of the NIST92 libra rom the response fac	ny of mass spectra. tor of an internal star idule for our labora	The ndard. ttory

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	SAMPLE: CABIN BACKGROUN RECEIVED: 07/06/07 TIME:		ER: LAB:H LAB N	
	DETERMINAND	METHOD	RESULTS	
	MASS SPEC. IDENTIFICATION	030*	87594	
Analysis for components	Volatile Organic Compounds by thermal de :	sorption GC/MS showed the pres	ence of the following major	
Benzene (<	3 ng)	Styrene (<3 ng)		
Toluene (18	tng)	1,2,4-Trimethylbenzene (<3 ng)		
	nylbenzene (<3 ng) Tributylphosphate (3.1 ng) <sup>T</sup>			
m&p-Xylene o-Xylene (<				
	e of other compounds in the sample may h ounds produced as a result of fibre bleed d		mber of siloxanes and other	
concentratio	marked <sup>T</sup> are tentative identifications based ns of these compounds are approximations te only to the items tested.	estimated from the response fac	tor of an internal standard.	
	ed **" in this report are NOT included in	n the UKAS accreditation sche	dule for our laboratory	
Tests mark				
Authorised	l by : John Donalson Senior Scienti authority of P Burton, Analytical Ma			
Authorised Under the	authority of P Burton, Analytical Ma IENT FOR TRANSPORT		al Services Ltd. bad	

<b>ARS</b> ANALYTICAL REPORT			
SAMPLE: CABIN +APU SPME RECEIVED: 07/06/07 TIM		SAMPL	ER: LAB:H
			LAB N
DETERMINAND		METHOD	RESULTS
MASS SPEC. IDENTIFICATION		030*	S7 595
Analysis for Volatile Organic Compounds by thermal components:	desorption GC	/MS showed the pres	ence of the following major
Benzene (<3 ng) Toluene (25 ng) Ethylbenzene (<3 ng) m&p-Xylene (<3 ng) o-Xylene (<3 ng)		3 ng) athylbenzene (<3 ng) sphate (<3 ng) <sup>⊤</sup>	
The presence of other compounds in the sample may silicon compounds produced as a result of fibre bleed			mber of siloxanes and other
Compounds marked <sup>T</sup> are tentative identifications bas concentrations of these compounds are approximatio Results relate only to the items tested.			
Tests marked **" in this report are NOT included	l in the UKAS	accreditation sche	edule for our laboratory
Authorised by : John Donalson Senior Scien Under the authority of P Burton, Analytical N		Signature: Date: 20/0	
DEPARTMENT FOR TRANSPORT fao : BEN ANSTEE AES	Northur Wallser Tyne & NE28 0	Wear QD	
ref S7595	·	ł	Page 1 of 1

aes	ANALYTICAL REPORT
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	SAMPLE: CABIN +APU + SOLV RECEIVED: 07/06/07 TIME:		R: LAB:H		
	DETERMINAND	METHOD	RESULTS		
	MASS SPEC. IDENTIFICATION	030*	87 596		
Analysis for components	l Volatile Organic Compounds by thermal de s:	sorption GC/MS showed the prese	nce of the following major		
Benzene («	<3 ng)	Styrene (<3 ng)			
Toluene (7	600 ng)	1,2,4-Trimethylbenzene (<3 ng)			
	Ethylbenzene (9.9 ng) Tributylphosphate (<3 ng) <sup>T</sup>				
m&p-Xylene o-Xylene (<	( a)				
	ce of other compounds in the sample may h pounds produced as a result of fibre bleed d		nber of siloxanes and other		
	s marked <sup>T</sup> are tentative identifications based ons of these compounds are approximations ate only to the items tested.				
Results rela					
	ked **" in this report are NOT included in	the UKAS accreditation scheo	lule for our laboratory		
Tests mari Authorise	ked **" in this report are NOT included ir d by : John Donalson Senior Scientis e authority of P Burton, Analytical Ma	st Signature:	AN (		
Tests mart Authorise Under the DEPARTI	d by : John Donalson Senior Scientis	st Signature:	107 J. Dank I Services Ltd. Id		

aes	ANALYTICAL REPORT
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SAMPLE: CABIN +APU + SOL				
RECEIVED: 07/06/07 TIME:		SAMPL	ER: L/	AB:HO
			L	AB N <sup>o</sup>
DETERMINAND		METHOD	RESULTS	
MASS SPEC. IDENTIFICATION		030*	87597	
Analysis for Volatile Organic Compounds by thermal de components:	ssorption GC/	/MS showed the pres	ence of the following maje	or
Benzene (<3 ng)	Styrene (<	3 ng)		
Toluene (7800 ng)	1,2,4-Trime	thylbenzene (<3 ng)		
Ethylbenzene (11 ng)	Tributylpho	aphate (<3 ng) <sup>T</sup>		
m&p-Xylene (480 ng)		,		
o-Xylene (<3 ng)				
The presence of other compounds in the sample may i silicon compounds produced as a result of fibre bleed of Compounds marked <sup>T</sup> are tentative identifications base concentrations of these compounds are approximations Results relate only to the items tested.	during sample d on searche	e Injection. s of the NIST92 libra	ry of mass spectra. The	
Tests marked *** in this report are NOT included i	in the UKAS	accreditation sche	dule for our laboratory	
Authorised by : John Donalson Senior Scienti Under the authority of P Burton, Analytical Ma		Signature: Date: 20/0		4
DEPARTMENT FOR TRANSPORT fao : BEN ANSTEE AES	Northun Wallsen Tyne & NE28 0	Wear QD		
ref S7597		I	Page 1 of 1	

APPENDIX 8.2 aes
CABIN AIR SAMPLING FEASIBILITY STUDY ON BEHALF OF THE DEPARTMENT FOR TRANSPORT, DURING A TEST FLIGHT USING A B757
REPORT AES-DfT-1 4355-WAMv2
27 <sup>th</sup> SEPTEMBER 2007
AES (ANALYTICAL & ENVIRONMENTAL SERVICES) 8 St. Paul's House, Armitage Bridge, Huddersfield, West Yorkshire, HD4 7NR Tel: 01484 660630 Fax: 05601 162854

AES (Analytical & Environmental Services) has produced this report within the terms of the contract with the client and taking account of the resources devoted to it by agreement with the client.

We disclaim any responsibility to the client and others in respect of any matters outside the scope of the above. This report is confidential to the client and we accept no responsibility of whatsoever nature to third parties to whom this report, or any part thereof, is made known. Any such party relies on the report at their own risk.

Report ty	ype: Air Mor	litoring
Report is	sue: Fir	nal
Report issue d	late: 27 <sup>th</sup> Septen	nber 2007
File reference num	ber: AES-DfT-1 4	355-WAMv2
Issuing of	fice: H udde	rsfield
<b>Originator:</b> M Thomas	Senior Consultant (Occupational Hygiene)	September 2007
Checked & approved:		
H Wilkins	Occupational Hygiene Manager	September 2007

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#### **RESULTS TABLES**

## APPENDIX 1 – SCHEMATIC ARRANGEMENT OF THE AIRCRAFT COCKPIT SHOWING SAMPLING POSITIONS

#### **EXECUTIVE SUMMARY**

- 1 .0 As part of the Department for Transport's feasibility study into sampling techniques for use in the assessment of aircraft cabin air quality, **AES** (Analytical & Environmental Services) have undertaken a basic workplace air sampling exercise. This exercise was carried out during specified stages of a test flight on the 31<sup>st</sup> July 2007. The aim of the exercise was to assess the suitability of specified sampling techniques in a 'live' environment.
- 2.0 The sampling for volatile and semi-volatile compounds using thermal desorption tubes at various stages of the test flight resulted in the detection of; Benzene, Toluene, Xylene, 1,2,4-Trimethyl benzene, Naphthalene, Heptanal, C9-C1 5 Aliphatic hydrocarbons, Phenol, 3-Carene, Phenylethyne, C17 Aliphatic hydrocarbons, Ethyl hexyl phthalate, C20-C30 Aliphatic hydrocarbons and Hexadeconoic acid. The results of the sampling highlight that none of the detected compounds were present at concentrations in excess of 0.2 mg/m<sup>3</sup> (200 μg/m<sup>3</sup>). For all samples, Toluene was the predominant analyte detected.
- 3.0 It should be noted that in all instances the detected concentrations from the sampling using thermal desorption tubes were significantly below the relevant HSE specified WEL where applicable. It should also be noted that wherever possible, WELs are set at a level at which there is no evidence of adverse effects on human health.
- 4.0 The sampling for volatile and semi-volatile compounds using SPME tubes at various stages of the test flight resulted in the detection of; Toluene, Heptanal, C9-C15 Aliphatic hydrocarbons, C15 Aromatic hydrocarbons, C17 Aliphatic hydrocarbons and C21 Aromatic hydrocarbons. It should be noted that it is not possible to quantify the results obtained using this sampling technique. It should also be noted that the presence of other compounds in the samples may have been masked by the large number of siloxanes and other silicon compounds produced as a result of the fibre bleed during sample injection.
- 5.0 A number of recommendations have been made and are included within the main report.

#### 1. INTRODUCTION

- 1.1 As part of the Department for Transport's feasibility study into sampling techniques for use in the assessment of aircraft cabin air quality, AES (Analytical & Environmental Services) have undertaken a basic workplace air sampling exercise. This exercise was carried out during specified stages of a test flight on the 31<sup>st</sup> July 2007. The aim of the exercise was to assess the suitability of specified sampling techniques in a 'live' environment. This monitoring exercise was undertaken by Matthew Thomas of AES (Analytical & Environmental Services).
- 1 .2 This exercise is intended to allow each of the assessment techniques to be assessed in a 'live' environment. Once suitable methods have been identified, it is then proposed that assessments can be undertaken on a specified number of aircraft as a means of assessing cabin air quality with emphasis on 'fume events'.
- 1 .3 The exercise was carried out under normal operations during the test flight. This report and the sampling refer to prevailing conditions at the time of the survey and the findings should not be extrapolated to estimate potential exposures under other conditions.

#### 2. PROCESS & OBSERVATIONS

- 2.1 Air sampling was undertaken to assess levels of volatile and semi volatile compounds using specified sampling techniques as part of a feasibility exercise in preparation for a wider programme aimed at looking into cabin air quality and 'fume events' on aircraft. This sampling exercise is a follow up to an exercise undertaken on the 6th June 2007.
- 2.2 Sampling using both pumped (thermal desorption tubes) and diffusive (SPME fibres) was undertaken. All sampling was undertaken in duplicate, half of the samples were analysed by AES's UKAS accredited in-house laboratory, the other half of the samples were taken for independent analysis by the Cranfield Institute.
- 2.3 Monitoring was undertaken during a test flight aboard a cargo aircraft. The aircraft in use for this exercise was a Boeing 757. The flight was undertaken purely for testing purposes, with the aircraft taking-off and landing from East Midlands Airport, the flight had a duration of just over one hour with monitoring also undertaken before and after the flight. Discussion with the pilots indicated that for this exercise, the aircraft was operated as it would have been under normal operating conditions.

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- 2.4 Pumped sampling using thermal desorption tubes was undertaken across a number of specified stages of the aircrafts flight cycle i.e. at a stand-still prior to engine activation, at a stand-still following engine activation, during taxiing, during take-off & climb, during cruise, during descent & landing and during final taxi.
- 2.5 Note that due to the lack of availability of SPME sampling consumables, sampling using this method was only possible during taxiing, during take-off & climb, during cruising and during descent & landing.
- 2.6 Monitoring was carried out within the cockpit at a location behind the left hand pilot's seat. During sampling the door between the cockpit and the cabin was kept closed with five people occupying the cockpit including the two pilots. A schematic showing sampling locations is presented in Appendix 1.

#### 3. METHODOLOGY

Sampling was carried out in accordance with Health & Safety Executive Guidance, booklet HSG1 73 "Monitoring strategies for toxic substances" 1997.

#### 3.1 Volatile & Semi-volatile Compounds (Pumped samples - thermal desorption tubes)

Samples for the above were taken by drawing air at a known flow rate of approximately 80 to 100 millilitres per minute through a thermal desorption tube (packed with a front layer of Tenax (for less volatile material) and a back up layer of Unicarb (carbon molecular sieve for volatiles)) connected to a suitable low flow sampling pump. The sampling pumps used during this exercise were all SKC Pocketpumps 210-1 002TX air sampling pumps, the serial numbers for the individual sampling pumps are provided in the results tables. Flow rates were determined at the start and end of each batch of sampling using a BIOS DC Lite DryCal (serial no. 3357) which was calibrated against a traceable UKAS primary standard. Monitoring was undertaken in accordance with MDHS 70, "General methods for sampling airborne gases and vapours".

Static samples were taken at a location representative of ascertaining background conditions in the aircraft cabin. Sampling was carried out in duplicate, with the sampling pumps positioned approximately 15 cm apart.

Following sampling, half of the samples were analysed using a gas chromatogram by our UKAS accredited in-house laboratory, the other half of the samples were taken for independent analysis by the Cranfield Institute. The samples to be analysed by AES were hand delivered to the laboratory so as to minimise the potential for cross contamination. The results of the analysis of the samples retained by AES are expressed in the units  $\mu$ g/m<sup>3</sup> and are provided in Tables 1 (i) to 1 (iv). The information for the field blank is presented in Table 1 (v).

#### 3.2 Volatile & Semi-volatile Compounds (Diffusive samples - SPME fibres)

Samples for the above were taken using pre-prepared SPME fibres. The sampling methodology involved the SPME fibres being exposed during the required period. Once the required period had expired and the duration noted, the fibres were retracted in preparation for transit to the laboratory. The SPME tubes were used as per the manufacturer's instructions.

The SPME fibres were exposed at a location representative of ascertaining background conditions in the aircraft cabin. Sampling was carried out in duplicate, with the fibres positioned AES (Analytical & Environmental Services)

in direct proximity of each other.

Following sampling, half of the samples were analysed using a gas chromatogram by our UKAS accredited in-house laboratory, the other half of the samples were taken for independent analysis by the Cranfield Institute. The samples to be analysed by AES were hand delivered to the laboratory so as to minimise the potential for cross contamination. The results of the analysis of the samples retained by AES are expressed in the units  $\mu$ g and are provided in Tables 2 (i). Note that it is not possible to quantify the results obtained from the SPME fibres. The information for the field blank is presented in Table 2 (ii).

#### 4. **HYGIENE STANDARDS**

In the UK the Health and Safety Executive publish a list of Occupational Exposure Limits (OELs) in their publication EH40, which form part of the requirements of the Control of Substances Hazardous to Health Regulations 2002 (COSHH), as amended by the Control of Substances Hazardous to Health (Amendment) Regulations 2004.

The COSHH (Amendment) Regulations 2004 came into force on **17th January 2005.** The existing requirements under the COSHH Regulations to follow good practice in controlling exposure to substances hazardous to health were clarified and consolidated by the introduction of eight principles, which apply regardless of whether a substance has been assigned an Occupational Exposure Limit:

- i. Design and operate processes and activities to minimise emission, release and spread of substances hazardous to health.
- ii. Take into account all relevant routes of exposure-inhalation, skin absorption and ingestion when developing control measures.
- iii. Control exposure by measures that are proportionate to the health risk.
- iv. Choose the most effective and reliable control options which minimise the escape and spread of substances hazardous to health.
- v. Where adequate control of exposure cannot be achieved by other means, provide, in combination with other control measures, suitable protective equipment.
- vi. Check and review regularly all elements of control measures for their continuing effectiveness.
- vii. Inform and train all employees on the hazards and risks from the substances with which they work and the use of control measures developed to minimise the risks.
- viii. Ensure that the introduction of control measures does not increase the overall risk to health and safety.

From **6**<sup>th</sup> **April 2005**, a single type of occupational exposure limit has been introduced; the AES (Analytical & Environmental Services)

*Workplace Exposure Limit (WEL).* This replaces both the Maximum Exposure Limit and Occupational Exposure Standard. An updated list of Workplace Exposure Limits is due to come into force on the 1<sub>st</sub>October 2007.

WELs are OELs set under COSHH, in order to help protect the health of workers. WELs are concentrations of hazardous substances in air, averaged over a specified period of time referred to as a time-weighted average (TWA). Two time periods are used: long term (8-hour TWA) and short term (15 minutes). Long term exposure limits are intended to control the health effects associated with prolonged or accumulated exposure. Short-term exposure limits are set to prevent acute health effects even from brief exposure.

WELs are derived by the following criteria:

 The WEL value would be set at a level at which no adverse effects on human health would be expected to occur based on the known and/or predicted effects of the substance. However, if such a level cannot be identified with reasonable confidence, or, if this level is not reasonably achievable, then, 2) The WEL value would be based at a level corresponding to what is considered to represent good control, taking into account the severity of the likely health hazards and the costs and efficacy of control solutions. Wherever possible, the WEL would not be set at a level at which there is evidence of adverse effects on human health.

Adequate control of exposure will require employers to:

- a) Apply the eight principles of good practice for the control of substances hazardous to health;
- b) Ensure that the WEL is not exceeded; and
- c) Ensure that exposure to substances that can cause occupational asthma; cancer; or damage to genes that can be passed from one generation to another; is reduced as low as is reasonably practicable.

The absence of a substance from the list of WELs does not indicate that it is safe. For these substances, exposure should be controlled to a level to which nearly all the working population could be exposed, day after day without adverse effects on health. As part of the risk assessment required under regulation 6 of COSHH, employers should determine their own working practices and in-house standards for control. Further advice can be found in the following Health and Safety Executive (HSE) sources:

Monitoring strategies for toxic substances (HSG 173), 1997;

COSHH Essentials: Easy steps to control chemicals. Control of Substances Hazardous to Health Regulations. HSG 193 (Second Edition), 2003 – an internet access version is also available at <u>www.coshh-essentials.org.uk</u>; and

All Chemicals Hazard Alert Notices (CHANS) have been suspended. Those seeking advice on substances for which a CHAN had previously been issued should follow the same approach as they would for any other hazardous substance, e.g. apply the CHIP and COSHH regulations.

The limits relevant to this survey are as follows:-

	Workplace Expo	sure Limit (WEL)	Notation &
Substance	8hr TWA Limit (mg/m <sup>3</sup> )	15 Minute STEL (mg/m <sup>3</sup> )	Comments
Benzene	3 (1 ppm)	-	Carc, Sk, R45, R46, R11, R36/38, R43/23/24/25, R65
Toluene	191	574	Sk, R11, R38, R48/20, R63, R65, R67
Xylene (mixed isomer)	220	441	Sk, Bmgv R10, R20/21, R38
Naphthalene	**	*	-
C9-C1 5 Aliphatic hydrocarbons	*	*	-
Heptanal	*	*	-
1,2,4-Trimethyl benzene	125	-	-
Phenol	7.8 (2 ppm)	-	Sk, R23/24/25, R34, R48/20/21/22, R68
3-Carene	***	***	-
C17 Aliphatic hydrocarbons	*	*	-
Dibutyl phthalate	5	10	R61, R62, R50
Hexadeconoic acid	*	*	-
Ethyl hexyl phthalate	*	*	-
C20-C30 Aliphatic hydrocarbons	*	*	-
C15 Aromatic hydrocarbons	*	*	-
C21 Aromatic hydrocarbons	*	*	-
Phenylethyne	*	*	-

At present there is no Workplace Exposure Limit (WEL) in place for this substance as specified by the HSE. It is cautioned however that despite these substances not having been assigned a WEL, it should not be assumed that they pose no hazard and should be treated accordingly.

\*\*

At present there is no HSE specified WEL for *Naphthalene*. Occupational exposure limits of 50 mg/m<sup>3</sup> (8 hour time weighted average) and 80 mg/m<sup>3</sup> (STEL) were published in EH40/02 & EH40/03 but were subsequently withdrawn from the 2005 list due to concern by the UK Advisory Committee on Toxic Substances that health may not be adequately protected because of doubts that the limits were not

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#### soundly-based.

At present there is no HSE specified WEL for 3 - Carene. Sweden currently has occupational exposure limits for this substance, the limits are as follows; 150 mg/m<sup>3</sup> (8 hour time weighted average) and 300

mg/m<sup>3</sup> (STEL).

- Carc Capable of causing cancer and/or heritable genetic damage.
- Sk Can be absorbed through the skin.

Bmgv Biological Monitoring Guidance Value – A Health Guidance Value for Xylene (mixed isomer) of 650 mmol methyl hippuric acid/mol creatinine in urine should not be exceeded when sampled post-shift.

Health Guidance Values (HGV) are set at a level at which there is no indication from the scientific evidence available that the substance being monitored is likely to be injurious to health. Values not greatly in excess of a HGV are unlikely to produce serious short or long term effects on health. However, regularly exceeding the HGV does indicate that control of exposure may not be adequate. Under these circumstances employers will need to look at current work practices to see how they can be improved to reduce exposure.

#### 5. **RESULTS & CONCLUSIONS**

- 5.1 A full set of tabulated results from this monitoring survey are included at the rear of the report.
- 5.2 From the results provided in Tables 1 (i) to 1 (iv), it can be seen that the sampling for volatile and semi-volatile compounds using thermal desorption tubes at various stages of the test flight resulted in the detection of; Benzene, Toluene, Xylene, 1 ,2,4-Trimethyl benzene, Naphthalene, Heptanal, C9-C15 Aliphatic hydrocarbons, Phenol, 3-Carene, Phenylethyne, C17 Aliphatic hydrocarbons, Ethyl hexyl phthalate, C20-C30 Aliphatic hydrocarbons and Hexadeconoic acid. The results of the sampling highlight that none of the detected compounds were present at concentrations in excess of 0.2 mg/m<sup>3</sup> (200 μg/m<sup>3</sup>). For all samples, Toluene was the predominant analyte detected.
- 5.3 It should be noted that in all instances the detected concentrations from the sampling using thermal desorption tubes were significantly below the relevant HSE specified WEL where applicable. It should also be noted that wherever possible, WELs are set at a level at which there is no evidence of adverse effects on human health.
- 5.4 From the results provided in Table 2 (i), it can be seen that the sampling for volatile and semi-volatile compounds using SPME tubes at various stages of the test flight resulted in the detection of; Toluene, Heptanal, C9-C1 5 Aliphatic hydrocarbons, C15 Aromatic hydrocarbons, C17 Aliphatic hydrocarbons and C21 Aromatic hydrocarbons. It should be noted that it is not possible to quantify the results obtained using this sampling technique. It should also be noted that the presence of other compounds in the samples may have been masked by the large number of siloxanes and other silicon compounds produced as a result of the fibre bleed during sample injection.
- 5.5 During the flight, a 'fume event' occurred, the event was noted during the take-off and climb stage, as take-off thrusters were replaced by flight thrusters. The 'fume event' was of very short duration but was noticeable to all in the cockpit as a distinct oily type odour, the odour persisted for less than one minute before completely dissipating. The results obtained during this stage of the flight indicate no prominent compound that was either unique to this stage of sampling or was present at a significantly elevated concentration.

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#### 6. RECOMMENDATIONS

- 6.1 It is strongly recommended that further monitoring be undertaken over a significant number of flights/sectors (i.e. in excess of 100 flights) as a means of studying the prevalence/frequency, composition and triggers for 'fume events'.
- 6.2 Ideally any further sampling should be undertaken using techniques that allow quantification of the concentrations of the contaminants present so as to allow direct comparison between sets of results.
- 6.3 To ensure the reliability of any future monitoring, it is strongly recommended that sampling either be undertaken by or under the supervision of a competent, suitably trained, qualified and experienced individual/individuals.

#### 7. **REFERENCES**

Control of Substances Hazardous to Health Regulations 2002

Control of Substances Hazardous to Health (Amendment) Regulations 2002 Control of Substances

Hazardous to Health (Amendment) Regulations 2004

Control of Substances Hazardous to Health Regulations 2002 as amended - Approved Code of Practice

EH40/2005 Workplace Exposure Limits & 2006 supplement

HSG1 73 - Monitoring Strategies for Toxic Substances

EH64 - "Summary Criteria for Occupational Exposure Limits".

MDHS 70, "General methods for sampling airborne gases and vapours"

AES (Analytical & Environmental Services)

**RESULTS TABLES** 

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### TABLE 1 (i): CORRECTED RESULTS FROM THE SAMPLING USING THERMAL DESORPTION TUBES FOR VOLATILE & SEMI VOLATILECOMPOUNDS DURING A TEST FLIGHT ON BEHALF OF THE DFT – 31<sup>st</sup> JULY 2007

	Sample Number &	Fl		Flow rate (L/min)			Contaminant Weight	Measured Airborne Concentration (µg/m <sup>3</sup> )
Sampling Details	Sampling Pump S/No	Time	On	Off	Mean	(Litres)	(hâ)	Volatile and Semi-volatile compounds
							Benzene – 0.012	10
							Toluene – 0.15	125
							m&p-Xylene - 0.01	8.3
							o-Xylene – 0.004	3.3
Static sample - Sampling equipment	S146415					1.2	1 ,2,4-Trimethyl benzene , – 0.0058	4.8
positioned behind the left hand pilots	12	12:18 –	0.100	0.100	0.100		Naphthalene – 0.008	6.7
seat. Sampling of cabin air – Aircraft at stand still, engines off, cabin doors		12:40					Heptanal – 0.0037	3.1
open.							C9-C15 Aliphatic	22.5
							Phenol – 0.0047	3.9
							3-Carene – 0.0099	8.3
							Phenylethyne – 0.0031	2.6
							C17 Aliphatic hydrocarbons – 0.0068	5.7
							Toluene – 0.11	123.6
Static sample – Sampling equipment	\$146417						Naphthalene – 0.003	3.4
positioned behind the left hand pilots seat. Sampling of cabin air – Aircraft	S/No 050479	12:50 – 13:02	0.074	0.075	0.0745	0.89	hydrocarbons - 0.008	9.0
oush back and engine start, cabin	(a)						3-Carene – 0.0043	4.8
doors closed.							Ethyl hexyl phthalate – <lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>

\* Note that all sampling was undertaken in duplicate and that the contaminant weight and measured airborne concentration results presented above have been corrected against the blank.

# TABLE 1 (ii): CORRECTED RESULTS FROM THE SAMPLING USING THERMAL DESORPTION TUBES FOR VOLATILE & SEMI VOLATILECOMPOUNDS DURING A TEST FLIGHT ON BEHALF OF THE DFT – 31<sup>st</sup> JULY 2007

Sampling Details	Sample Number &	Sample	Flow rate (L/min)			Volume	Contaminant Weight	Measured Airborne Concentration (µg/m <sup>3</sup> )
	Sampling Pump S/No	Time	On	Off	Mean	(Litres)	(µg)	Volatile and Semi-volatile compounds
							Benzene – 0.0021	2.0
							Toluene – 0.091	85.8
							<u>m&amp;p-Xylene – 0.0035</u> 1 ,2,4-Trimethyl benzene – 0.0031	3.3 2.9
							Naphthalene – 0.0055	5.2
Static sample – Sampling equipment	S146419						C9-C15 Aliphatic	19.8
positioned behind the left hand pilots		13:02 – 13:16	0.076	0.076	0.076	1.06	hydrocarbons – 0.021	4.0
seat. Sampling of cabin air – Aircraft taxi to take off position.	S/No 050479 13:02 (a)	13.02 - 13.10	0.070	0.076	0.076	1.00	3-Carene – 0.0042 C17 Aliphatic Hexadeconoic acid – 0.008	3.1 7.5
							Ethyl hexyl phthalate – 0.031	29.2
							C20-C30 Aliphatic hydrocarbons – 0.023	21.7
						-	Benzene – 0.0138	7.6
							Toluene – 0.16	88.4
Static sample – Sampling equipment							Naphthalene – <lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
positioned pilot's seat Sampling of cabin air – Aircraft take off and climb. Note that fume	S146423	13:16	0.101	0.100	0.1005	1.81	C9-C15 Aliphatic	17 7
take on and chimp. Note that fume			0.101	0.100	0.1005	1.01	hydrocarbons – 0.032	
	S/No 050449	13:34					Phenol – 0.0031	1.7
event occurred during this sample period following the transition from full	(d)						Heptanal – 0.0039	2.2
thrust to standard climb.							3-Carene – 0.006	3.3
							C17 Aliphatic hydrocarbons – 0.0036	2.0

### TABLE 1 (iii): CORRECTED RESULTS FROM THE SAMPLING USING THERMAL DESORPTION TUBES FOR VOLATILE & SEMI VOLATILE<br/>COMPOUNDS DURING A TEST FLIGHT ON BEHALF OF THE DFT – 31st JULY 2007

Sampling Details Sa	Sample Number &	Sample Time	Flo	w rate (L/	min)	Volume (Litres)	Contaminant Weight	Measured Airborne Concentration (µg/m <sup>3</sup> )
	Sampling Pump S/No	On		Off	Mean		(µg)	Volatile and Semi-volatile compounds
							Benzene – 0.0108	4.1
							Toluene – 0.110	41.5
							Naphthalene – 0.0025	0.9
							C9-C1 5 Aliphatic hydrocarbons – 0.006	2.3
							Heptanal – 0.0033	1.2
Static sample – Sampling equipment behind left hand	S146427						Phenol – 0.0039	1.5
positioned the pilot's		13:36 –					3-Carene – 0.0039	1.5
seat. Sampling of cabin air – Aircraft at			0.102	0.102	0.102	2.65		
	S/No 050449	14:02						
end of ascent and cruise. Note possible							C17 Aliphatic	
ume event residue.	(d)						hydrocarbons – 0.0055	2.1
							Dibutyl phthalate – <lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
							Hexadeconoic acid – 0.011	4.2
							Ethyl hexyl phthalate – 0.0184	6.9

\* Note that all sampling was undertaken in duplicate and that the contaminant weight and measured airborne concentration results presented above have been corrected against the blank.

### TABLE 1 (iv): CORRECTED RESULTS FROM THE SAMPLING USING THERMAL DESORPTION TUBES FOR VOLATILE & SEMI VOLATILE<br/>COMPOUNDS DURING A TEST FLIGHT ON BEHALF OF THE DFT – 31<sup>st</sup> JULY 2007

	Sample Number &	-			/min)	Volume	Contaminant Weight	Measured Airborne Concentration (µg/m <sup>3</sup> )
Sampling Details	Sampling	Time				(Litres)	(µg)	Volatile and Semi-volatile
	Pump S/No		On	Off	Mean			compounds
							Benzene – 0.0037	1.3
							Toluene – 0.180	64.5
							Naphthalene – <lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
							C9-C15 Aliphatic	13.3
Static sample – Sampling equipment	S146431						<u>Heptanal – 0.0048</u> 3-	1.7 3.
positioned behind the left hand pilots	0140401	44.00 44.00	0.400	0.404	0.4005	0.70	Carene – 0.011	
seat. Sampling of cabin air – Aircraft	S/No 050449	14:03 – 14:30	0.103	0.104	0.1035	2.79	C17 Aliphatic	
descent and landing.	(d)						hydrocarbons – 0.017	6.1 <lod< td=""></lod<>
							Dibutyl phthalate – <lod< td=""><td></td></lod<>	
							Ethyl hexyl phthalate –	4.1
							0.0114	
							C20-C30 Aliphatic hvdrocarbons – 0.0034	1.2
							Benzene – 0.0034	4.6
							Toluene – 0.150	161.3
							Naphthalene – 0.0078	8.4
							C9-C15 Aliphatic	
Static sample – Sampling equipment							hydrocarbons - 0.019	20.4
	S146435							
positioned behind the left hand pilot's		14:31 –					Heptanal – 0.004	4.3
seat. Sampling of cabin air – Aircraft			0.104	0.103	0.1035	0.93		
	S/No 050449	14:42					3-Carene – 0.01	10.8
axi from runway including engine	(d)						C17 Aliphatic	
switch off.							hydrocarbons – 0.004	4.3
							Ethyl hexyl phthalate – 0.0044	4.7

Note that all sampling was undertaken in duplicate and that the contaminant weight and measured airborne concentration results presented above have been corrected against the

# TABLE 1 (v): RESULTS OF THE ANALYSIS OF THE THERMAL DESORPTION TUBE FIELD BLANK (VOLATILE & SEMI VOLATILE<br/>COMPOUNDS) TEST FLIGHT ON BEHALF OF THE DFT – 31<sup>st</sup> JULY 2007

Sompling Details	Sample Number &	Sample Time	Flow rate (L/min)			Volume (Litres)	Contaminant Weight	Measured Airborne Concentration (µg/m <sup>3</sup> )
Sampling Details	Sampling Pump S/No	On	Off I		Mean	(Enres)	(µg)	Volatile and Semi-volatile compounds
							Benzene – 0.0042	N/A
							Naphthalene – 0.0042	N/A
Field blank – sample handled in an identical way to the field samples	S146439	N/A	N/A	N/A	N/A	N/A	C9-C1 5 Aliphatic hydrocarbons – 0.013	N/A
above.	S/No N/A						Dibutyl phthalate – 0.01	N/A
							Ethyl hexyl phthalate – 0.0066	N/A

### TABLE 2 (i): CORRECTED RESULTS FROM THE SAMPLING USING SPME TUBES FOR VOLATILE & SEMI VOLATILE COMPOUNDSDURING A TEST FLIGHT ON BEHALF OF THE DFT – 31<sup>st</sup> JULY 2007

Sampling Details	Sample Number	Sample Time	Sample Duration (mins)	Contaminant Weight (µg)
				Toluene – 0.012
Static sample – Sampling equipment positioned behind the				Heptanal – 0.0002
left hand pilot's seat. Sampling of cabin air – Aircraft taxi to	S146421	13:03 – 13:16	13	C9-C15 Aliphatic hydrocarbons – <lod< td=""></lod<>
take off position.				C15 Aromatic hydrocarbons – 0.0038
				C17 Aliphatic hydrocarbons – 0.0036
Static sample – Sampling equipment positioned behind the left hand pilot's seat. Sampling of cabin air – Aircraft take off				Toluene – 0.0012
and climb. Note that fume event occurred during this sample	S146425	13:17 – 13:36	19	Heptanal – 0.0009
period following the transition from full trust to standard climb.		· · · · · · · · · · · · · · · · · · ·		C9-C1 5 Aliphatic hydrocarbons – <lod< td=""></lod<>
				Toluene – 0.0095
Static sample – Sampling equipment positioned behind the				Heptanal – 0.0023
left hand pilot's seat. Sampling of cabin air – Aircraft at end of	S146429	13:39 – 14:02	23	C9-C15 Aliphatic hydrocarbons – 0.3
ascent and cruise. Note possible fume event residue.				C15 Aromatic hydrocarbons – 0.0038
				C21 Aromatic hydrocarbons – 0.0052
behind				Toluene – 0.0005
Static sample – Sampling equipment positioned the				C9-C15 Aliphatic hydrocarbons – <lod< td=""></lod<>
left hand pilots seat. Sampling of cabin air – Aircraft descent	S146433	14:05 – 14:30	25	C15 Aromatic hydrocarbons – 0.0036
and landing.				C17 Aliphatic hydrocarbons – 0.0033

NB: The presence of other compounds in the sample may have been masked by the large number of siloxanes and other silicon compounds produced as a result of the fibre bleed during sample injection.

\* Note that all sampling was undertaken in duplicate and that the contaminant weight and measured airborne concentration results presented above have been corrected against the blank.

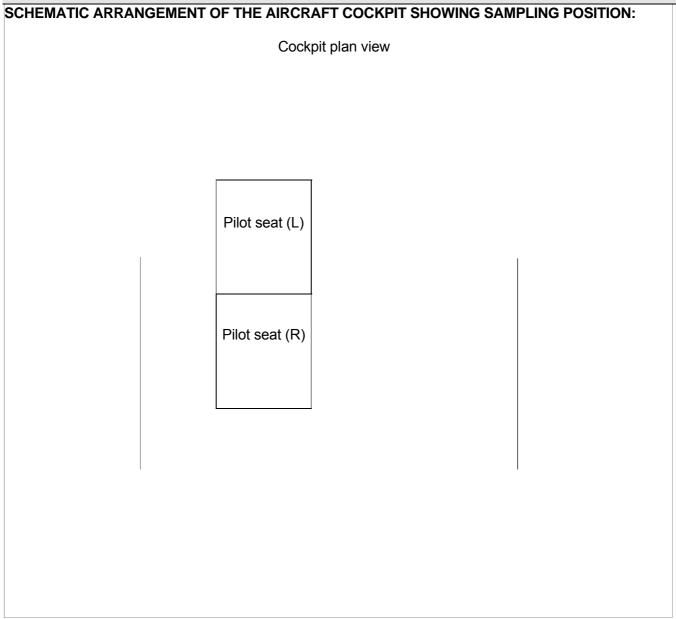
# TABLE 2 (ii): RESULTS OF THE ANALYSIS OF THE SPME TUBE (VOLATILE & SEMI VOLATILE COMPOUNDS)TEST FLIGHT ON BEHALF OF THE DFT – 31<sup>st</sup> JULY 2007

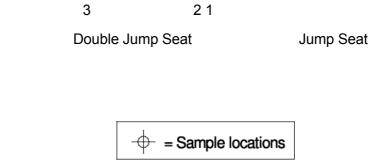
Sampling Details	Sample Number	Sample Time	Sample Duration (mins)	Contaminant Weight (µg)						
	S146437	N/A	N/A	N/A						Toluene – 0.0085
Field blank – sample handled in an identical way to the field samples above.					Heptanal – 0.0033					
				C9-C1 5 Aliphatic hydrocarbons – 1.0						

#### **APPENDIX** 1

#### SCHEMATIC OF SAMPLE LOCATIONS

#### **APPENDIX 1:**





1 - Pumped samples - samples retained by AES for analysis

2 - Pumped samples - samples retained by Cranfield Institute for analysis

3 - SPME samples - samples split between AES & Cranfield Institute for analysis

(Not to Scale)

Work reported in this document, unless otherwise stated, was carried out under the terms of the UKAS accreditation for UKAS Laboratory No 0967. Opinions and interpretations contained herein are outside the scope of UKAS accreditation.

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### **APPENDIX 8.3**

### **Cranfield Report on the**

use of photoionization detectors

**Dr Christopher Walton** 

**Cranfield Health** 

September 2007

#### Use of photoionization detectors

#### Background

Photoionization detectors (PIDs) are general-purpose, hand-held, battery-powered instruments which are capable of responding to a wide range of gases and vapours. The sample is drawn through a chamber where it is exposed to high-energy ultraviolet (UV) light. Ionization occurs when a molecule in the sample absorbs a UV photon which has an energy (measured in electron volts or eV) greater than the ionization potential of the molecule. The chamber also contains electrodes to which a potential is applied. Ionisation results in a current between the electrodes which can be measured and used to estimate the concentration of species of interest in the sample.

The purpose of this exercise was to determine the utility of PIDs in aircraft cabin air quality monitoring. The instruments used were designed to detect the majority of volatile organic compounds (VOCs) thought most likely to be present in the air, but neither the major components of air itself nor low molecular weight compounds such as methane. Although PIDs can be calibrated with some accuracy against a pure sample of a given compound, they are non-specific devices and will continue to respond to other VOCs present in the environment in which they are used. They are therefore unsuitable as the sole analytical method for cabin air quality assessment.

Two potential roles for the PID were considered:

- 1. Monitoring of overall VOC concentration across all phases of a flight.
- 2. Detection of anomalous elevations of VOC concentrations ("fume incidents").

Since the increased concentrations in 2 were considered likely to be transient, consideration was also given to the feasibility of using a PID as a method for triggering other VOC sampling methods such as pumped thermal desorbtion (TD) tubes, which might be expected to allow identification of specific VOCs released during an incident.

#### Instruments and preparation

Two instruments were tested:

- 1. The MiniRAE 2000 (RAE systems, San Jose, CA. <u>www.raesystems.com</u>) was used in the ground test.
- 2. The Phocheck+ 5000 (Ion Science, Cambridge, UK. <u>www.ionscience.com</u>) was used for the flight test.

These units are essentially similar in appearance, size and operation, the major difference between them being the increased sensitivity of the PhoCheck, which is designed to respond to concentrations in the parts per billion (ppb) range.

Both units were hired for a one-week period from Shawcity Ltd (Faringdon, Oxon, UK <u>www.shawcity.co.uk</u>) which allowed sufficient time for familiarisation and instrument setup prior to the test and download of data afterward. Familiarisation included basic checks of functionality by exposing the instruments to high and low concentrations of VOCs. High concentrations were achieved using solvents soaked into a piece of

laboratory tissue. Response to low concentrations was investigated by such activities as sampling evaporation from around the caps of closed solvent bottles or offgassing from neoprene laboratory gloves. No attempt was made to examine samples of known concentration, though each unit was supplied with a calibration certificate.

Both the MiniRAE and the Phocheck produced large responses (in the hundreds of ppm) to high concentrations of solvent. Paradoxically, however, the Phocheck failed completely to respond to low concentrations while the MiniRAE proved capable of detecting VOCs in both low-concentration scenarios described above. Although the performance of the Phocheck was a cause for concern, there was insufficient time for corrective action, and the unit was used as planned on the flight test.

#### Ground test

This test was designed to determine the ability of the PID to detect significant fume incidents by deliberately releasing a test VOC into the cabin. The results of the solvent release test are shown in Figure 1. Peaks representing concentrations up to approximately 150ppm are clearly visible, with the whole incident occupying approximately 6 minutes. The MiniRAE was set to sample every 2 seconds, and at this resolution, wide variations in concentration within incident are also clearly visible.

In contrast, prior to solvent release the MiniRAE failed to register the presence of VOCs. However, the data recorded during the decay phase of the trial clearly demonstrate the instrument's ability to record concentrations below 1 ppm, suggesting that routine Voc concentrations in this environment are at or below the detection limit of this particular PID.

#### Flight test

This exercise produced no useful information, since the PID, although operated during all phases of the flight, failed to register anything above baseline. Since the analytical results from both flight and ground tests demonstrate that VOCs are present in some degree in normal aircraft operation, this suggests a problem with the PID itself. This view is reinforced by the results obtained during instrument familiarisation.

It is not clear at present whether this is a problem with all Phocheck+ 5000 instruments, or with the particular example used. However, the latter seems most likely.

#### Conclusions

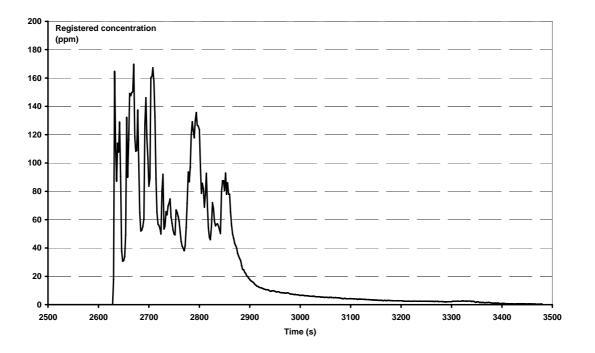
- 1. The PID is a suitable instrument for detecting fume incidents in aircraft cabins.
- 2. It will be possible to use the PID as a means of triggering full analytical sampling of cabin air during fume events in any future trials.
- 3. An instrument with ppb sensitivity is required for monitoring of general background levels, and for detecting "normal" variations in cabin air VOC concentration.

#### Recommendations

1. That a PID be included as part of the instrumentation used in any future trials.

- 2. That as part of the pre-work for such trials a number of PIDs be assessed for suitability in terms of:
  - a. Ease of use
  - b. Data logging capability (sampling rate and available memory).
  - c. Data download (data rate, reliability, export).
  - d. Sensitivity and accuracy.
  - e. Maintainability.
  - f. Cost of instrument and consumables (including comparison of purchase and hire costs).
- 3. That this aspect of the pre-work be carried out by School of Engineering and Cranfield Health in collaboration, using Cranfield Health's selected ion-flow tube mass spectrometer (SIFT-MS) as the reference method.

**Figure 1.** VOC concentration registered by photoionisation detector (PID: MiniRAE 2000) during release of test volatiles in an aircraft cabin. The PID correction factor was set for Toluene. The data shown represent average concentrations over two-second sampling periods. Time is given in seconds from start of data acquisition.



# Appendix 8.4 BRE : Executive Summary & Key Recommendations

The results of the analysis undertaken by BRE during the feasibility study to date are of great interest.

Key components of hydraulic fluid and of engine oil have been identified and measured in the cabin environments studied. These compounds, which are mainly in the semivolatile and non-volatile (oil) ranges, have been determined both in the presence of and in the absence of a "fume event" (i.e. an oil/hydraulic fluid fume event such as those widely reported by flight and cabin crew).

It must be stressed that only two aircraft and a limited number of air samples have been tested during the feasibility study, therefore a cautious approach should be adopted in the interpretation of the results.

In order to obtain more information on the types and concentrations of the contaminants involved, and to provide data for future work on their possible health effects, a more comprehensive testing programme is required.

BRE's recommendations for further studies are as follows :-

- Test a selection of "problem" aircraft types (e.g. BAE-146, B-757) in flight ; in order to provide robust and meaningful data this testing phase should comprise at least 100 sectors per aircraft type over a period of 3-6 months.
- Include a significant number of sectors involving individual aircraft on which an above average frequency of reported fume events has occurred.
- If practical, monitor a subset of such 'troublesome' aircraft on several consecutive sectors.
- Monitor chemical contaminants over a range of flight phases with pumped adsorbent tube samplers (and other devices as agreed).
- > Monitor ultra fine particles on as many flights as possible.

On selected flights it would be useful to attempt to quantify more closely the actual peak concentration of airborne contaminants during a fume event, by using high-density sampling. Should such an event occur, it would then be possible to more accurately quantify the potential peak exposure of the flight crew to the contaminants.

### Appendix 8.5 BRE Report : Test Sampling on a BAe146 Aircraft

#### Results from Feasibility Study at Teesside Airport – 6<sup>th</sup> June 2007

This report and its Appendix summarise the results that were obtained by BRE during the measurements conducted at Airport A as part of the First Stage of the Feasibility Study for the DfT cabin air project.

In line with the instructions given at the meeting held in the hangar after the monitoring, no communication has been made between BRE and the staff at AES since the monitoring.

The discussion of results here is intended to help one to make comparisons between the various sampling techniques and subsequent analyses that were employed by BRE, AES and Cranfield University.

#### Test conditions during which samples were taken

The test conditions, during which the samples were taken, are given more fully in Appendix A and are summarised below;-

- Test 1 Aircraft hangar background.
- Test 2 Aircraft cabin background.
- Test 3 Aircraft with APU and ECS packs on.
- Test 4 Aircraft with APU and ECS packs on chemical released.

#### Measurements of temperature, RH, carbon dioxide and ultra-fine particles

The main feature to note was the rise in the ultra-fine particle concentrations when the APU and ECS were operating. These particles may have come from the APU directly, or from re-ingestion of the APU exhaust into the aircraft.

Changes in the carbon dioxide concentration measured arise from the presence of staff on the aircraft and whether or not the doors were open, or whether the ECS system was providing cabin ventilation.

The measurements of temperature and relative humidity exhibited typical characteristics for a ground test in an aircraft.

#### Sampling and analysis of chemical samples

Air samples were collected on adsorbent tubes using a hand held sampler.

The tubes were analysed at the BRE laboratories using GC and GC-MS, with external calibration.

Hyjet4 is a hydraulic fluid containing tributyl phosphate, dibutylphenyl phosphate and butyldiphenyl phosphate. It was measured using an authentic sample of the fluid (as

used in the BAe146 aircraft tested) as an external standard through the response to the butylphenyl phosphates.

Jet2 is an engine oil containing a range of synthetic esters and is reported to contain 1-3% tricresyl phosphate and 1-2% aromatic amines. It was measured using an authentic sample of the oil (as used in the aircraft tested) as an external standard using the mass spectrometer response to the esters.

Other compounds observed in Test 3 that were above the aircraft and hangar background, but that were not fully quantified, included, 2,4-toluene di-isocyanate (TDI) and tri-(1-chloro-2-propyl) phosphate (fire retardant TCPP).

The main analytical findings may be summarised as follows:-

- Large concentrations of toluene and xylene were found in samples taken during Test 4 (when the chemical sample was deliberately released).
- Concentrations of Hyjet4 hydraulic fluid were similar (2 3 μg m<sup>-3</sup>) for all of the samples taken within the aircraft cabin (Tests 2, 3 & 4), and higher than that found as a background in the hangar (Test 1 0.4 μg m<sup>-3</sup>).
- Tri-butyl phosphate (typically found in hydraulic fluid and used as an additive in plastics) was found in all of the samples from the aircraft cabin (Tests 2, 3 & 4) in concentrations ranging from 23 42 μg m<sup>-3</sup>. Background level (Test 1) was 2 μg m<sup>-3</sup>.
- Higher concentrations (11 14 μg m<sup>-3</sup>) of Jet2 engine oil were found in the cabin during tests where the APU and ECS systems were running (Tests 3 & 4). Background levels (Tests 1 & 2) were 2 μg m<sup>-3</sup>.
- Higher concentrations (0.6 1.3 μg m<sup>-3</sup>) of total tri-cresyl phosphate, a component of engine oil, were found in the cabin during tests where the APU and ECS systems were running (Tests 3 & 4), compared to concentrations of 0.02 0.03 μg m<sup>-3</sup> in Tests 1 & 2.
- The relative concentration of the different components in the hydraulic fluid found in the air samples was different to that found in the sample of Hyjet4 used as a reference material. This may be because in the vapour phase concentration is dependent on the relative volatilities of the components of the fluid. In addition, the ratio could be further changed in the aircraft cabin due to evaporation/condensation conditions and possible other sources of the components.
- Similarly, the ratio of tri-cresyl phosphates to the synthetic esters contained in Jet2 oil found in the aircraft atmosphere is different to the ratio found in the liquid reference material.

#### Conclusions

The sampling and analytical techniques that BRE has developed have been able to identify and measure low-level airborne concentrations of engine oil and hydraulic fluid,

and of their components including total tri-cresyl phosphate, in the aircraft cabin during the tests conducted at Teesside on 6<sup>th</sup> June 2007.

It should be noted that no "bleed air contamination event" was noticed or reported by the people conducting the tests, thus supporting our assertion that our techniques are able to monitor contaminant chemicals of relevance to this study - at concentrations below the detection threshold of most people.

#### Appendix A. General Information - Airport A Feasibility Study. 6<sup>th</sup> June 2007

Test / Sample	APU / Engine	ECS Pack	BRE Samplers Time on	BRE Samplers Time off
1	Hangar background.	-	14.49	15.06
2	Aircraft background.	-	15.11	15.28
3	APU on.	1&2	15.47	16.05
4	APU. Chemical released.	1&2	16.08	16.27

For tests 3 & 4, the times for the BRE sampler operation roughly coincide with the running of the APU / ECS system.

APU on: **15.45** ECS Packs 1&2 on: **15.49** Pack temperatures increased throughout Test 3. End of Test 3 packs turned to "cool" (APU & Packs still running) Pack temperatures increased from ~half-way through Test 4 APU and ECS Packs turned off: **16.24** 

#### **Aircraft Tested**

OO-TAU

#### **General Information**

The air system takes off each engine at 41 psi, 71 lb/min and temp of 220 deg C. The packs control from 18 to 27 deg C.

Engine type: ALF502R-5's rated @ 6700 lbs thrust Engine oil pressure 90psi @ 110 deg C APU oil pressure 48 psi @ 135 deg C. Main oil seals are carbon seating on a face plate.

# APPENDIX 8.6 BRE Report : Test Sampling on Boeing 757 fitted with the RR 535c Engine

#### Results from Feasibility Study at Airport B - 31<sup>st</sup> July 2007

This letter report and its Appendix summarise the results that were obtained by BRE during the in-flight measurements conducted on a DHL Air Boeing 757 aircraft flying out of Airport B as part of the Second Stage of the Feasibility Study for the DfT cabin air project.

Appendix A contains general details of the tests and the aircraft on which the monitoring was conducted.

In line with the instructions given at the meetings held before and after the monitoring, no communication has been made between BRE and the staff at AES since the monitoring.

The discussion of results here is intended to help one to make comparisons between the various sampling techniques and subsequent analyses that were employed by BRE, AES and Cranfield University.

#### Test conditions during which samples were taken

The test conditions, during which the samples were taken, are given more fully in Appendix A and summarised below;-

- Sample 1. Aircraft Background.
- Sample 2. Aircraft Background (APU & ECS on).
- Sample 3. Taxi.
- Sample 4. Ascent.
- Sample 5. Cruise.
- Sample 6. Descent.
- Sample 7. Descent/Landing/Short Taxi.
- Sample 8. Stand (APU & ECS on).

All tests were conducted on the flight deck of the aircraft, with the door to the cargo bay closed.

Air samples for chemical testing were collected on adsorbent tubes using a hand held sampler.

The tubes were analysed at the BRE laboratories using GC and GC-MS, with external calibration.

Skydrol 500B4 is a hydraulic fluid containing tributyl phosphate, dibutylphenyl phosphate and butyldiphenyl phosphate. It was measured using an authentic sample of the fluid (as used on the B757 aircraft tested) as an external standard using the GC

response to the butylphenyl phosphates. It should be noted that the ratio of these components was different in the air samples from that found in the fluid. Jet2 in is an engine oil containing a range of synthetic esters and reported to contain 1-

3% tricresyl phosphate and 1-2% aromatic amines. It was measured using an authentic sample of the oil (as used on the aircraft tested) as an external standard using the mass spectrometer response to the esters. It should be noted that the ratio of the components was different in the air samples from that found in the fluid.

#### **Discussion and Conclusions**

The sampling and analytical techniques that BRE has developed were applied to air in the flight deck throughout various phases of a flight on a DHL Air Boeing 757 aircraft. The tests have been able to identify and measure low-level concentrations of engine oil and hydraulic fluid and their components including total tricresyl phosphate.

The "bleed air contamination event" reported by those conducting the tests and the flight crew during the ascent phase (in particular the "thrust to climb" period) of the flight was coincident with a sharp, brief rise in ultra-fine particles.

There was a higher concentration (5  $\mu$ g m<sup>-3</sup>) of Jet 2 engine oil found within the sample taken during this stage of the flight (Sample 4), compared with those found during other stages of the flight (2  $\mu$ g m<sup>-3</sup> or below). Interestingly, some of the concentrations of Jet 2 on the first feasibility study (on a BAe146 aircraft at Teesside Airport) were higher than this level (at 11 - 14  $\mu$ g m<sup>-3</sup>) although no "bleed air contamination event" was noted by those present on that occasion. The concentration of total tri-cresyl phosphate found in Sample 4 (0.04  $\mu$ g m<sup>-3</sup>) was higher than that found in other flight phases (though a concentration of 0.05  $\mu$ g m<sup>-3</sup>was found in the background sample (Sample 1).

Skydrol hydraulic fluid was found at similar levels (at 1 - 4  $\mu$ g m<sup>-3</sup>) in air samples from all stages of the flight, and at similar concentrations to those found for Hyjet hydraulic fluid during the first feasibility study at Airport A. Tributyl phosphate, a major component of hydraulic fluids and also an additive in plastics, was found at concentrations of 2 - 8  $\mu$ g m<sup>-3</sup> (i.e. at somewhat lower levels than found at Teesside when the APU and ECS were on).

It should be noted that the concentrations measured were the average concentrations over each sampling period. During the period over which Sample 4 was taken (when the "event" occurred) the particle monitor recorded high readings over a period of around two minutes within the total tube sampling time of 18 minutes. Therefore, if we assume that the particles emitted account for at least part of the bleed air contamination, it is possible - if all of the Jet2/Skydrol was emitted during these two minutes - that the *instantaneous* Jet2/Skydrol concentrations *could have been* around ten times the average value.

The sharpness of the peak in the ultra-fine particle concentrations indicates that the contamination "event" was very brief, probably only lasting for a few seconds before being ventilated away. Although the number concentration of the particles measured during this period was high (with instantaneous readings representing >500,000 particles per cm<sup>3</sup> of air), due to their small size ( $20nm - 1\mu m$ ) their mass concentration would have been extremely small. The result of this is that the pumped sample taken for analysis during this flight phase (taken over 18 minutes) is likely to have collected only a small additional mass arising from the *particle* phase during the "event".

It is likely that the changes in carbon dioxide concentration measured arose from the presence of staff on the aircraft and whether or not the doors were open, or whether the ECS system was providing cabin ventilation.

The measurements of temperature and relative humidity exhibited typical in-flight characteristics; with the temperature varying a little and the relative humidity dropping during the flight phase of the monitoring.

As was the case in Phase One of this Feasibility Study (where no event was discerned by those present) our results for those flight phases where there was not a discernible event show that our techniques are also able to monitor contaminant chemicals of relevance to this study at concentrations below the detection threshold of most people.

#### Appendix A.

Test / Sample	APU / Engine	BRE Samplers Time on	BRE Samplers Time off
1	Aircraft Background.	12:28	12:38
2	Aircraft Background (APU & ECS on).	12:47	12:57
3	Taxi.	13:01	13:11
4	Ascent.	13:18	13:36
5	Cruise.	13:42	13:53
6	Descent.	13:59	14:11
7	Descent/Landing/Taxi.	14:18	14:31
8	Stand (APU & ECS on).	14:33	14:41

#### General Information – Airport B Feasibility Study 31<sup>st</sup> July 2007

All tests were conducted on the flight deck of the aircraft, with the door to the cargo bay closed.

#### **Aircraft Tested**

G-BMKC

#### Engines

Engine type: RB211-535C37 rated @ 37,400 lbs thrust (sea level) Engine oil pressure 18-45 psi APU oil pressure 60-70 psi (oil cooler bypass below 170°F. Skydrol 500B4 used.

#### ECS

Pressure and temperature at engine off-take for ECS 40-50 psi at 450°F. Temperature range for ECS control in cabin 65-85°F.



# APPENDIX 8.7

# **Intertek MSG**

Separation Science Wilton Centre Tel: 01642 435745

Test Report: No. SEP/W002571RL001 **Volatile organic compounds present in airliner cabin air** Date: 16/10/2007

For **C Walton** Cranfield University

Prepared by: Bernard Fields GC/HPLC Laboratory

# TEST REPORT Volatile organic compounds present in airliner cabin air

Report Number	SEP/W002571RL001
Chit Number	209915
Receipt Date	25/09/2007
Lab Book Reference	
File Reference Location	D128
Number of Samples	8
Description of Work Required	Identification and quantification of air sampling tubes
Method Reference	SOP/GC/MS/9

# Samples Submitted

Sample Identifier	Sample Description	Customer Identifier
SEP/W002571-1	Air sampling tube	S146416 1.2
SEP/W002571-2	Air sampling tube	S146418 1.21
SEP/W002571-3	Air sampling tube	S146420 1.4
SEP/W002571-4	Air sampling tube	S146424 1.8
SEP/W002571-5	Air sampling tube	S146428 2.6
SEP/W002571-6	Air sampling tube	S146432 2.73
SEP/W002571-7	Air sampling tube	S146436 0.91
SEP/W002571-8	Air sampling tube	S146440 0

# Procedures

## **Description of procedure**

Samples were analyzed as submitted in Perkin Elmer steel thermal desorption tubes packed with tenax and Unicarb. The tubes were heated for 20 minutes and the volatiles contained in the samples were released and swept by a flow of gas to a cold trap where they were reconcentrated. Finally, the trap was heated rapidly while a stream of gas swept the desorbed volatiles into the connected GC for separation and detected by mass spectrometry. Signals at mass 45, 57, 71, 91 and 93 were used for analysis and quantification of isopropyl alcohol, nonanal, dodecane, toluene and  $\alpha$ -pinene respectively and for estimation of similar compounds. These named compounds were the compounds found at the most significant concentrations.

#### **Thermal desorption conditions**

#### System

Perkin Elmer ATD400 with Agilent 6890GC and 5973MSDS

The conditions were shown as below:

Oven temperature:	240 °C
Primary desorption:	20 minutes
Line temperature :	225 °C
Valve temperature:	225 °C
Trap low:	-30 °C
Trap high:	260 °C
Trap hold:	5min
Pressure	8psi He
Out split:	20ml/min
Desorb flow:	50ml/min

## GC conditions

Column Alltech  $EC^{TM-1}$  30m×320µm×1.00µm was used. Temperature was programmed from 30 °C (hold for 10 min) to 200 °C (hold for 2 min) at the rate of 10 °C /min. Pressure was 8.00 Psi He.

#### **MS conditions**

MS were used as the detector, scan mode was chosen. Mass range was from 20-400. EM voltage was at 2400. Mass 45, 57, 71, 91, 93 were elected and the calibrations were based on those peak areas.

## Preparation of standards and calibration procedure

Three standards of mixtures of isopropyl alcohol, nonanal, dodecane, toluene and  $\alpha$ -pinene in methanol were prepared, 0.02 ug/ul, 0.2 ug/ul and 1 ug/ul respectively for each of the five compounds. Each standard was analyzed by injecting 1ul onto a tube packed with tenax followed by spherocarb. (NB spherocarb and Unicarb, which are both used together with tenax on the calibration tubes and sampling tubes respectively are essentially identical in retention properties). These standards were run under the same conditions as the samples (without removing the methanol). 100% transfer of these standards into the system under the conditions of test was validated by a second desorption of the standards which showed that all of the standards were transferred.

The calibration curves of ug of isopropyl alcohol, nonanal, dodecane, toluene and  $\alpha$ -pinene vs areas of mass 45, 57, 71, 91 and 93 respectively were prepared. Good linear plots were obtained. A typical calibration for toluene is given.

## Analysis of samples

As many as possible of the compounds in the samples were identified by their mass spectra.

Selected compounds : isopropyl alcohol, toluene, dodecane, nonanal and alpha-pinene were quantified from the calibration curves. The ppb concentrations of those compounds were calculated by the equation given below.

Estimates of the concentrations of homologous alkanes and aldehydes were obtained on the basis that the higher alkanes and aldehydes would give a similar response on a mass/mass basis as the dodecane and nonanal standards

Concentration in air (ppb) =  $\frac{m \times 24 \times 10^9}{M \times v}$ 

M: molecular weight m: mass of compounds g v: sample volume L

# Results

# Chromatograms

Chromatograms of samples were given below from Figure 1 to Figure 8:

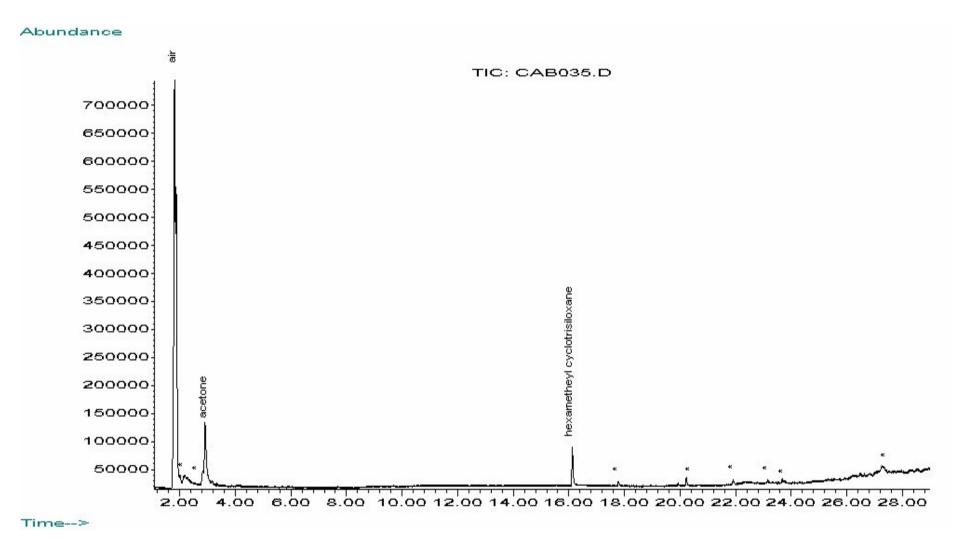


Figure 1: Chromatogram of S146440 (blank) generated by GC-MS



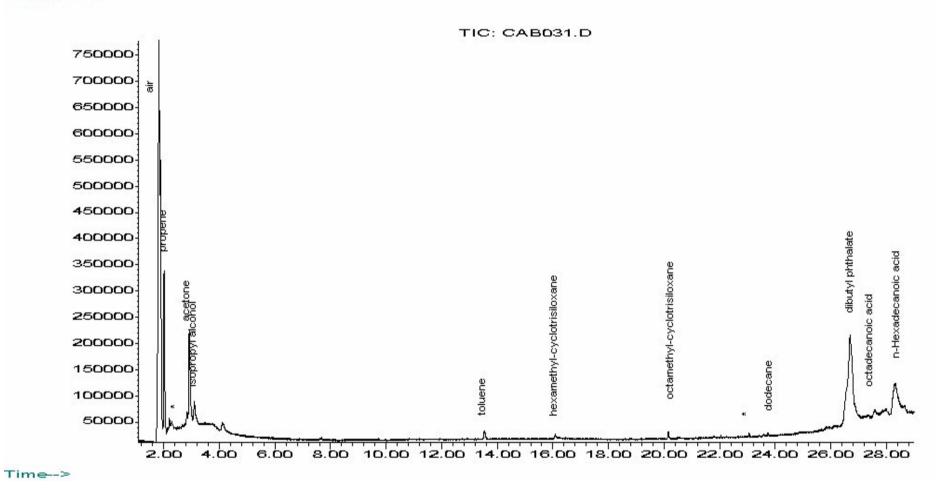
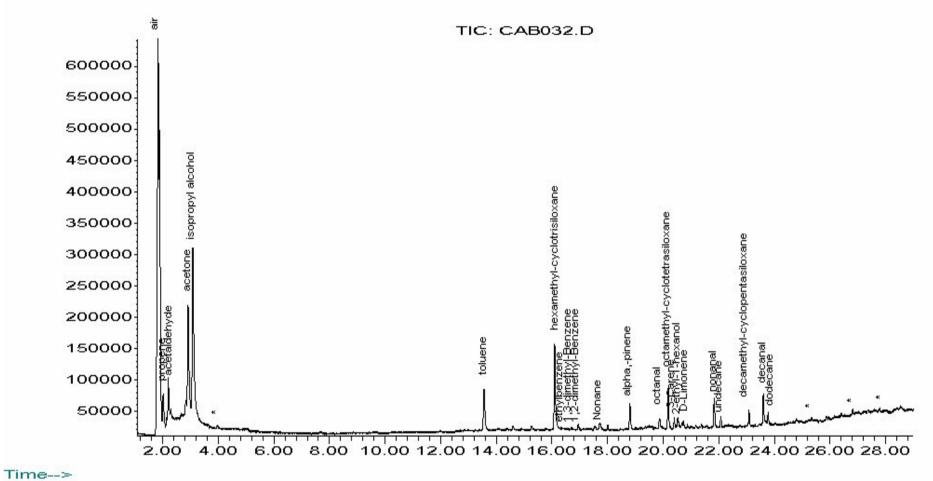


Figure 2: Chromatogram of S146416 generated by GC-MS









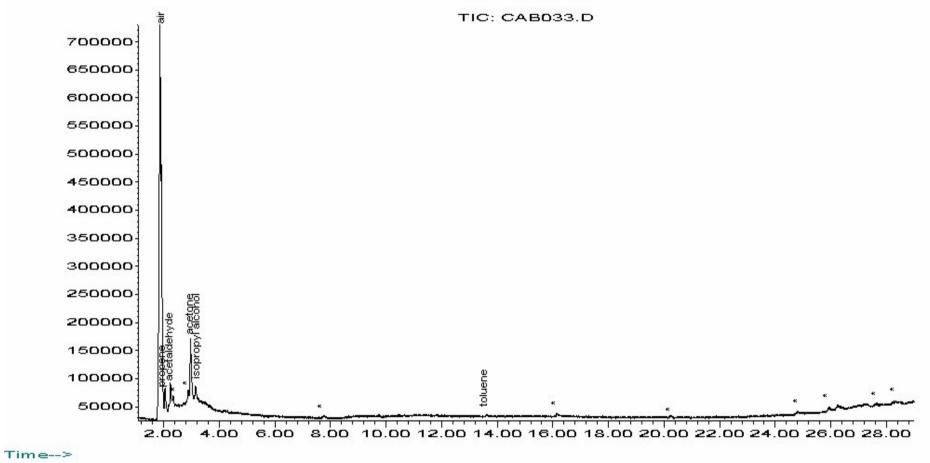
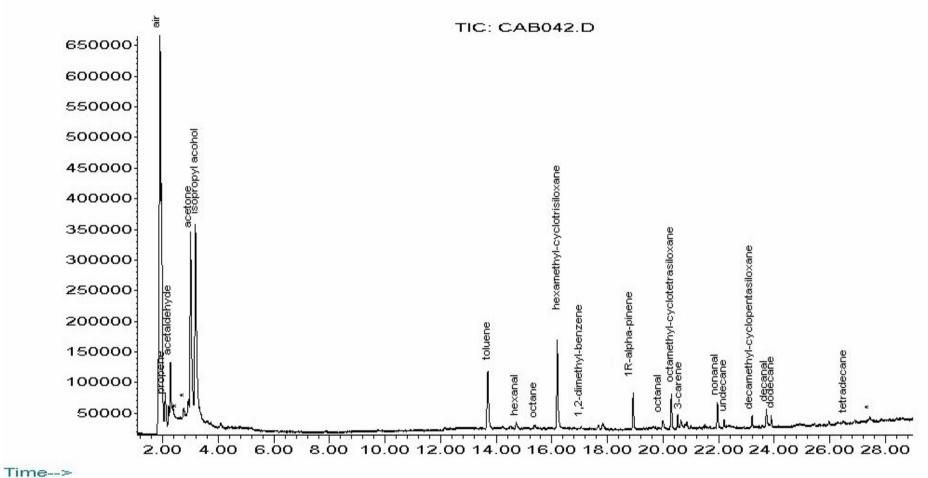


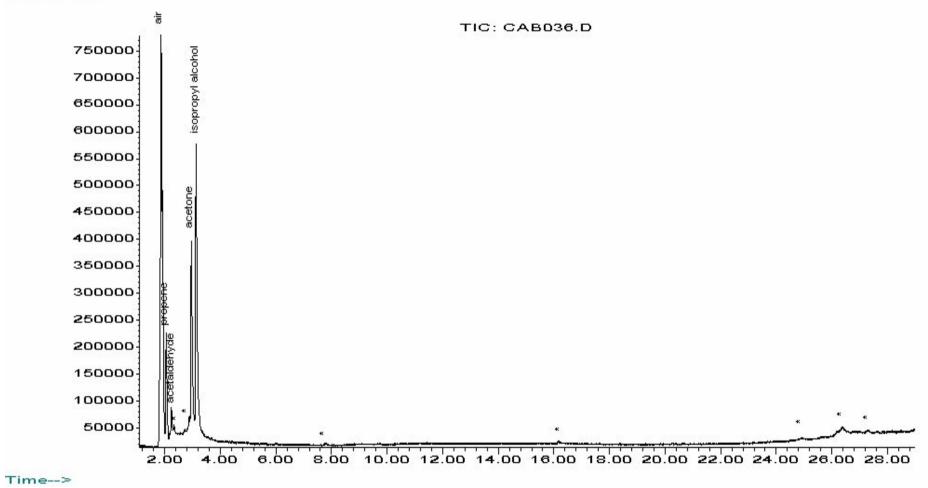
Figure 4: Chromatogram of S146420 generated by GC-MS













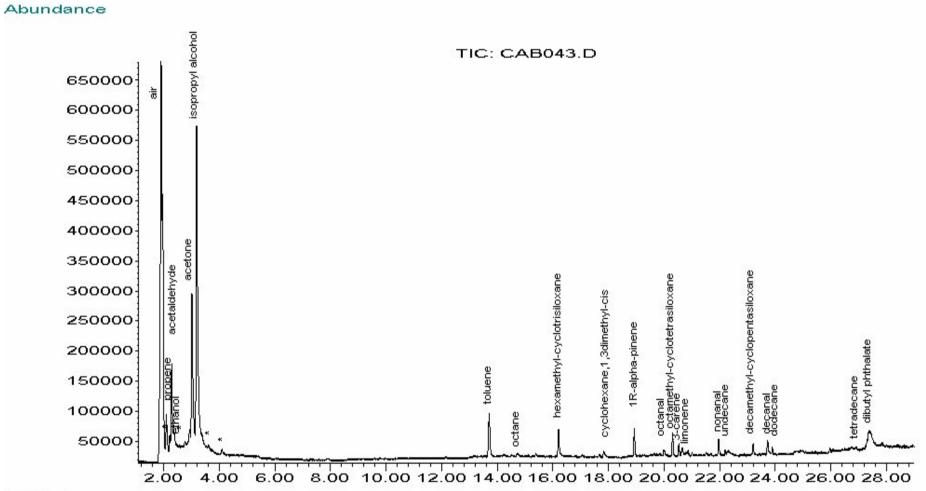




Figure 7: Chromatogram of S146432 generated by GC-MS



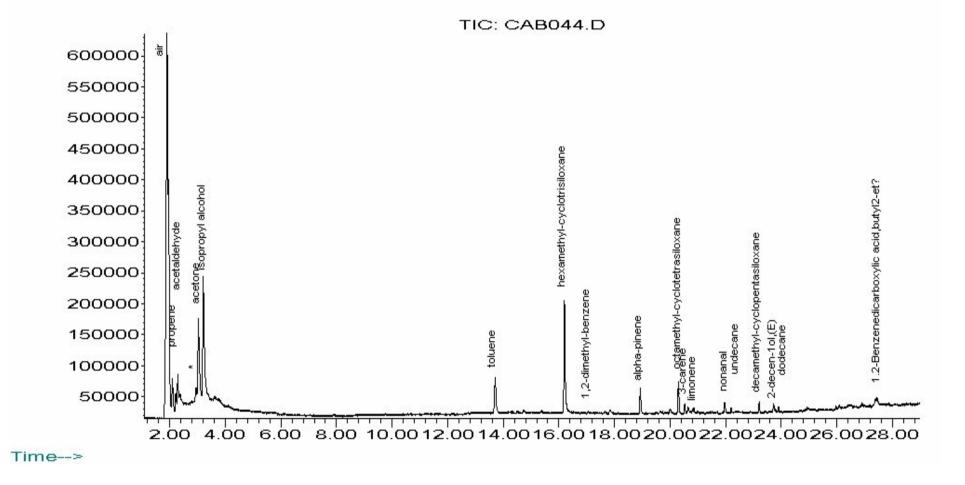
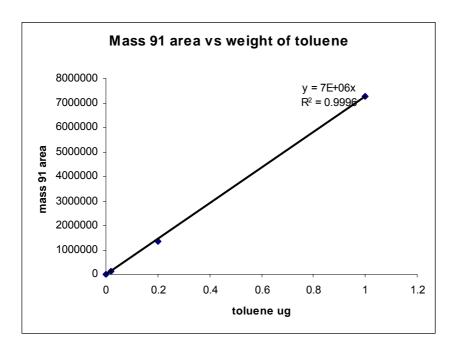


Figure 8: Chromatogram of S146436

## **Calibration graphs**

The calibration graphs were produced by plotting the Mass areas of the specific ion in the standards to the weight of the injected compound. A typical calibration graph is given below, with a correlation coefficient of 0.9996. For the purpose of calibration we force the response through the origin.



**Figure 9: Calibration graph for toluene** 

Identified	S146440	S146416*	S146418	S146420*	S146424	S146428*	S146432	S146436
compounds								
propene		+	+	+	+	+	+	
ethanol							+	
acetaldehyde			+	+	+	+	+	+
2-propanol			+	+	+	+	+	+
toluene		+	+	+	+		+	+
Hexamethyl-	+	+	+		+		+	+
cyclotrisiloxane								
hexanol					+			
octane					+		+	
Ethyl benzene			+					
1,3-dimethyl-			+					
benzene								
1,2-dimethyl-			+		+			
benzene								
nonane			+					
α-pinene			+		+		+	+
octanal			+		+		+	
Octamethyl-		+	+		+		+	+
cyclotetrasiloxane								
3-carene			+		+		+	+
2-ethyl-hexanol			+					
limonene			+				+	+
nonanal			+		+		+	+
undecane			+		+		+	+

 Tables of results

 Table 1 Compounds identified in the samples. \*Samples taken incorrectly - compounds could be present which are not observed.

Decamethyl-		+	+	+	+
cyclopentasiloxane					
2-decen-1(ol) (E)					+
decanal			+	+	
decanol		+			
dodecane	+	+	+	+	+
tetradecane			+	+	
Dibutyl-phathlate				+	+
Octadecanoic acid	+			+	+
n-Hexadecanoic	+				+
acid					

# Table 2 Quantitative results. Decanal and undecane are estimated from the nonanal and dodecane calibration.

Quantified	S146440		S146418		S146424		S146432		S146436	
compounds	(blank)		ug	ppb	ug	ppb	ug	ppb	ug	ppb
	ug	ppb								
2-propanol			0.177	58.4	0.203	45.2	0.326	47.8	0.077	33.7
toluene			0.016	3.5	0.022	3.2	0.017	1.6	0.013	3.8
α-pinene			0.012	1.7	0.016	1.6	0.013	0.8	0.011	2.1
nonanal			0.011	1.6	0.011	1.1	0.007	0.5	0.004	0.7
decanal			0.003	0.4	0.002	0.2	0.001	0.1		
undecane					0.001	0.1	0.002	0.1	0.002	0.3
dodecane					0.003	0.2	0.003	0.1	0.001	0.2

# **Discussion of results**

#### Figure 1 S146440 tube blank

Peaks present in the chromatogram are air, acetone and hexamethyltrisiloxane. The acetone and hexamethyltrisiloxane are contaminants which we are unable to avoid and may have arisen in the prior handling of the tube or in our laboratory (acetone) or in the thermal desorption system itself (hexamethyltrisiloxane - which appears to be ubiquitous). Consequently we ignore the present of acetone and only consider the hexamethyltrisiloxane to be present in samples if the sample contains significantly more than the blank.

#### Sample tubes containing cabin air

These samples fall into two groups. One group, where the air samples have been taken onto the tubes the wrong way and where all the quantitative data is invalid (and not presented in the table) and the other where the samples have been taken correctly.

These sampling tubes contain two adsorbent beds in series in the tube so that the tubes can quantitatively sample and analyses a wide range of compound volatilities. The tubes work by taking air samples through the weaker absorbent first followed by stronger absorbent. Any involatile compounds which are likely to be held strongly by absorbents are trapped on the front of the weak absorbent bed. Volatile compounds pass through the weak absorbent but are still trapped on the stronger absorbent. In the laboratory desorption takes place in the reverse direction so that both types of compound are easily recovered from the tubes. It is vital that the samples are taken onto the tube the right way round otherwise the strongly held involatile compounds will go onto the strong absorbent and it will be very difficult to get them off. This has been the case with the three samples S146416, S146420, and S 146428. We are sure about this because the direction of sample entry was marked on each tube. It is evident from the chromatograms where much less of the compounds present are found on these tubes than in the normal samples. There is a second unfortunate consequence of this and that is that these compounds will still be present on the tubes and small, amounts may be detected in subsequent analyses unless they can be exhaustively cleaned. Clearly if the project is to progress using these tubes then means must be found to make it clear on the tubes which direction the sample has to be taken.

#### Compounds identified in cabin air

The compounds identified from their mass spectra are listed in table 1. Many of these compounds : toluene, limonene, cyclic siloxanes, alkanes, and aldehydes were reported as being detected in commercial aircraft cabin air in reference 1.

## Quantification of compounds present

The compounds quantified are given in table 2. They are presented only for those samples where the sample was taken correctly. There are a number of compounds (consistently) present above 0.5ppb : propanol (ca 50ppb), toluene (ca 3ppb), alphapinene (ca 2ppb) and nonanal (ca 1ppb). Propene and the cyclic siloxanes were not quantified and so could be present above 0.5ppb. Propene may not be quantifiable by the sampling method because it is too volatile. The cyclic siloxanes could and should be quantified by this method in any future work.

## Validation of sampling and analysis methodology.

For a valid analysis of the compounds present it is necessary to show that:

1 all of the compound entering the tube during the sampling period is retained on the tube.

2 all of the compound on the tube at the end of the sampling period is transferred to the analysis system when analysed

3 all of the reference materials on the calibration tubes are transfered to the analysis system when analysed.

Items 2 and 3 were validated for the range of volatilities of propanol to dodecane by a second desorption of both sample tubes and calibration tubes containing these compounds. This showed that these two validation criteria were met. The thermal desorption efficiencies using data from the standards were propanol 99.7%, toluene 98.8% and dodecane 99.4%.

Item 1 is not yet validated. The combination of tenax and unicarb (which is similar to spherocarb in its retention characteristics) would normally allow quantitative retention of compounds in the range C3-C30 (C8-C30 for tenax and C3-C7 for Unicarb - reference 2) under suitable sampling and desorption conditions. The quantification results depend on this being confirmed at least for the range of results C3-C14. The validation of item 1 for the range of analytes is a necessity if the project continues and if the work is undertaken within our UKAS accreditation (or done to any reliable standard) and is the subject of a proposal for further work.

#### Summary of work

Chemicals present in the cabin air of aircraft in the C3 to C14 range have been identified.

The method for these has been shown, for most compounds, to enable detection at 0.5ppb or less using 2-3 litre air samples.

There are several compounds present at levels above 0.5ppb ie propanol (ca 50ppb), toluene (ca 3ppb), alpha-pinene (ca 2ppb) and nonanal (ca 1ppb).

## **Future work**

1 There is a need to ensure breakthrough volumes are not exceeded and quantitative recoveries are obtained for compounds found in cabin air. This would involve spiking two sets of clean sampling tubes with the same amounts of propanol, toluene and dodecane and a range of higher hydrocarbons. We would pump 3 litres of air (the maximum used in sampling) at 100ml/min for 30 minutes through one set of the tubes. We would then analyse both sets to establish that (a) the same amounts are found on both sets of tubes (b) no residual amounts are left on the tubes after the first desorption. Analysing a range of higher hydrocarbons will establish the upper carbon number limit for which this is true.

2 The GC method currently will elute up to C14 in the time range of the analysis. Reference 1 indicates compounds found in cabin air of C17. The range of application of the method should be extended to include this by ensuring appropriate absorbent tubes and thermal desorption conditions are used and by extending the GC run time. This is expected to be quite straightforward. We would do this prior to the validation under 1 above.

## Costs of analysis and future work.

To validate the quantification of compounds in the range propanol to the upper method alkane limit would cost 1600GBP

Experience with this work indicates that costs of analysis of similar samples from a survey of flights would be as follows.

Where the sample does not appear to show the presence of different chemicals to those described herein then we would analyse those samples for 80GBP per sample.

Where samples indicate the presence of any unusual compounds then we would quantify the normal range of compounds, identify the additional compounds if possible (the analysis up to this point costing 80GBP as before) and estimate the concentration of additional compounds using the dodecane standard response at 20GBP per additional compound. Quantifying any additional compounds using the actual compound as reference material would cost 200GBP per compound. We would do this where a significant health hazard could be associated with the new compound.

In order to perform the analyses at this cost samples would need to be retained until 10 samples could be analysed together. Sealed TD tubes should allow this storage without compromising the analysis.

There could be less expensive options which could be appropriate for example performing no quantitative analyses on samples which do not appear out of the ordinary.

#### References

1 Volatile organics present in recycled air aboard a commercial airliner. J Brady, S Overton and J J Manura. Scientific Instrument Services Application note 26a. 23 December 1999.

2 Thermal Desorption Technical Support Note 5: Advice on sorbent selection and conditioning sample tubes. Markes International Ltd.

#### **Report Authorisation**

Bernard Fields	
Date 16/10/2007	

Copies to: