# Determination of organophosphate contaminants in jet fuel

E. Spila*, G. Sechi, M. Bernabei

*Divisione Aerea Studi Ricerche e Sperimentazioni, Reparto Chimico Tecnologico, Aeroporto Pratica di Mare, 00040 Pomezia (Rome), Italy*

## Abstract

The aircraft used by the Italian Air Force as tanker in flight refuelling operations is the Boeing 707; the features of the pumping system can generate jet-fuel contamination by the organophosphoric hydraulic fluid, Skydrol. This contamination could have negative effects on the technological properties of jet-fuel, and thus the jet fuel has to be periodically checked to measure its Skydrol concentration. In the present work two methods to determine organophosphate-based hydraulic fluids in jet fuels are described. Both methods are based on gas chromatographic techniques: in the first one a mass spectrometer detector in the selected ion monitoring mode was used, whereas in the second one a flame photometric detector with a optical filter selective for phosphorus compounds was employed.  © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Jet fuel; Petrochemical analysis; Organophosphate compounds; Skydrol; Triethyl phosphate; Tribenzylamine

## 1. Introduction

The aircraft used the as tanker by Italian Air Force in the air refuelling operations is the Boeing 707; the air refuelling procedures are based on a pumping system fully immersed in the jet fuel [1]. The pumping system is based on an hydraulic mechanism, whose operating fluid, Skydrol, is a mixture of organic phosphates [2]. Due to the complete immersion of the pumps in the tankers, fuel contamination by the hydraulic fluid can occur. The organophosphorus compounds can have a negative effect on the fuel thermal stability [3]; moreover the effect of phosphorus compounds in the hot corrosion on the aircraft turbines are known [4]. In order to prevent these negative effects, the jet fuel has to be periodically checked to measure the contamination level.

In the present work two specific methods to carry out this determination are described; both of them are based on gas chromatographic techniques: in the

*Corresponding author.

first one mass spectrometry operating in the selected ion monitoring mode (GC–MS-SIM) [5,6] was used, whereas in the second one flame photometric detection with a optical filter selective for phosphoric compounds (GC–FPD) was employed [7,8].

These techniques, because of their specificity, do not require sample pre-treatments other than the addition of an internal standard. The analysis of aviation fuel samples can be performed in less than 15 min in a sample of 5–10 ml.

## 2. Experimental

### 2.1. Reagents

The standard solutions were prepared with commercial products: triethyl phosphate (TEP) (99%, Aldrich), tribenzylamine (TBA) (>99%, Aldrich), Skydrol (Monsanto). The Jet A1 fuel used to prepare the standard solutions was according to present directive for the civil and military aviation [9].

Table 1
Chromatographic conditions for GC–MS analysis

| | |
|---|---|
| Injector temperature | 250°C |
| Initial temperature | 130°C for 1 min |
| Programmed temperature | 10°C/min |
| Final temperature | 250°C for 1 min |
| Carrier gas | Helium |
| Linear speed in column | 24.5 cm/s |

Table 2
Chromatographic conditions for GC–FPD analysis

| | |
|---|---|
| Injector temperature | 240°C |
| Detector temperature | 240°C |
| Air/hydrogen detector ratio | 0.7/1.4 kg/cm$^2$ |
| Initial temperature | 180°C for 2 min |
| Programmed temperature | 10°C/min |
| Final temperature | 270°C for 5 min |
| Carrier gas | Helium |
| Linear speed in column | 24.5 cm/s |

## 2.2. Instrumentation

The apparatus used for GC–MS-SIM analysis consisted of a gas chromatograph Fisons GC 8000 Series, equipped with a methylsilicone capillary column (25 m×0.25 mm I.D., 0.25 μm phase film). The GC–MS analysis was carried out by a Fisons MD 800 MS system operating in the mass range of 33–500 u.

The apparatus used for the GC–FPD analysis consisted of a Carlo Erba gas chromatograph Model 4200, equipped with a methylsilicone capillary column (30 m×0.32 mm I.D., 1.0 μm phase film). The GC–FPD analysis was carried out by a Fisons FPD-700 FPD system operating with an optical filter selective for phosphoric compounds (passing band centred at 526 nm).

## 2.3. Procedure

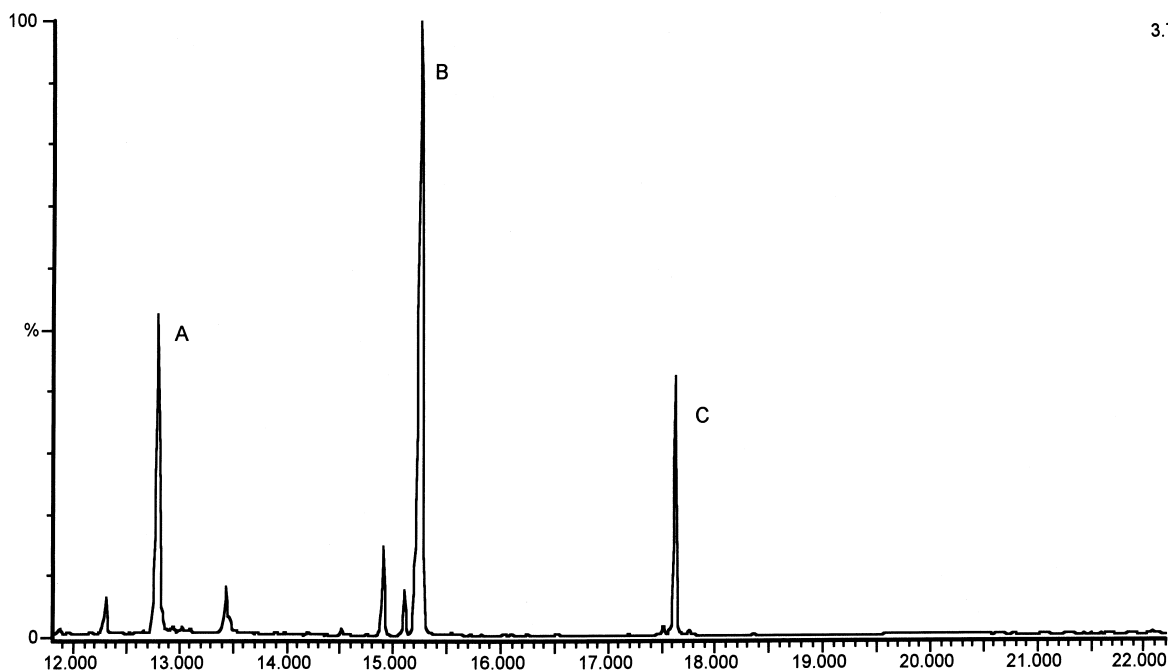The fuel samples for the GC–MS-SIM determinations of hydraulic fluid were prepared by the



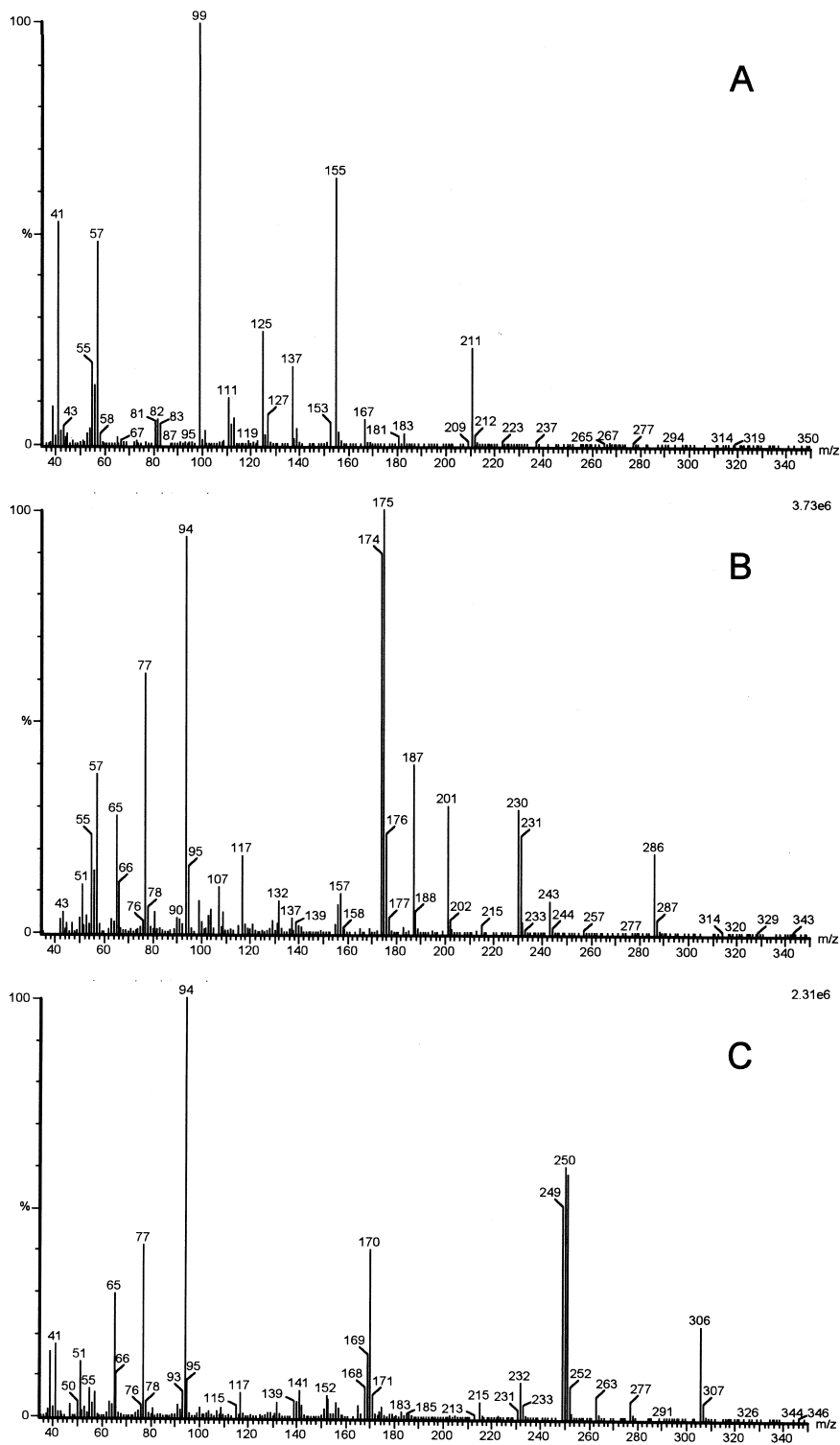Fig. 1. Total ion current chromatogram of Skydrol.

Fig. 2. Mass spectra of compounds A, B and C.

addition, in a 10-ml volumetric flask, of 20 μl of a 0.1% (m/v) TBA solution in jet fuel to a fuel sample; 1 μl of each sample was injected into the GC–MS system.

The fuel samples for the GC–FPD determination of hydraulic fluid were prepared by addition of a known volume of TEP (10 μl) into a known volume of fuel (10 ml) placed in a volumetric flask; 1 μl of each sample was injected into the GC–FPD system.

## 2.4. Conditions

The measurements for the GC–MS-SIM and GC–FPD determinations were carried out under the chromatographic conditions, respectively, shown in Tables 1 and 2.

## 3. Results and discussion

The total ion current chromatogram of Skydrol shows three main peaks, labelled in Fig. 1, respectively, with letters A, B and C. In addition a fourth component was detected at a higher retention time (D).

The mass spectrum of compound A (Fig. 2a) is characterized by the presence of signals 99, 155, 211 and 266; it can be originated from the ester structure shown in Fig. 3a, together with the proposed fragmentation pattern. The spectrum of compound B (Fig. 2b) differs from the previous one because of the 94 signal, due to a phenolic group, whose presence is confirmed by the 175, 230 and 286 peaks; the chemical structure attributable to this compound, reported in Fig. 3b together with the proposed fragmentation pattern, is obtained by the formal substitution, in compound A, of a phenyl group to a butyl group.

On the same basis, compound C, showing the spectrum reported in Fig. 2c, can be identified with structures in Fig. 3c. In addition compound D was identified as triphenylphosphate.

Summarizing, Skydrol hydraulic fluid is a mixture of butyl and phenyl esters of phosphoric acid.

TBA, having a retention time higher than the main components of Skydrol, has been chosen as the internal standard; it shows the mass spectrum reported in Fig. 4.
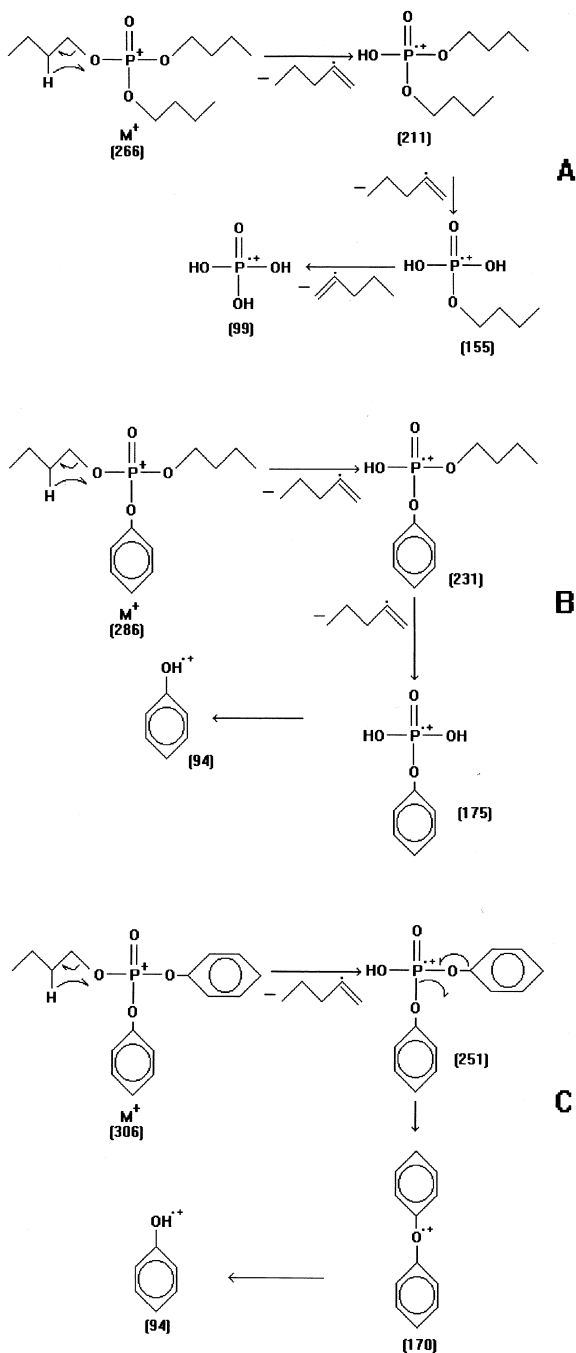


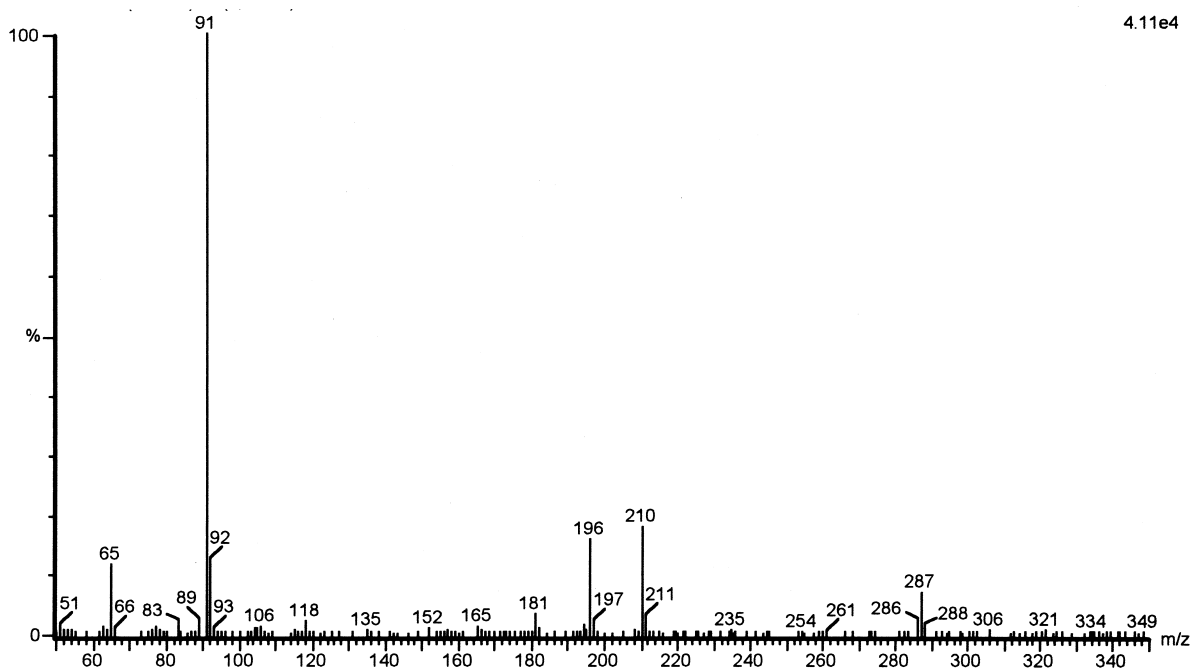Fig. 3. Structure and proposed fragmentation pattern of compounds A, B and C.

Fig. 4. Mass spectrum of TBA.

The signals obtained for compounds A and D were not considered significant enough for an analytical measurement, the former because of the interference of a matrix hydrocarbon peak showing the same ion masses, and the latter because it was too low.

Above described data have constituted the basis to build the acquisition program in the SIM mode shown in Table 3.

Calibration curves in the range 5–100 ppm have been built by injecting standard solutions with a Skydrol concentration of 5, 10, 50 and 100 ppm, all containing 2 ppm of TBA. They show a linear relationship between the instrumental response and the analytes concentration according to the following equations: Skydrol (ppm)=1.152+44.453 $[\text{Area}_{(\text{Compound B})}/\text{Area}_{(\text{TBA})}]$; Skydrol (ppm)= $0.854+187.232[\text{Area}_{(\text{Compound A})}/\text{Area}_{(\text{TBA})}]$.

Table 3
Selected ions for GC–MS-SIM analysis

|  | $m/z$ | Retention time (min) |
|---|---|---|
| Compound B | 94, 175 | 6.53 |
| Compound C | 94, 251 | 8.82 |
| TBA | 91, 210 | 10.20 |

A useful alternative route to the quantitative analysis of phosphorated hydraulic fluids in jet fuel is based on the use of FPD. Such a detection method, when equipped with a optical filter having a passing band centred at 526 nm, is sensitive to the HPO radical formed during the combustion of phosphorous-based organic compounds. Also a phosphorus-containing compound has to be chosen as an internal standard: TEP is suitable and has been employed in this work. Fig. 5 shows a chromatogram obtained for a jet fuel sample added with 100 ppm of Skydrol and 10 ppm of TEP, for an injected volume of 1 μl.

Also, in this case a linear behaviour of the calibration curve is observed in the range 5–100 ppm according to the following equation: Skydrol (ppm)= $-1.419+17.388[\text{Area}_{(\text{Compound B})}/\text{Area}_{(\text{TBA})}]$.

Table 4 summarizes the data on the reproducibility of the two analytical methods.

## 4. Conclusions

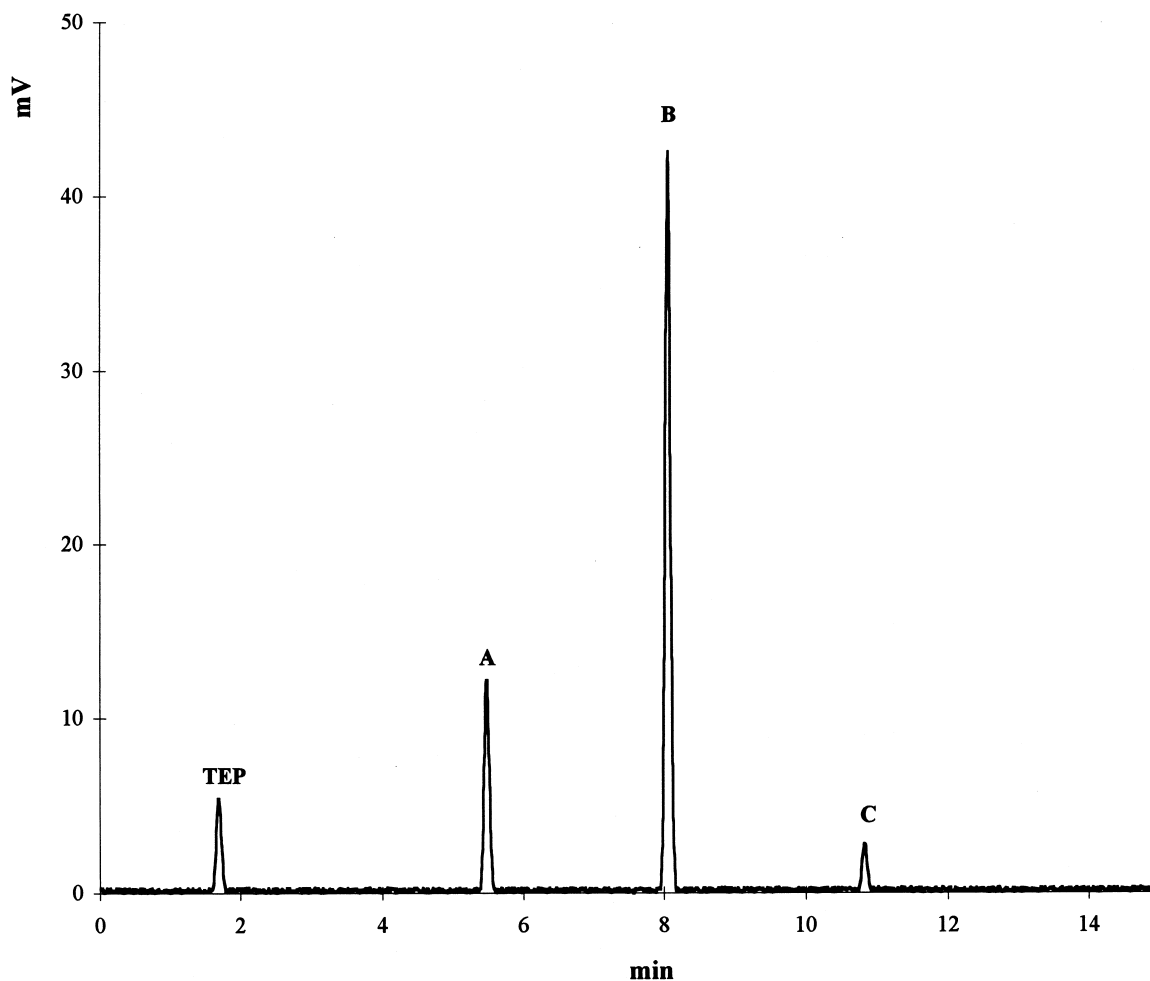Due to their specificity, both GC–MS and GC–FPD analyses represent an useful tool to determine

Fig. 5. GC–FPD chromatogram of a jet fuel sample added with 20 ppm of Skydrol and 10 ppm of TEP.

organophosphate contamination in complex mixtures such as fuels. This characteristic enables one to perform accurate determinations without pre-treating samples but just adding the internal standards at a given concentration and injecting into the column. This technique has two relevant advantages: shorter time needed to carry out the analysis and low amount of sample needed.

Table 4
Accuracy data for GC–MS-SIM and GC–FPD analytical methods

|  | GC–MS-SIM | GC–FPD |
|---|---|---|
| Linearity range (ppm) | 5–100 | 5–100 |
| Linear regression ($R^2$) | 0.997 | 0.998 |
| Sensitivity (ppm) | 2 | 2 |
| RSD (%, $n=5$, 50 ppm)/inter-day | 5.1 | 6.8 |
| RSD (%, $n=5$, 50 ppm)/intra-day | 3.0 | 4.0 |

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