



Determination of total and polycyclic aromatic hydrocarbons in aviation jet fuel

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Abstract

The aviation jet fuel widely used in turbine engine aircraft is manufactured from straight-run kerosene. The combustion quality of jet fuel is largely related to the hydrocarbon composition of the fuel itself; paraffins have better burning properties than aromatic compounds, especially naphthalenes and light polycyclic aromatic hydrocarbons (PAHs), which are characterised as soot and smoke producers. For this reason the burning quality of fuel is generally measured as smoke formation. This evaluation is carried out with UV spectrophotometric determination of total naphthalene hydrocarbons and a chromatographic analysis to determine the total aromatic compounds. These methods can be considered insufficient to evaluate the human health impact of these compounds due to their inability to measure trace (ppm) amounts of each aromatic hydrocarbon and each PAH in accordance with limitations imposed because of their toxicological properties. In this paper two analytical methods are presented. Both are based on a gas chromatographic technique with a mass detector operating in the selected ion monitoring mode. The first method was able to determine more than 60 aromatic hydrocarbons in a fuel sample in a 35-min chromatographic run, while the second was able to carry out the analysis of more than 30 PAHs in a 40-min chromatographic run. The linearity and sensitivity of the methods in measuring these analytes at trace levels are described.

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1. Introduction

The combustion quality of jet fuels is largely influenced by their hydrocarbon composition. In particular, products with a large proportion of aromatic hydrocarbons have worse combustion properties and a greater tendency to produce smoke after combustion. For these reasons the present military and civil directives [1,2] require the determination of the burning quality of fuels, monitoring the smoke formation tendency [3], total naphthalene hydrocar-

bon concentration, with UV spectrophotometry [4], and total aromatic hydrocarbons [5].

Nevertheless, the atmospheric pollution of fuel combustion products is also strongly related to their composition, especially the polycyclic aromatic hydrocarbon (PAH) content [6–8].

The reference methods actually used [3–5] are not designed to measure the different contributions of each PAH and each aromatic hydrocarbon in aviation jet fuel. Therefore, these methods can be considered inadequate to evaluate the human health impact of these compounds because of their inability to measure trace (ppm) levels in accordance with limitations imposed by their toxicological properties [9].

In the present paper two analytical methods are

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proposed to measure PAHs and total aromatic hydrocarbons in aviation jet fuel; they are based on a gas chromatographic technique with mass spectrometric detection in the selected ion monitoring mode (GC–MS–SIM) [10–15]. The first method was able to determine more than 60 aromatic hydrocarbons in a fuel sample in a 35-min chromatographic run, while the second was able to carry out the analysis of more than 30 PAHs in a 40-min chromatographic run. Several real samples have been analysed and the results obtained have been compared with those obtained by reference methods [4,5].

2. Experimental

2.1. Reagent

The standard solutions were prepared with analytical grade reagent (>99%, Aldrich). All aviation jet fuels samples were in accordance with the actual specifications [1,2]. All the remaining reagents were of analytical grade.

2.2. Instrumentation

The apparatus used for GC–MS analysis consisted of a Fisons GC (model 8000), equipped with a methylpolysiloxane (5% phenyl) capillary column (25 m×0.2 mm I.D. and 0.33- μ m phase film), an autosampler (model AS 800) and a Fisons mass spectrometer detector (model MD 800).

2.3. Procedure

The fuel samples for GC–MS analyses were prepared without any pre-treatment other than dilution and internal standard addition. The working solutions of fuel samples were obtained by dilution of 10 μ l of fuel with *n*-hexane in 5-ml volumetric flasks. As internal standard (I.S.) was added, with a 100- μ l micropipette, 40 μ l of a 200-mg/l stock solution of [²H₁₀]phenanthrene in *n*-hexane (for aromatic hydrocarbons analysis) and an analogue solution of diphenylamine (for PAH analysis); 1 μ l of each sample was injected with a 5- μ l micro-syringe.

Table 1
GC–MS–SIM: chromatographic conditions

<i>Column</i>	
Stationary phase	Methylpolysiloxane (5% phenyl)
Film thickness	0.33 μ m
Length	25 m
Inner diameter	0.2 mm
<i>Chromatographic set-up</i>	
Inlet temperature	250 °C
Inlet type	Split/splitless
Split ratio	1:30
Split/splitless valve time	1.0 min
Initial temperature	40 °C for 3 min
Programmed temperature	5 °C/min
Final temperature	280 °C
Carrier gas	Helium
Helium flow rate	0.7 ml/min

2.4. Conditions

The measurements for GC–MS–SIM determinations were carried out under the chromatographic conditions reported in Table 1. The ions chosen to

Table 2
GC–MS–SIM: mass spectrometer conditions

<i>MS detector</i>		
Interface temperature	230 °C	
Ionisation energy	70 eV	
Scan speed	0.3 s/spectrum	
Compounds	Ion (<i>m/z</i>)	RRT (I.S.), range
<i>PAHs</i>		
Naphthalene	128	0.62
Methylnaphthalene	115, 141, 142	0.74–0.75
C ₂ -Naphthalene	141, 155, 156	0.82–0.86
C ₃ -Naphthalene	155, 170	0.90–0.97
C ₄ -Naphthalene	155, 169, 184	1.01–1.10
Acenaphthylene	152	0.86
Acenaphthene	152, 154	0.89
Phenanthrene	178	1.12
Anthracene	178	1.13
Methylanthracene	165, 191, 192	1.21–1.23
Diphenylamine (I.S.)	168	1.00
<i>Aromatic hydrocarbons</i>		
$\Phi + C_2$	91, 92, 105, 106	0.206–0.239
$\Phi + C_3$	($\Phi + C_2$), 119, 120	0.275–0.354
$\Phi + C_4$	($\Phi + C_3$), 133, 134	0.354–0.518
$\Phi + C_5$	($\Phi + C_4$), 147, 148	0.471–0.581
$\Phi + C_6$	($\Phi + C_5$), 161, 162	0.553–0.638
[² H ₁₀]Phenanthrene	94, 187, 188	1.00

Table 3
Validation parameters for PAH analyses

	Naphthalene	Acenaphthylene	Acenaphthene	Phenanthrene	Anthracene
Linearity range ($\mu\text{g/l}$)	100–2500	100–1300	100–2500	100–1900	100–2000
Correlation coefficient (R^2)	0.999	0.999	0.999	0.999	0.999
Quantitation limit ($\mu\text{g/l}$)	9.0	7.5	9.0	24.0	8.4
Detection limit ($\mu\text{g/l}$)	3.0	2.5	3.0	8.0	2.8
RSD ($n=5$) (%) /inter-day	2.1	1.5	1.1	1.9	2.5
RSD ($n=5$) (%) /intra-day	1.8	0.7	0.5	2.2	2.7

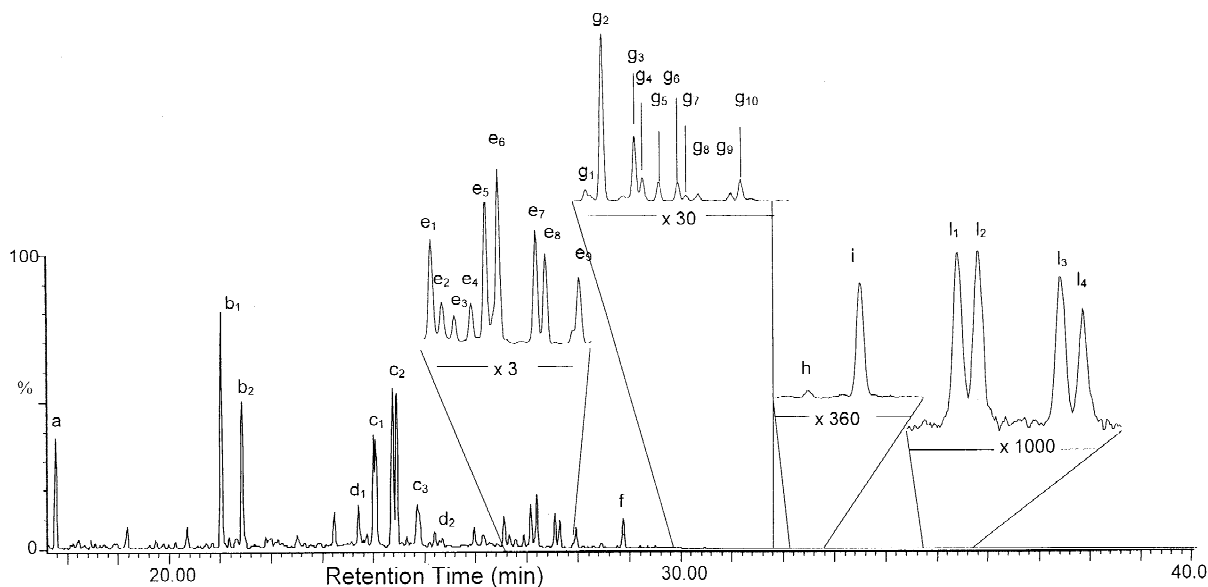


Fig. 1. GC-MS-SIM chromatogram of fuel sample. PAH analysis: naphthalene (a), methylnaphthalenes (b), dimethylnaphthalenes (c), ethylnaphthalenes (d), C₃-naphthalenes (e), I.S., diphenylamine (f), C₄-naphthalenes (g), phenanthrene (h), anthracene (i), methylanthracenes (l).

Table 4
PAHs (ppm, v/v) in fuel sample

Compound	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Naphthalene	398.0	174.7	167.4	493.3	353.4	435.0	83.0	1309.0	413.8	321.5
Methylnaphthalene	3171.0	986.5	1417.8	2160.8	1792.6	2327.3	480.6	4871.8	2786.6	2548.5
Dimethylnaphthalene	3422.5	343.7	299.7	1251.0	512.0	1646.5	140.3	874.3	2473.7	2464.3
Ethylnaphthalene	424.6	72.0	95.2	241.0	141.6	352.2	24.1	287.9	317.6	293.5
C ₃ -Naphthalene	1362.1	0.1	29.1	205.6	68.7	326.6	26.6	186.1	1128.1	1144.0
C ₄ -Naphthalene	40.2	5.3	ND	7.1	5.6	15.1	ND	18.1	36.7	32.3
Acenaphthylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	ND	ND	ND	0.7	ND	ND	ND	1.8	ND	ND
Phenanthrene	0.4	0.3	0.1	0.1	0.1	0.6	ND	ND	0.1	0.1
Anthracene	1.4	0.2	0.5	2.3	1.7	2.4	1.7	17.2	17.0	16.0
Methylanthracene	1.3	0.7	1.7	3.1	4.4	3.0	ND	50.9	12.2	8.4

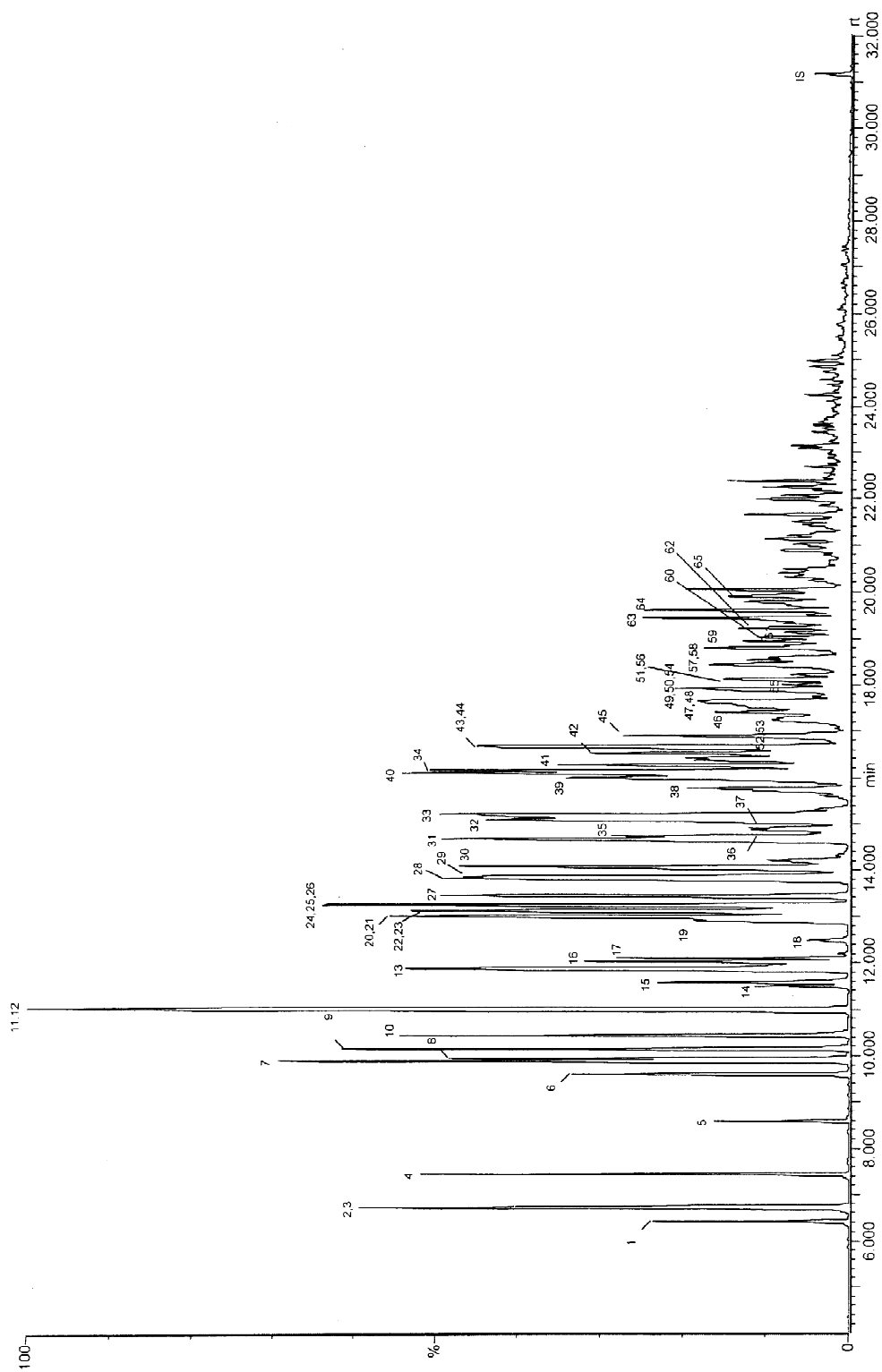


Fig. 2. Identified aromatic hydrocarbons.

#	RT	RRT (IS)	name	#	RT	RRT (IS)	name
1	6.419	0.206	Ethylbenzene	17	12.098	0.388	1-Methyl-4-i-Propylbenzene
2	6.716	0.215	m-Xylene	18	12.481	0.400	1-Methyl-2-i-Propylbenzene
3	6.716	0.215	o-Xylene	19	12.906	0.414	1-Methyl-3-n-Propylbenzene
4	7.445	0.239	p-Xylene	20	12.992	0.417	1,3-di-Ethylbenzene
5	8.580	0.275	i-Propylbenzene	21	12.992	0.417	1,4-di-Ethylbenzene
6	9.596	0.308	n-Propylbenzene	22	13.138	0.422	1-Methyl-4-n-Propylbenzene
7	9.891	0.317	1-Methyl-3-Ethylbenzene	23	13.138	0.422	n-Butylbenzene
8	9.945	0.319	1-Methyl-4-Ethylbenzene	24	13.237	0.425	1,3-di-Methyl-5-Ethylbenzene
9	10.146	0.326	1,3,5-tri-Methylbenzene	25	13.237	0.425	1,2-di-Ethylbenzene
10	10.441	0.326	1-Methyl-2-Ethylbenzene	26	13.237	0.425	1-Methyl-2-n-Propylbenzene
11	11.017	0.354	1,2,4-tri-Methylbenzene	27	13.443	0.431	1,4-di-Methyl-2-Ethylbenzene
12	11.017	0.354	t-Butylbenzene	28	13.813	0.443	1,2-di-Methyl-4-Ethylbenzene
13	11.864	0.381	1,2,3-tri-Methylbenzene	29	13.860	0.445	1,3-di-Methyl-2-Ethylbenzene
14	11.485	0.369	i-Butylbenzene	30	14.079	0.452	1,2-di-Methyl-3-Ethylbenzene
15	11.571	0.371	s-Butylbenzene	31	14.660	0.470	1,3-di-Methyl-4-Ethylbenzene
16	12.025	0.386	1-Methyl-3-i-Propylbenzene	32	15.082	0.484	1,2,4,5-tetra-Methylbenzene
17	12.098	0.388	1-Methyl-4-i-Propylbenzene	33	15.195	0.488	1,2,3,4-tetra-Methylbenzene
18	12.481	0.400	1-Methyl-2-i-Propylbenzene	34	16.131	0.518	1,2,3,5-tetra-Methylbenzene

35 - # 51 Pentybenzene isomers (Φ -5), # 52 - # 65 Hexylbenzene isomers (Φ -6)

Fig. 2. (Continued)

measure PAHs and aromatic hydrocarbons are reported in Table 2.

3. Results and discussion

3.1. Determination of PAHs

Calibration curves, in the concentration range 0.1–2.5 mg/l, have been obtained for naphthalene, acenaphthylene, acenaphthene, anthracene and phenanthrene. Table 3 gives the validation parameters for the analytical method proposed.

Several aviation jet fuel samples, originating from different Italian producers, have been analysed. The GC–MS–SIM chromatogram of a fuel sample is reported in Fig. 1. The results obtained are reported in Table 4. The GC–MS–SIM method was able to identify naphthalene, methyl-naphthalene, more than 20 different alkyl-naphthalenes, acenaphthene, phenanthrene, anthracene and 4 alkylanthracenes.

The total naphthalene hydrocarbon content of fuel samples has also been analysed according to a UV spectrophotometric reference method [4]; a linear relation was found: PAHs (GC–MS–SIM)=0.7331 PAHs (UV), with $R^2=0.92$. The low slope observed is due to the ion used to measure PAHs with the

GC–MS–SIM method: the current produced by this ion is a only part of the total ion current. The concentrations of naphthalene, methyl-naphthalene, dimethyl-naphthalene, ethyl-naphthalene, and C₃-naphthalene have been considered to predict the total naphthalene hydrocarbons of jet fuel samples.

3.2. Determination of aromatic hydrocarbons

Calibration curves have been obtained for 16 different aromatic hydrocarbons in the distillation range of jet fuel. Table 5 gives the validation parameters for the analytical method used. Several aviation jet fuel samples, originating from different Italian producers, have been analysed. The GC–MS–SIM chromatogram of a fuel sample is reported in Fig. 2. The results obtained are reported in Table 6. The GC–MS–SIM method was able to identify more than 60 different aromatic hydrocarbons in a 30-min chromatographic run. The concentration of each identified aromatic hydrocarbon has been considered to measure the total aromatic hydrocarbon content of jet fuel samples; the response factors of aromatic hydrocarbons have been determined by measuring the ratio signal/concentration of different standard solutions containing the first 34 aromatic hydrocarbons described in Fig. 2; the response factors of

Table 5
Validation parameters for total aromatic hydrocarbon analyses

Name	R^2	Quantitation limit ($\mu\text{g/l}$)	Detection limit ($\mu\text{g/l}$)	RSD ($n=5$) (%), inter-day	RSD ($n=5$) (%), intra-day
Ethylbenzene	0.998	1.5	0.5	2.1	1.2
<i>p</i> -Xylene	0.996	2	0.7	2.1	1.4
<i>n</i> -Propylbenzene	0.994	2.1	0.7	2.3	1.8
1-Methyl-4-ethylbenzene	0.998	2.2	0.7	2.2	1.6
1-Methyl-2-ethylbenzene	0.995	2.2	0.7	2.9	1.9
1,2,4-Trimethylbenzene	0.994	1.4	0.5	2.7	1.8
1,2,3-Trimethylbenzene	0.994	1.5	0.5	3.1	1.9
<i>sec.</i> -Butylbenzene	0.994	1.7	0.6	3.2	2
1-Methyl-4-isopropylbenzene	0.996	1.6	0.5	2.5	1.2
<i>n</i> -Butylbenzene	0.998	2.3	0.8	2.3	1.1
(2,2-Dimethyl)propylbenzene	0.993	1.8	0.6	3.1	1.9
1-Methyl-4- <i>tert.</i> -butylbenzene	0.993	1.7	0.6	3.3	2.1
1,3-Diisopropylbenzene	0.998	2.1	0.7	2	1.1
<i>n</i> -Pentylbenzene	0.999	1.9	0.6	1.2	0.8
1-Phenylhexane	0.994	1.5	0.5	2.9	1.8
1,4-Diisopropylbenzene	0.998	1.9	0.6	2.1	1.1

Table 6
Aromatic hydrocarbons (% v/v) in fuel sample

Compound	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
Φ -2 (M_r 106)	0.88	1.12	0.57	0.46	0.58	1.23	1.15	1.07
Φ -3 (M_r 120)	2.40	3.14	2.01	2.12	3.22	3.07	3.16	2.88
Φ -4 (M_r 134)	4.54	5.18	5.00	4.23	6.03	5.32	4.85	4.70
Φ -5 (M_r 148)	3.72	3.29	3.70	2.96	4.35	3.45	3.81	3.67
Φ -6 (M_r 162)	2.12	1.38	2.41	2.14	1.56	1.43	1.18	1.54
Total aromatics (%)	13.67	14.11	13.68	11.91	15.75	14.49	14.14	13.86
Ref. method (ASTM D 1319)	13.90	14.89	14.19	12.80	16.75	14.94	14.58	14.29

pentylbenzene isomers (from 35 to 51 in Fig. 2) and hexylbenzene isomers (from 52 to 65 in Fig. 2) have been determined by measuring the ratio signal/concentration of different standard solutions, containing isomers with different number of substituents on the aromatic ring. Each pentyl- and hexylbenzene isomer has been identified in fuel sample on the basis of its retention time and its mass spectrum. The abundance ratio of the ion produced in the fragmentation process has been used to determine the number of substituents in the aromatic ring and to assign the response factor. The correlation with the reference method [5] is reported in Table 6.

4. Conclusion

The proposed GC–MS–SIM methods are able to measure trace levels of PAHs and total aromatic hydrocarbon in aviation jet fuel; the GC–MS–SIM, due to its selectivity, represents a simple way to measure low levels of PAHs without sample pre-treatment other than dilution and internal standard addition. The PAH content of several aviation jet fuel samples, originating from different Italian producers, have been analysed with the proposed methods. More than 30 PAHs have been identified in each sample with the GC–MS–SIM method. The data obtained by GC–MS–SIM determinations are related to the UV spectrophotometric reference method (ASTM D 1840). The total aromatic hydrocarbon content of jet fuel samples has been measured. More than 60 aromatic hydrocarbons have been identified in each sample. The data obtained by GC–MS–SIM determinations correlate well with the reference method (ASTM D 1319).

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