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DETERMINATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN PETROLEUM OILS BY COMBINATION OF THIN-LAYER CHROMATOGRAPHY AND GAS CHROMATOGRAPHY–MASS SPECTROMETRY*

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SUMMARY

A procedure is described for the determination of polynuclear aromatic hydrocarbons (PAHs) in petroleum oils, involving extraction of the sample, dissolved in cyclohexane, with N-methylpyrrolidone–water–phosphoric acid, separation of the PAH fraction from the total extract by thin-layer chromatography and an analysis by gas chromatography or gas chromatography–mass spectrometry with selected ion monitoring. The determination of some PAHs in a lubricating and in fuel oil is reported.

INTRODUCTION

The analysis of polynuclear aromatic hydrocarbons (PAHs) in petroleum oils is extremely interesting because of the wide distribution of these materials and their environmental impact. Unfortunately, such analyses are very difficult owing to the great complexity of the aromatic fractions present in different types of oils. The difficulties lie either in the extraction of the PAHs from the oil, owing to the presence of large amounts of aromatic hydrocarbons polysubstituted with aliphatic chains, or in the complexity of the PAH fraction, the separation of which can be achieved only with high-resolution capillary columns.

Different analytical techniques, combined with various clean-up procedures, have been used for analyses of oil samples for PAHs[1–6]. In this paper we propose a procedure for the determination of PAHs in lubricating oils used in internal combustion engines and in fuels oils, which are more diffuse types of petroleum oils. The procedure consists in extraction of the sample, separation of the PAH fraction from the total extract by thin-layer chromatography (TLC) and analysis by gas chromatography (GC) or gas chromatography–mass spectrometry (GC–MS) with selected ion monitoring (SIM).

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EXPERIMENTAL

Materials

All solvents were of analytical-reagent grade and were obtained from Merck (Darmstadt, F.R.G.). The purity of the solvents used for extraction was checked before use.

Silica gel TLC plates of dimension 20 × 20 × 0.2 cm were obtained from Merck.

Standard samples of PAHs were commercial products (Fluka, Buchs, Switzerland; Aldrich, Milwaukee, WI, U.S.A.) with purities of 95–99%. Standard solutions were prepared in tetrahydrofuran and stored at 4°C in the dark.

The lubricating and fuel oils examined were commercial products; the lubricating oils were of the type commonly used in motor vehicle engines.

Apparatus

The analyses were performed on a DANI (Monza, Italy) Model 6800 instrument equipped with a flame-ionization detector and a split-stream injector.

A bonded-phase fused-silica capillary column (22 m × 0.25 mm I.D.; thickness of SE-54 cross-linked stationary phase film, 0.52 μm) was employed.

GC–MS analyses were performed on a Hewlett-Packard Model 5846 A gas chromatograph connected with a Model 5985 mass spectrometer and equipped with a Hewlett-Packard data system. A fused-silica capillary column of the same type as that used in GC was employed. The column was connected directly to the ion source of the mass spectrometer and the sample was introduced with a splitter in the ratio 1:8. Helium at a flow-rate of 2 ml/min was used as the carrier gas. Spectra were obtained by electron impact at 70 eV.

Extraction

A 0.5-ml volume of oil was dissolved in 5 ml of cyclohexane and extracted three times with 5 ml of N-methylpyrrolidone (NMF)–water–phosphoric acid (80:19:1). The separation of layers was facilitated by the use of a centrifuge. The combined extracts were diluted with water (45 ml) and back-extracted into cyclohexane (10 ml). The cyclohexane phase was dehydrated using anhydrous sodium sulphate. The dry extract was filtered through a glass filter (16–40 μm), washed with fresh cyclohexane and then reduced to 300–500 μl under a stream of nitrogen in a test-tube placed in a water-bath at ambient temperature.

Thin-layer chromatography

The concentrated extract was applied to a silica gel plate about 15 cm long and developed with *n*-hexane–benzene (1:1) in the dark. After removal of the mobile phase, the plate was irradiated with UV light (254 nm). The PAH spot was marked, scraped off, powdered and transferred into a small glass column (10 cm × 2 cm I.D.) with a glass frit. The PAHs were eluted from the silica gel with 5 ml of tetrahydrofuran. The solution was concentrated to 100–200 μl under nitrogen in the dark.

Analysis

The analyses were performed with two different systems, according to the type

of oil. The lubricating oil analysis was performed by GC, whereas the fuel oil analysis was performed by GC–MS in the SIM mode. The chromatograms of standard and unknown mixtures were obtained by recording the current intensity of the molecular ion of known PAHs. The chromatograms obtained were very simple and peak identification was effected on the basis of the coincidence of both the *m/e* ratios and the retention times.

The determination of individual PAHs was carried out by comparison of the peak areas with that of *n*-octacosane added as an internal standard and corrected for the different response factors.

The extent of PAH recovery was evaluated following the described GC procedure. This determination was carried out on a new lubricating oil (previously extracted and analysed) to which was added a known amount of a standard PAH mixture. The recovery was 90 ± 10%.

RESULTS AND DISCUSSION

To optimize the extraction from the oil, the partition coefficients (K_d) of three-to-five-ring PAHs, including some mono- and dimethyl derivatives, were determined. The partition coefficients of some PAHs between cyclohexane and various solvents are given in Table I. The K_d values for the extraction of PAHs into dimethyl sulphoxide and NMP–water–phosphoric acid are more favorable than those into dimethylformamide–water–phosphoric acid and nitromethane. For the extraction of PAHs from the oils we used NMP–water–phosphoric acid, which is normally used in industry to dearomatize lubricating oils.

TABLE I

PARTITION COEFFICIENTS OF PAHs BETWEEN DIFFERENT SOLVENTS AND CYCLOHEXANE

PAH	K_d*			
	DMF–H_2O–H_3PO_4	*NMP–H_2O–H_3PO_4*	*CH_3NO_2*	*DMSO*
Phenanthrene	1.30	3.71	1.46	4.65
1-Methylphenanthrene	0.64	2.04	1.69	2.75
2-Methylanthracene	0.95	1.67	1.92	3.34
Fluoranthene	1.31	4.63	1.19	3.97
Pyrene	1.01	3.96	0.70	3.10
3-Methylpyrene	1.05	3.31	1.45	3.31
Benz[*a*]anthracene	2.09	6.40	2.42	10.80
7-Methylbenz[*a*]anthracene	1.37	4.13	1.53	7.08
7,12-Dimethylbenz[*a*]anthracene	0.38	1.57	0.80	1.00
Chrysene	1.13	5.40	1.13	5.80
2-Methylchrysene	1.50	4.10	0.85	7.08
Benzo[*b*]fluoranthene	1.20	8.43	1.20	8.17
Benzo[*a*]pyrene*	0.83	7.47	0.57	6.32

* DMF = dimethylformamide; H_3PO_4 = orthophosphoric acid; NMP = Methylpyrrolidone; CH_3NO_2 = nitromethane; DMSO = dimethyl sulphoxide.

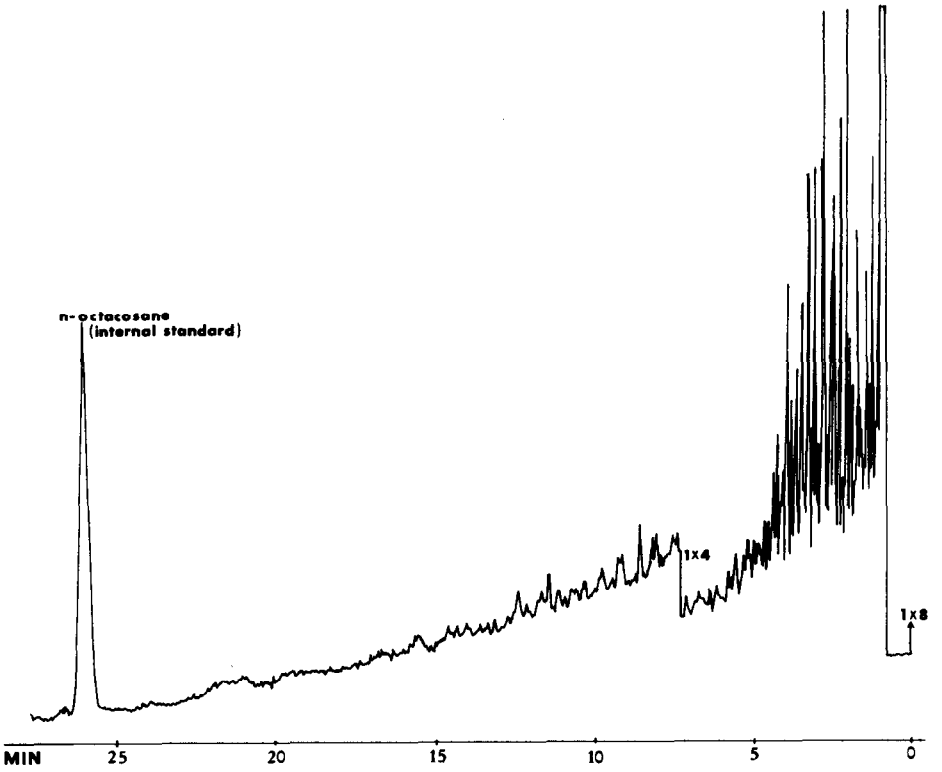

Fig. 1. Capillary column gas chromatogram of a new lubricating oil extract. Column, 22 m × 0.25 mm I.D. fused-silica capillary with SE-54 bonded phase. Column temperature, 225°C; injector temperature, 250°C; detector temperature, 250°C. Carrier gas, hydrogen (flow-rate 6 ml/min); flame ionization detector.

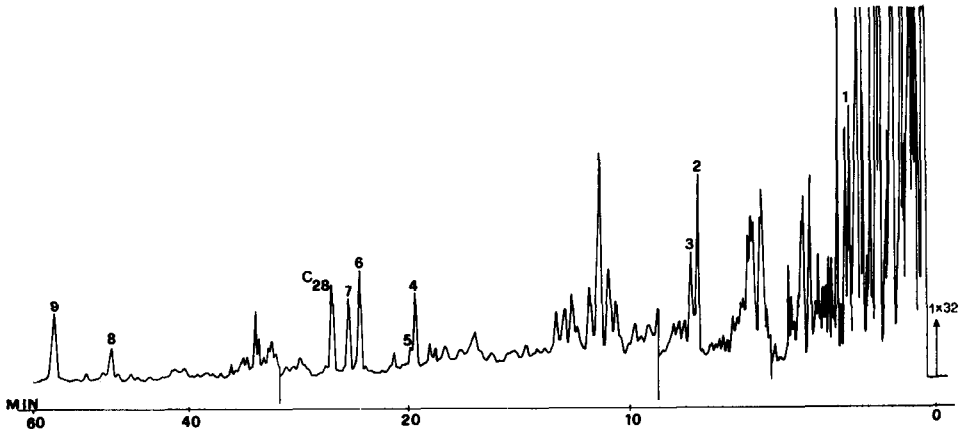

Fig. 2. Capillary column gas chromatogram of lubricating oil extract after use in a motor vehicle engine. Column and conditions as in Fig. 1. Internal standard, *n*-octacosane. Peaks: 1 = fluoranthene; 2 = benz[*a*]anthracene; 3 = chrysene; 4 = benzo[*b*]fluoranthene; 5 = benzo[*k*]fluoranthene; 6 = benzo[*e*]pyrene; 7 = benzo[*a*]pyrene; 8 = indene(1,2,3-*cd*)pyrene; 9 = benzo[*ghi*]perylene.

Lubricating oils

With the described procedure, new lubricating oils and oils used in motor vehicle engines were analysed. Figs. 1 and 2 show the chromatograms of a new lubricating oil and of the same oil after 10 000 km of urban and extra-urban use. It was found that the oil became rich in PAHs, prevalently non-alkylated and of greater interest for their carcinogenicity, only after such prolonged use.

Capillary columns with an efficiency great enough to produce complete resolution of isomer pairs such as benz[*a*]anthracene–chrysene, benzo[*k*]fluoranthene–benzo[*b*]fluoranthene and benzo[*a*]pyrene–benzo[*e*]pyrene are required (see Fig. 3).

The reproducibility of the quantitative analysis was determined by carrying out five different extractions of an identical sample of used engine oil and executing

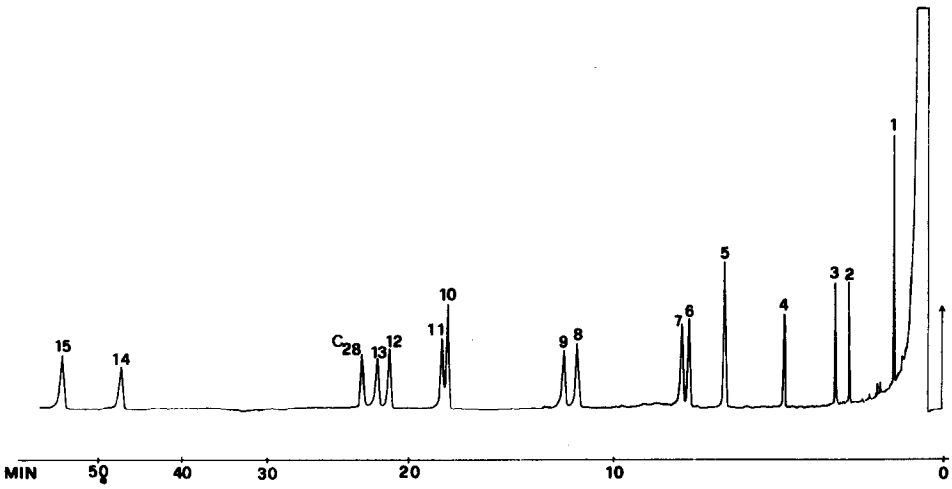

Fig. 3. Capillary column gas chromatogram of standard PAH mixture. Column and conditions as in Fig. 1. Peaks: 1 = phenanthrene, 2 = fluoranthene, 3 = pyrene, 4 = 3-methylpyrene; 5 = benzo[*ghi*]fluoranthene; 6 = benz[*a*]anthracene; 7 = chrysene; 8 = 2-methylchrysene; 9 = 4-methylchrysene; 10 = benzo[*b*]fluoranthene; 11 = benzo[*k*]fluoranthene; 12 = benzo[*e*]pyrene; 13 = benzo[*a*]pyrene; 14 = indene[1,2,3-*cd*]pyrene; 15 = benzo[*ghi*]perylene.

TABLE II

MEAN CONCENTRATIONS AND RELATIVE STANDARD DEVIATIONS FOR SOME PAHs DETERMINED IN A USED LUBRICATING OIL

PAH	*Concentration (μg/g)*	*Standard deviation (μg/g)*
Fluoranthene	65.0	5.2
Benz[*a*]anthracene	48.8	4.5
Chrysene	20.9	2.4
Benzo[*b*]fluoranthene	28.2	1.8
Benzo[*k*]fluoranthene	4.0	0.8
Benzo[*e*]pyrene	38.6	2.7
Benzo[*a*]pyrene	31.0	2.5
Indene[1,2,3-*cd*]pyrene	19.2	4.3
Benzo[*ghi*]perylene	39.2	5.3

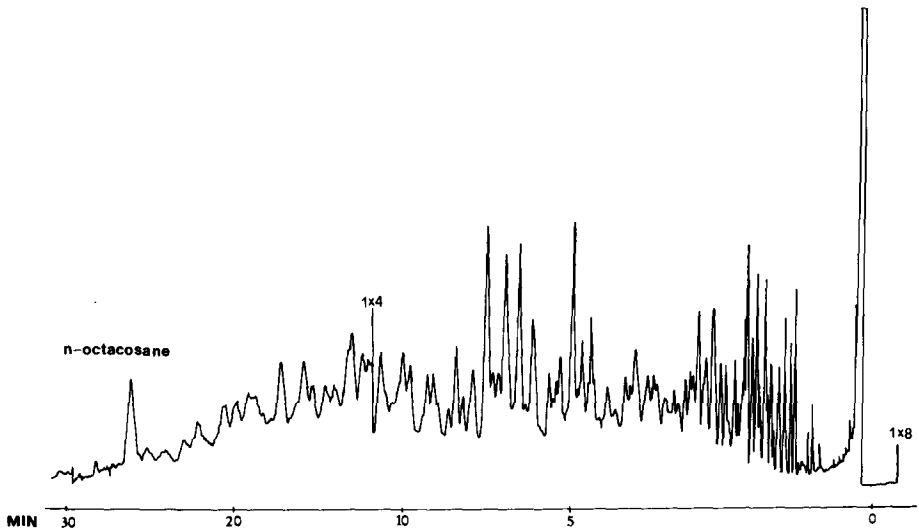

Fig. 4. Capillary column gas chromatogram of a fuel oil extract. Column and conditions as in Fig. 1.

four GC analyses on each extract. Table II reports the mean values and the relative standard deviation obtained for some selected compounds.

Fuel oils

Extracts from fuel oils are generally much more complex than extracts obtained from lubricating oils used in engines (see Fig. 4). They are, in fact, extremely rich in alkylated PAHs, which can interfere and render difficult the identification and quantitation of individual compounds. This problem can be resolved by using GC–MS in the SIM mode.

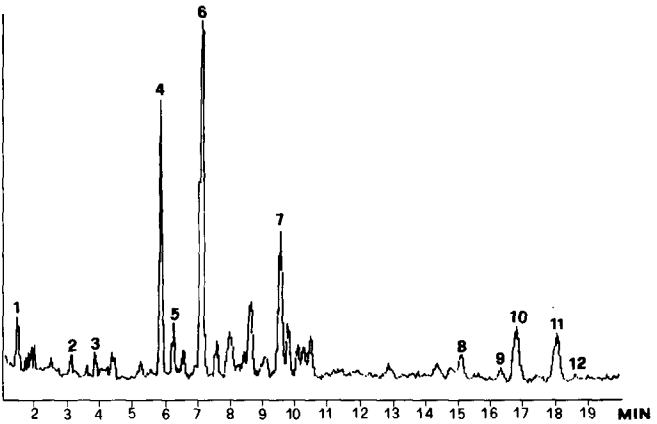

Fig. 5. Total ion current trace of PAH fraction of a fuel oil. Column temperature, 230°C; carrier gas, helium (flow-rate 2 ml/min). Column and other GC conditions as in Fig. 1. Peaks: 1 = phenanthrene; 2 = pyrene; 3 = methylpyrene; 4 = tetramethylphenanthrene; 5 = tetramethylphenanthrene; 6 = chrysene, 7 = methylchrysene; 8 = benzo[*b*]fluoranthene; 9 = dimethylchrysene; 10 = tetramethylpyrene; 11 = benzo[*e*]pyrene; 12 = benzo[*a*]pyrene.

TABLE III

RETENTION TIMES, m/e RATIOS AND CONCENTRATIONS OF SOME PAHs IN A FUEL OIL

PAH	*Retention time (230°C) (min)*	*m/e*	*Concentration (μg/g)*
Phenanthrene	1.28	178	3
Pyrene	2.97	202	3
3-Methylpyrene	4.17	216	16
Chrysene*	6.72	228	70
Methylchrysene	9.23	242	40
Methylchrysene	9.53	242	23
Benzo[*b*]fluoranthene*	14.23	252	6
Benzo[*k*]fluoranthene*	14.53	252	< 1
Benzo[*e*]pyrene*	16.98	252	7
Benzo[*a*]pyrene*	17.72	252	< 1
Indeno[1,2,3-*cd*]pyrene*	13.20**	276	< 1
Benzo[*ghi*]perylene*	15.58**	276	< 1

* These PAHs are the same as those determined in the engine oil.
** At 260°C.

In SIM, PAHs are determined without difficulty because the mass spectrometer is focused on *m/e* values characteristic of the compounds under consideration and therefore the spectrometer becomes a highly selective and sensitive detector.

Total ion current traces of an extract of fuel oil are shown in Fig. 5.

Table III reports the results of the analysis of a fuel oil; the compounds with asterisks are the same as those determined in the engine oils in Table II. Comparing the data for the two different type of oils, it is found that the unalkylated PAH concentration in the fuel oil is much lower than that in the used lubricating oils.

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