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A GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC STUDY OF ORGANIC COMPOUNDS ADSORBED ON PARTICULATE MATTER FROM DIESEL EXHAUST

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SUMMARY

A gas chromatographic-mass spectrometric analytical system is used to analyze the organic materials extracted from diesel exhaust particulates obtained by use of a direct sampling device. The analysis is performed by first subjecting the extracted organic mixtures to column chromatography, which yields four or more fractions. Each of these is further analyzed on a gas chromatographic-mass spectrometric system that employs high-resolution high-capacity support-coated open-tubular and large-bore open-tubular columns. Additional information is also obtained from an integrated gas chromatograph-mass spectrometer-computer system by identifying compound types via mass chromatography. Thirty-five hydrocarbons have been identified which include alkanes, polycyclic aromatic hydrocarbons, and six oxygenated compounds primarily of the phenolic type. Twenty-nine additional hydrocarbons and oxygenated compounds have also been tentatively identified.

INTRODUCTION

This study is part of a series of investigations concerning the identification of organic compounds in the gaseous exhaust of a diesel engine^{1,2}. In previous studies, compounds were recovered from aqueous solution condensates of the total gaseous exhaust from a 1972 Mercedes-Benz passenger car. Analysis of the organic species extracted from these condensates by a gas chromatographic-mass spectrometric (GC-MS) system subsequently revealed the presence of numerous oxygenated compounds, the major component being phenol. Details of these results are reported elsewhere^{1,3}, and are generally in agreement with data from similar studies by other workers⁴.

The analysis of particulate matter produced by internal combustion engines

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has not received the attention that has been given to gaseous emissions. The limited work reported for particulates is confined to the determination of inorganic content, and analysis for specific types of adsorbed organic compounds. A number of studies⁵⁻⁸ have centered on the sampling and analysis of the lead content of particulate matter emitted from spark ignition engines. The effects of temperature on the size distribution of exhausted particulate matter have also been examined by Sampson and Springer⁹. Hangerbrauck and co-workers¹⁰ have investigated the polycyclic aromatic hydrocarbon (PAH) content of the particulates exhausted from eight different spark ignition automobiles and four light trucks, using a cooled stainless-steel condenser system and glass-fiber filters to obtain samples of aqueous condensate and solid dry particulate matter. The total PAH content of the dry particulate was determined by benzene extraction, column chromatography and UV-fluorescence spectroscopy. A study conducted by Linnell and Scott¹¹ using a six-cylinder diesel engine revealed that the ash of the particulate matter was primarily copper, iron, and zinc. These authors also recovered an oily material from the particulate matter, the infrared absorption spectrum of which indicated that it consisted of the high-boiling components of the original diesel fuel, along with some aldehydes and acids. Using an infrared technique, McKee and co-workers¹² reached the same conclusions regarding the total organic emissions of diesel engines.

Much of the analytical work on environmental samples has been focused on detection and identification of the carcinogenic PAH compounds. Generally, techniques have involved some combination of column, thin-layer, gas chromatographic, and spectroscopic techniques¹³⁻¹⁵. The most recent work is by Lao and co-workers¹⁶: organic compounds adsorbed on air-borne particulate matter were extracted with cyclohexane and subjected to column chromatography, followed by analysis with a GC-MS system which employed high-resolution GC columns. These workers were able to identify 120 PAHs present in the complex organic mixture obtained from urban air particulate matter. No such extensive study, however, has been done on the organic compounds adsorbed on particulate matter emitted from internal combustion engines, which led us to undertake the present investigation. We used a diesel source for this study because the diesel engine produces larger volumes of particulate material than other types. Analyses were then carried out by sample pre-treatment using column chromatography, followed by GC-MS with high-resolution large-bore open-tubular (LBOT) or support-coated open-tubular (SCOT) columns.

EXPERIMENTAL

Collection

Exhausted particulate matter from a diesel engine was collected with the dry particulate sampling device shown in Fig. 1. Pads of glass wool filtering fiber (Pyrex filtering fiber No. 3950) approximately $\frac{1}{8}$ in. thick were used to accumulate diesel particulates. The damp pads were removed from the sampler, air-dried for a day at room temperature, and extracted for 24 h with chloroform in a Soxhlet extractor. The sampler was placed 18 in. from the exhaust outlet, and three different sampling collection runs were made, in which the sampling periods were 3, 6, and 9 h, respectively.

A second sample collection technique used a 0° condensation device that gave a dilute aqueous mixture of organics and particulates. The particulates were recover-

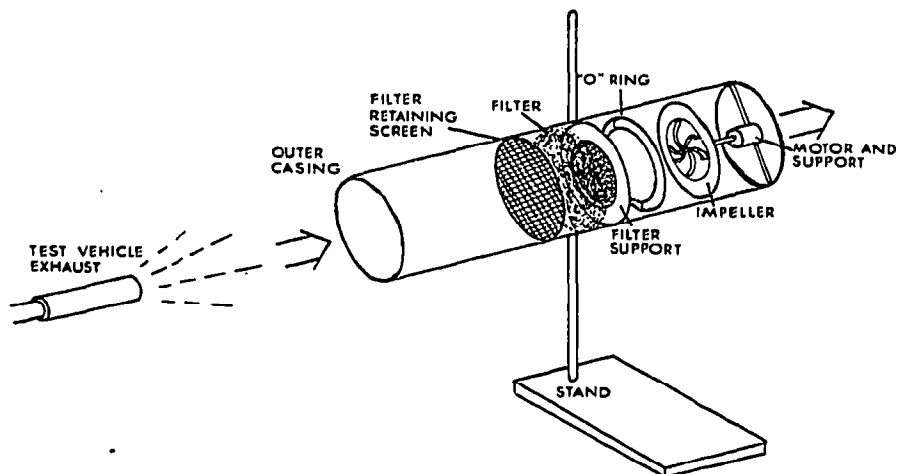


Fig. 1. Dry particulate sampler used to collect solid materials from a diesel passenger car.

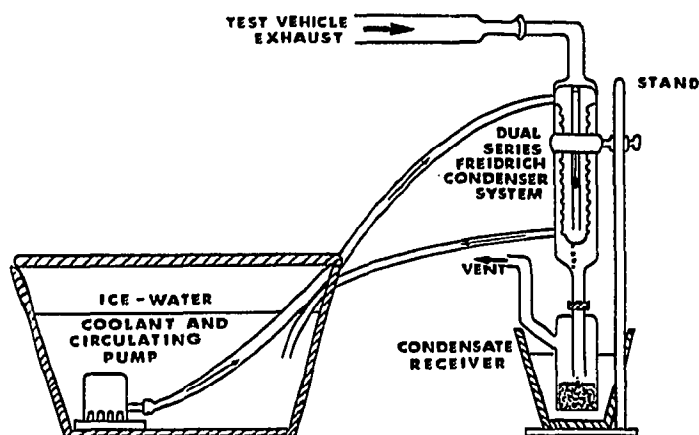


Fig. 2. Exhaust condenser system for auto emissions collection.

ed by gravity filtration, air-dried for a day, and Soxhlet extracted as above. The condensation apparatus is shown in Fig. 2.

The test vehicle was a new 1972 Mercedes-Benz 220 Diesel car. All exhaust sampling experiments were done with the engine throttle set to produce a fast idle. Fuels were obtained from local retail distributors. A chromatogram of each sample of the original fuel was run on a 500-ft. \times 0.03-in. I.D. LBOT column containing OV-101 to verify composition as largely paraffinic (Fig. 3); all fuel samples exhibited the same GC profile.

Sample pre-treatment

The chloroform Soxhlet extracts of the particulate matter were allowed to evaporate at room temperature to approximately 5 ml. Because of the complexity of the extracted mixtures and similar retention times of many of the compounds, column

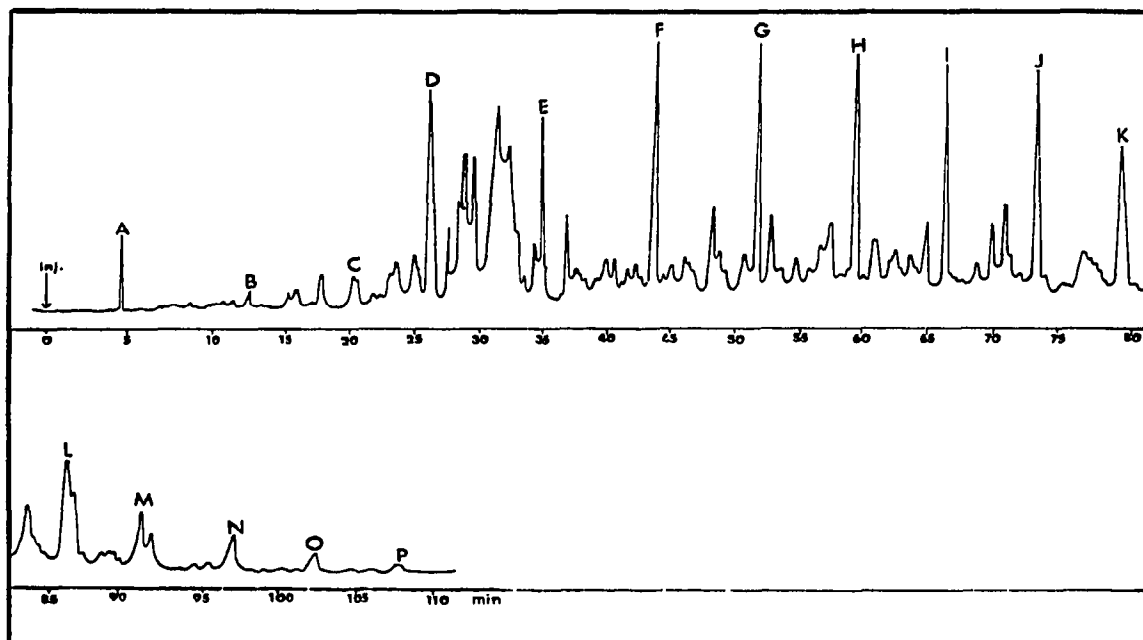


Fig. 3. Gas chromatogram of commercial diesel fuel. Column: 500-ft. \times 0.03-in. I.D. LBOT; liquid phase: OV-101 plus 5% Igepal CO-880; temperature: 40–220° at 2°/min; injector: 290°; detector: dual flame at 275°; carrier gas: helium at 30 ml/min; sample size: 0.5 μ l. Peak A is air; peaks B–P are n -C₇ to n -C₂₁ alkanes.

chromatographic fractionation prior to GC–MS analysis was required. The column chromatographic technique which successfully provided preliminary separation of the organic extract was a slight modification of the technique reported by Sawicki *et al.*¹⁷. Chromatographic-grade 80–200 mesh alumina (Fisher Scientific, Pittsburgh, Pa., U.S.A.) was heated at 280° for 30 h, cooled in a desiccator, and deactivated with 12% (w/w) water. The deactivated alumina was allowed to equilibrate in a glass-stoppered vessel for an additional 30 h, then dry-packed to a depth of 8 in. in a 1/2-in. \times 15-in. glass column. Aliquots of the chloroform extract solutions containing approximately 10–15 mg of organic material were mixed with 1 ml of alumina, air-dried at room temperature, and placed at the top of the column. The column was then developed with five 100-ml portions of n -pentane which contained increasing concentrations of diethyl ether in the order: 0, 3, 6, 9, and 12%. Individual fractions of 20 ml each were collected and allowed to evaporate to less than 1 ml overnight at room temperature. The alkanes were always found in the first 20-ml fraction. The remaining 24 fractions were recombined into five aliquots (according to the color and amount of residue contained in neighboring fractions), each finally being contained in 100 μ l of benzene solvent. These aliquots were then subjected to GC–MS analysis.

Gas chromatography

The GC columns used for this study were a 200-ft. \times 0.03-in. I.D. SCOT column containing OV-101 and SF-96, and a 500-ft. \times 0.03-in. I.D. LBOT column

coated with OV-101. These were prepared according to previously described methods¹⁸⁻²¹. The gas chromatograph was a Perkin-Elmer 900 dual-flame instrument. The relative composition of the individual column chromatography fractions was determined from GC area measurements made with an Infotronics CRS-208 digital integrator. The sum of the individual peak areas was used to approximate the relative percent composition of solutes contained in each fraction. The combination of residues from the individual 20-ml collection tubes was usually sufficient to make one or more GC injections. Fractions beyond the tenth tube rarely produced enough material for satisfactory mass spectra.

Mass spectrometry

Mass spectra for the separated components were obtained with a Hitachi RMU-6E mass spectrometer interfaced to the gas chromatograph with a Watson-Bieman effusive type separator²². To maximize detection of parent ions, mass scans were done from high to low masses. Ionizing voltage was 70 eV and the ion source temperature was 280°. A typical scan from approximately 450 to 28 a.m.u. required 15 sec. The reverse scan was always initiated as the solute maxima passed through the ion source, a procedure that ensured maximum possible intensity for the parent peak. The mass spectra were normalized and compared with currently available compendia to establish component identities²³⁻²⁵.

Mass spectra obtained from the column chromatography fractions were mass-scaled by hand and the peak heights measured. Each spectrum was then coded onto punched cards and processed with an IBM 360/65 computer. Spectra were corrected for background, normalized, and displayed in tabular form followed by a normalized bar graph representation of the data.

A sample of the total particulate chloroform extract was also analyzed in the applications laboratory of the Finnigan Instrument Company using a Model 1015 D quadrupole mass spectrometer interfaced to a Varian Aerograph gas chromatograph and computerized with the Finnigan System 150. Three hundred forty 3-sec mass spectra were taken and stored in computer memory during evolution of the gas chromatogram. From these data, mass chromatograms and individual background-corrected and normalized mass spectra were produced.

RESULTS AND DISCUSSION

The production of PAHs, oxygenated compounds, and soot particles from diesel fuels has been considered in detail by Ray and Long²⁶, and Fish²⁷, who have formulated various mechanisms for particulate formation. A diesel engine compresses inducted air to high pressure at elevated temperatures, and fuel is injected into the cylinder through nozzles at the top of the piston stroke. Combustion then originates spontaneously around the edges of the spray plume, increasing the pressure and temperature of the gaseous mixture. Particulates are thought to be formed from pyrolysis of the fuel spray-plume core, where a portion of the high-molecular-weight hydrocarbons in the fuel is converted to carbon with the simultaneous production of acetylenes and hydrogen. Unburned high-molecular-weight hydrocarbons are deposited on the cylinder walls where they may subsequently be pyrolyzed to form additional soot particulates²⁸. The large fraction of non-combusted *n*-alkanes we found in

TABLE I
RESULTS OF A TYPICAL EXHAUST COLLECTION EXPERIMENT

Total collection time, h	21½
Total fuel volume consumed, Brit. gal.	12.2
Total exhaust passed through condensor, l	18,890
Average exhaust velocity, l/h	887
Total particulates collected (sum of filter and condensor), g	3.1690
Organic material extracted from particulates, g	0.8948
Amount of particulates produced per gallon fuel consumed, g	0.2599
Amount of organic material on particulates per gallon fuel consumed, g	0.0733

particulates may therefore result from encapsulation by these soot particles. Encapsulated phenolic and other water-soluble compounds would be expected to be lost in our aqueous condensation collection procedure. However, in numerous comparative experiments^{1,2}, we saw no composition differences between particulate extracts obtained from wet or dry collection techniques.

Results of a typical particulates collection run are presented in Table I. The particulate matter from three exhaust collection runs (27,000, 18,000, and 12,000 l of

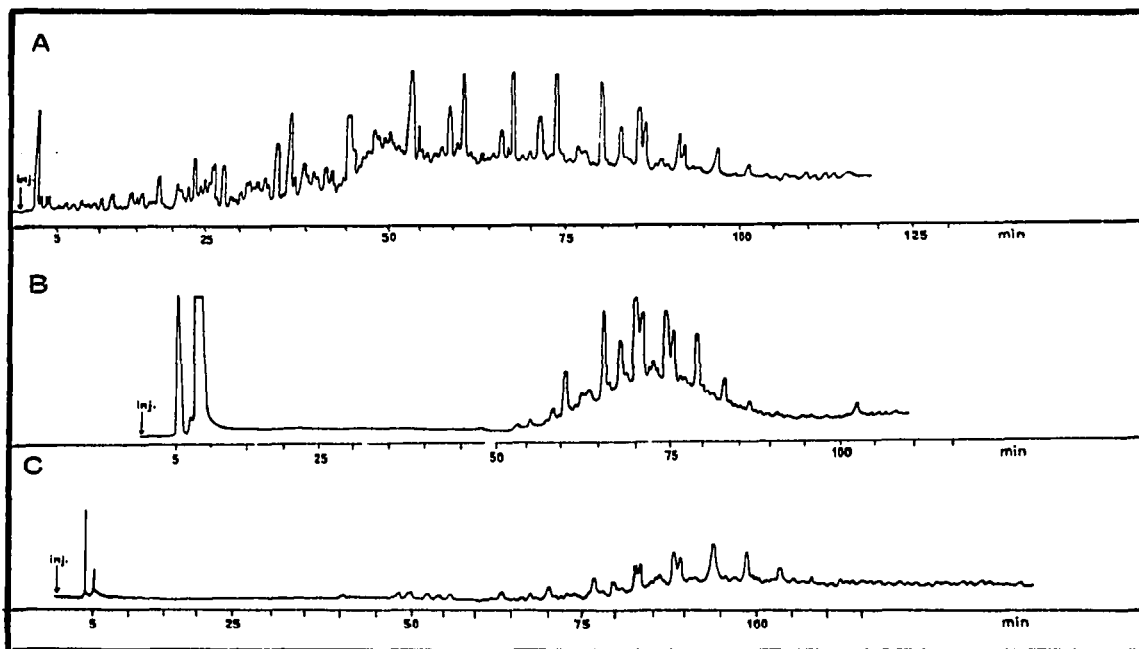


Fig. 4. Comparative gas chromatograms of diesel fuel, and exhaust particulates extract before and after column chromatography. (A) Chromatogram of diesel fuel, GC conditions are identical to Fig. 3. (B) Chromatogram of particulates extract in chloroform before column chromatography. Column temperature: isothermal at 205°; sample size: 1.5 μ l; all other conditions are identical to Fig. 3. (C) Chromatogram of first column chromatographic 20-ml fraction of particulates extract. GC column: 200-ft. \times 0.03-in. I.D. SCOT; liquid phase: OV-101 plus SF-96 (50:50, v/v); temperature: 30–295° at 2°/min; injector: 340°; detector: dual flame at 300°; carrier gas: helium at 8 ml/min; sample size: 0.5 μ l.

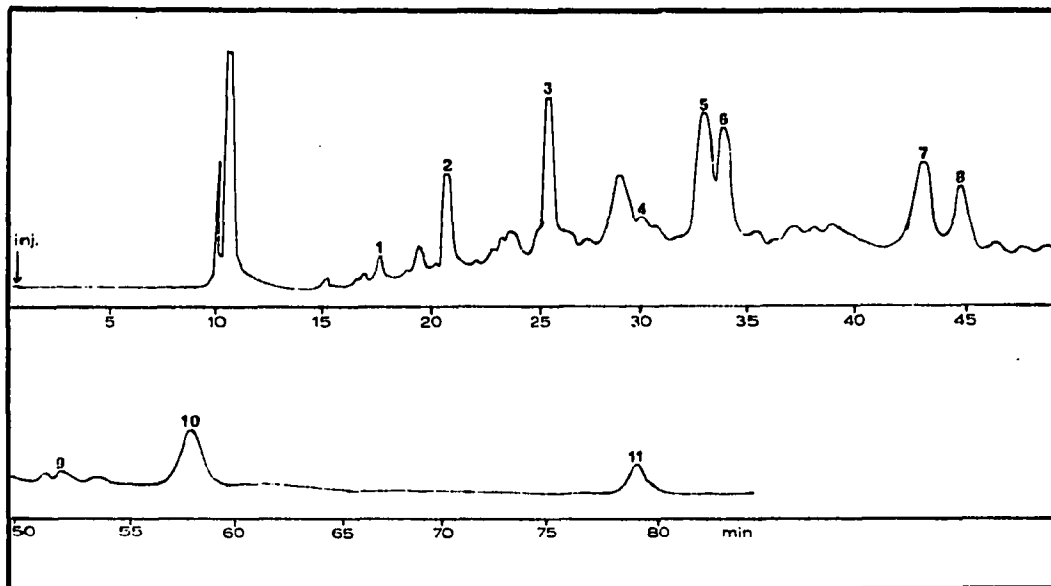


Fig. 5. Gas chromatogram of organic material extracted from auto particulate emissions. Column: identical to Fig. 4C; temperature: 100–295° at 2°/min; injector: 350°; detector: dual flame at 300°; carrier gas: helium at 8 ml/min; sample size: 10 μ l. Peaks 1–7 are *n*-C₄ to *n*-C₂₀ alkanes. Component percent composition is given in Table II.

exhaust) were combined to provide sufficient sample for development of the analytical methodology. A GC comparison of the initial fuel sample, and the particulate extract solution before and after column chromatographic fractionation (first 20 ml) is shown in Fig. 4. The column chromatography step appears to remove many of the high-molecular-weight components from the particulate extract solution, which simplifies subsequent analysis. In addition, the comparison in Fig. 4 indicates that a surprisingly

TABLE II

POSITIVELY IDENTIFIED ALIPHATIC CONSTITUENTS OF EXTRACTED PARTICULATE MATTER (Fig. 5)

Peak No.	Name	Component relative percent*
1	<i>n</i> -Tetradecane	0.9
2	<i>n</i> -Pentadecane	5.0
3	<i>n</i> -Hexadecane	13.8
5	<i>n</i> -Heptadecane	14.3
7	<i>n</i> -Octadecane	10.9
10	<i>n</i> -Nonadecane	5.7
11	<i>n</i> -Eicosane	2.3
	Total	52.9

* Approximated from normalized area percent calculations, assuming equal response factors for all constituents.

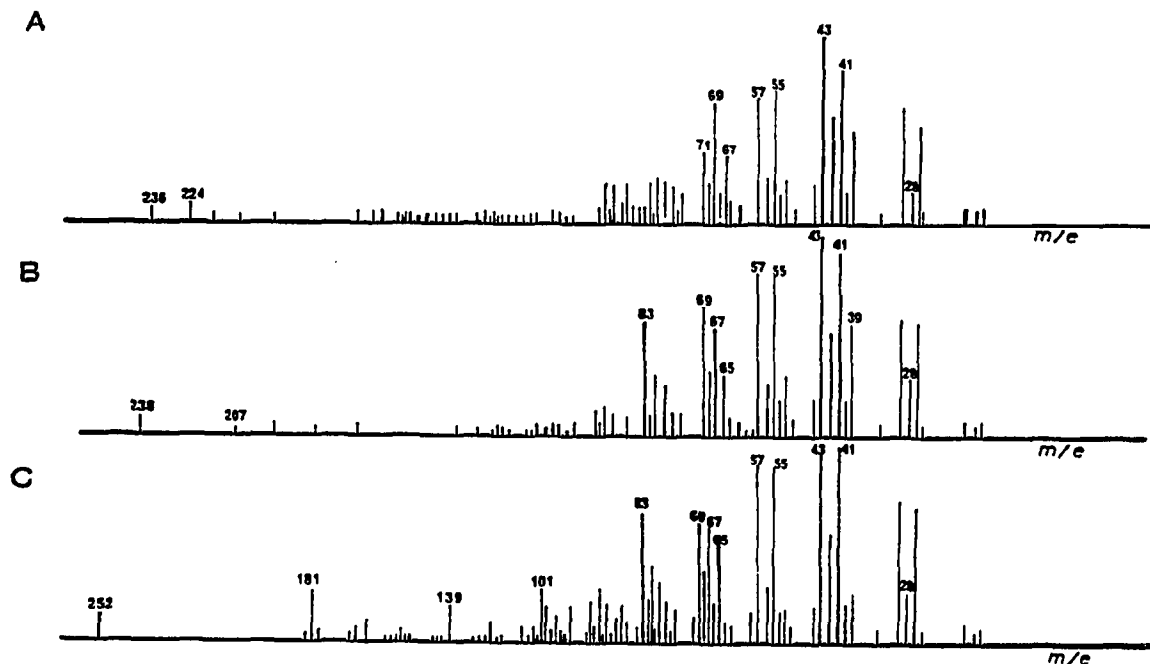


Fig. 6. Mass spectra of GC peaks shown in Fig. 5. (A) Peak No. 4: possible mixture: m/e of 218, 224, 236 indicate long-chain aliphatic hydrocarbons. (B) Peak No. 5: primarily *n*-heptadecene, (C) Peak No. 6: m/e at 252, strong 181 (loss of 71), remainder of pattern suggests unsaturated compound, possibly $C_{18}H_{36}$ containing a dimethylethyl-substituted position.

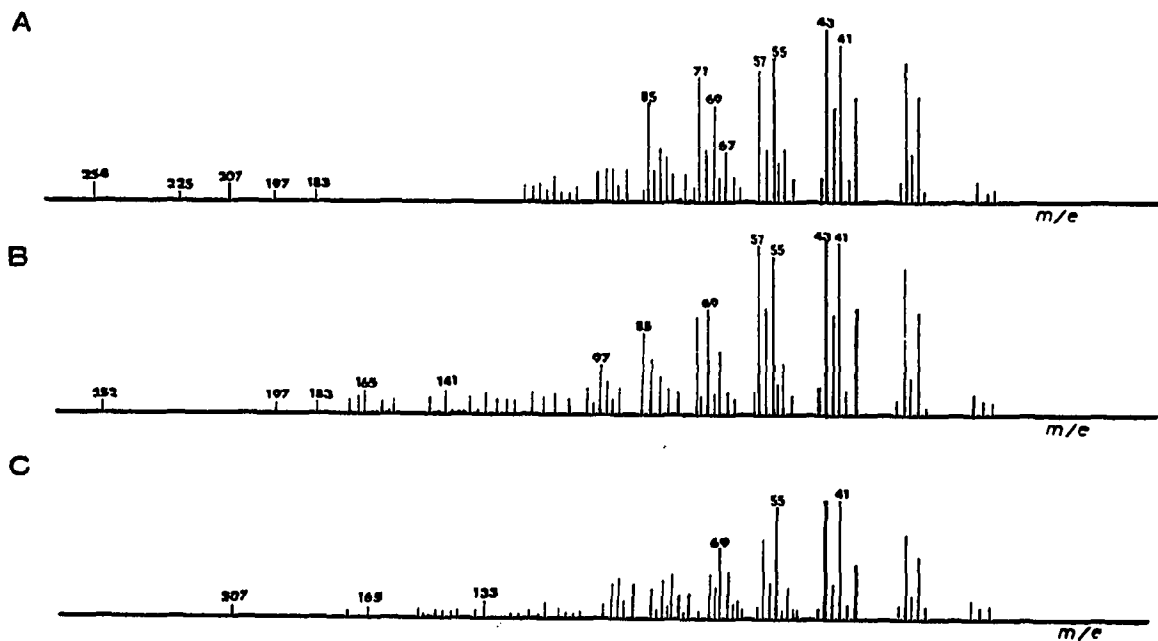


Fig. 7. Mass spectra of GC peaks shown in Fig. 5. (A) Peak No. 7: primarily *n*-octadecane. (B) Peak No. 8: m/e at 252, but aliphatic fragmentation pattern (dodecylcyclohexane possible). (C) Peak No. 9: aliphatic fragmentation pattern; some branching.

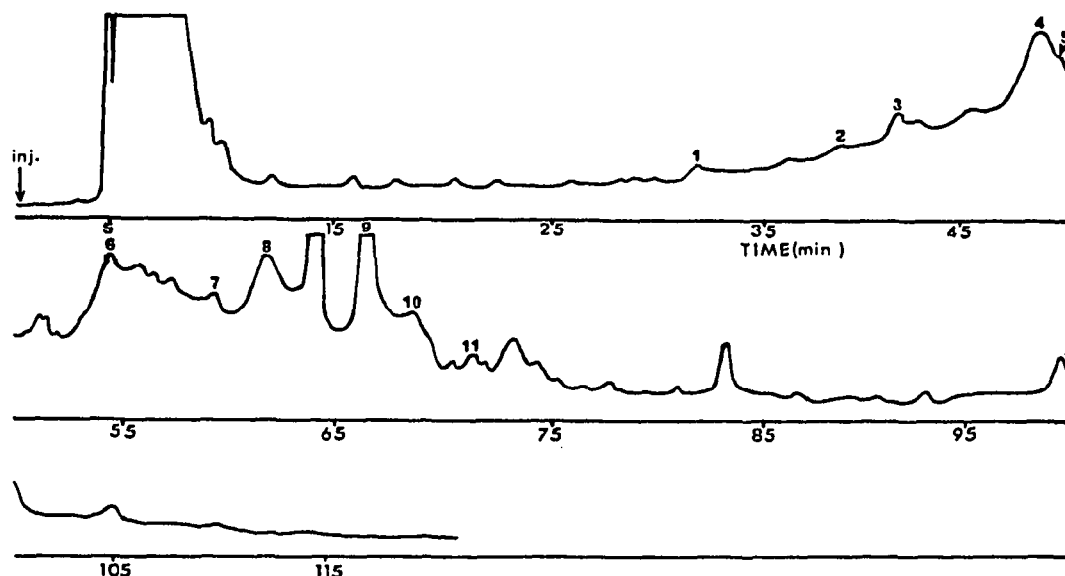


Fig. 8. Gas chromatogram of column chromatographic PAH fraction of particulates extract. Peak identity and percent composition are given in Table III. GC conditions are identical to Fig. 5.

large amount of the higher-fuel fraction does not combust in the engine, and is emitted as exhaust. Fig. 5 shows the gas chromatogram of the first 20-ml (alkanes) fraction after concentration to 100 μ l; the relative percent composition (obtained from peak area integration) of identified *n*-alkanes in the mixture is given in Table II. Figs. 6 and 7 show typical mass spectra of compounds found in the particulate matter before column chromatography. Fig. 8 illustrates the gas chromatogram of the combined

TABLE III

TENTATIVE IDENTIFICATION OF COMPOUNDS FOUND IN THE COLUMN CHROMATOGRAPHY FRACTION CONTAINING PAHs (Fig. 8)

Peak No.	Name	Component relative percent*
1	Biphenyl	0.02
2	Dimethyltetrahydronaphthalene	0.05
3	1,2-Dihydrotrimethylnaphthalene	4.0
4	Phenylpyrocatechol	9.0
5	Phenylphenol	0.8
6	Methylfluorene and tetramethyl-substituted naphthalene	9.0
7	Dimethylperhydronaphthalene	3.0
8	Dimethylfluorene and tetrahydrophenanthrene	8.6
9	9,10-Anthraquinone	9.2
10	Methoxyphenanthrene	4.5
11	Decalin	3.2
	Total	51.37

* Approximated from normalized area percent calculations, assuming equal response factors for all constituents.

TABLE IV

COMPOUNDS EXTRACTED FROM DIESEL FUEL PARTICULATE MATTER

(A) Identity based on comparison with published spectra

n-Tetradecane; *n*-Pentadecane; *n*-Hexadecane; *n*-Heptadecane; *n*-Octadecane; *n*-Nonadecane; *n*-Eicosane; *n*-Heneicosane; *n*-Docosane; Methyldecane; Methylundecane; 2-Methylpentadecane; Ethyltridecane; 1-Tetradecane; 1-Heptadecane; Decahydronaphthalene; Acenaphthylene; Acenaphthene; Biphenyl; Methylnaphthalene; 1-Ethyl-naphthalene; 2-Isopropyl-naphthalene; Trimethylnaphthalene; Butyl- or tetramethylnaphthalene; Ethylfluorene; Dimethylfluorene; Trimethylfluorene; 1,2-Dihydrotrimethylnaphthalene; Dimethyltetrahydronaphthalene; 4,5-Dimethylperhydrophenanthrene; Dimethylphenanthrene; *o*-, *m*- and *p*-Phenylphenols; 2,6-Di-*tert*-butyl-4-methylphenol; Methoxyphenanthrene; 9,10-Anthraquinone

(B) Structures based upon comparison of observed spectra with available published spectra for similar compounds or isomers

Methyldecane; $C_{17}H_{34}$; Dodecylcyclohexane; Long-chain methyl ketone $C_{18}H_{38}O$; Dinaphthyl-alkane, $m/e = 324$; Undecylnaphthalene; Tetrahydrophenanthrene; Dimethyltetrahydronaphthalene; Dimethylperhydrophenanthrene; C_7H_{13} -Substituted chrysene; C_9H_{13} -Substituted chrysene; Naphthalene; Binaphthyl; Methylfluorene; Perhydrophenanthrene; Octahydrophenanthrene; Trinaphthenebenzene; Diphenylacenaphthalene; Dimethylcyclopentanaphthylene; Isoamyl-substituted fluorene; Aromatic, $m/e = 134$; Aromatic, $m/e = 148$; Aromatic, $m/e = 148$; Fluorene; Dihydroxymethoxybenzene; Ethyl naphthoate; 1-Acetylnaphthalene; Phenylpyrocatechol

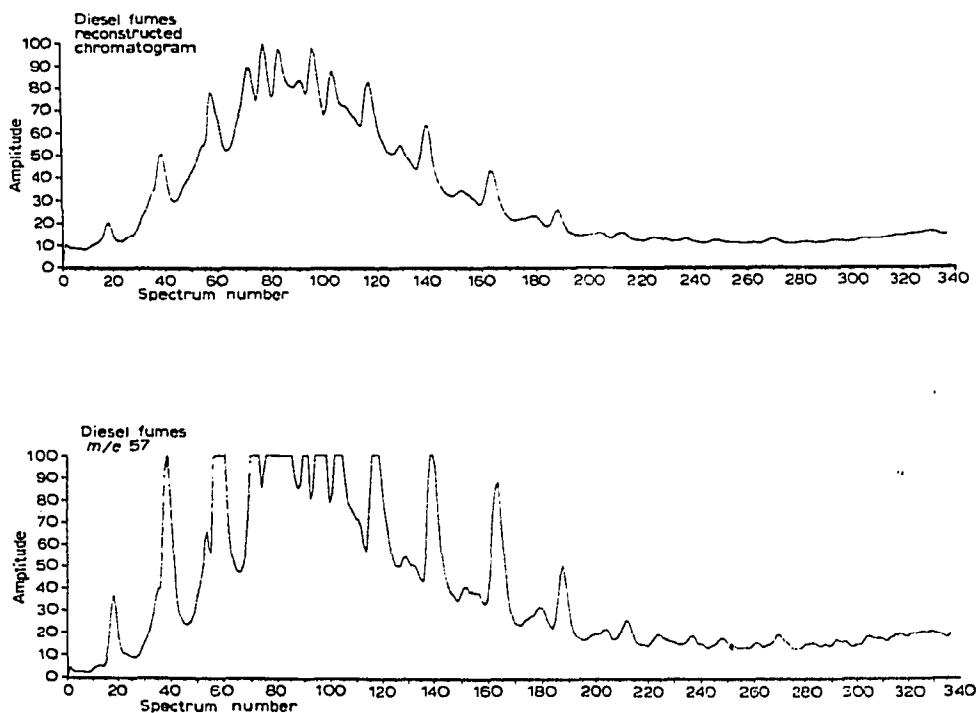


Fig. 9. Reconstructed gas chromatogram and mass chromatogram (m/e at 57) for particulates extract. Most of the extract appears to consist of aliphatic or olefinic material.

column chromatographic fractions which contain both PAH and oxygenated compounds; relative percent composition and tentative peak identities are given in Table III. Table IV summarizes all the compounds we have thus far identified that are present in diesel fuel exhaust particulate extracts.

Some difficulties were encountered with overlapping peaks for 1-olefins and *n*-alkanes in various GC runs; these were resolved by a gas chromatograph-mass spectrometer-computer system, which has previously been described in detail²⁹. The "off-line" system used for the major portion of this work requires near-complete GC component resolution, which could only be achieved with the aid of column chromatographic sample pre-treatment. The mass chromatogram technique, illustrated in Fig. 9 for *m/e* at 57, however, can be used to locate components in a GC profile in which peak resolution is minimal. Additionally, mass chromatograms of *m/e* at 78 or 165 could be used to locate components containing the benzene or fluorene structure of PAH. It is possible, therefore, to analyze particulate and exhaust extracts without using time-consuming column chromatographic sample pre-treatments. However, it should be recognized from the work presented here, that the use of a GC-MS system that lacks a dedicated computer still enables the separation and identification of components in very complex mixtures.

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