北海道大学工学部研究報告
第 138 号 (昭和 63 年)

Bulletin of the Faculty of Engineering,
Hokkaido University. No. 138 (1988)

Measurement of Polynuclear Aromatic Hydrocarbon in Particulates and Gaseous Unburnt Hydrocarbon from Diesel Engines

Koji YAMANE*, Takemi CHIKAHISA*, Noboru MIYAMOTO** and Tadashi MURAYAMA*

(Received September 30, 1987)

Abstract

This paper provides information on measurement techniques for the soluble organic fraction in the particulate and gaseous unburnt hydrocarbon in diesel exhaust. A dilution mini-tunnel and teflon coated glass fiber filter were used to collect the particulates. The soluble organic fraction (SOF) is extracted from particulates by soaking filters in dichloromethane, which was isolated by column-chromatography. Its PAH fraction was determined by high performance liquid chromatography (HPLC). Column-chromatography with a silica-gel column and HPLC with an octadecylsilan-bonded column kept at high temperatures improved the analytical efficiency. The gaseous hydrocarbon in raw exhaust was analysed by a gaschromatography (GC) with FID. The temperature of the sample glass syringe affected the measurements of the high boiling point hydrocarbon constituents.

Introduction

Regulations for diesel particulate and gaseous hydrocarbon emissions have become severe for smaller passenger cars. Thus, there is a growing need for dilution systems to collect/measure the particulates. Dilution systems are proposed by EPA. However they are not practical due to size and cost. In the present research a dilution mini-tunnel system was developed, and its accuracy and repeatability were investigated.

The goal of this study is to establish methods for chemical analysis of PAH(Polynuclear Aromatic Hydrocarbon) in particulates and gaseous unburnt hydrocarbon constituents.

There are some reports of techniques for extracting the SOF from the particulate matter [1-4]. With solvent extraction and analysis of SOF, Soxhlet extraction is most widely used. However, the extraction period and solvents are different in different reports. Obuchi et al. [2] showed the effect of extraction time on extraction rates of SOF by the Soxhlet method. It reports that the extraction is almost complete within 6 hours for all types of compounds. Petersen et al. [3] used toluene as the solvent, and extracted SOF for 16 hours. MacDonald et al.[1] used methylene-chloride (dichloromethane), and extraction were made for 4 hours.

There have been a number of reports on the determination of the polynuclear aromatic hydrocarbons (PAHs) in particulates [5-7]. Andrews et al. [5] separated SOF with silicagel

* Thermal Energy Conversion Laboratory
** Heat Engine II Laboratory
Department of Mechanical Engineering

in column chromatography, and analyzed the PAH fraction of SOF with a high-performance liquid chromatograph (HPLC). It had an octadecylsilane-bonded, reversed-phase column, with a high resolution efficiency for PAHs. Tabata et al. [7] analysed PAHs in airborne dust using capillary GC and a GC-MS-COM system.

There are also a number of reports with HPLC techniques [5, 6, 8, 9]. Prior to the use of an HPLC columns, it was commonly processed to eliminate aliphatic compounds from the SOF extract. The procedure include liquid-liquid separation [8], column chromatographic separation [5, 6, 9], and thin layer chromatographic separation [6]. Obuchi et al. [9] showed the effect of organic solvents on hydrocarbons eluted with the column chromatographic technique.

There are some reports on the determination of gaseous hydrocarbons (HCs) in exhaust using various gas chromatographic techniques [4, 10, 11]. O'Donnel et al. [10] analyzed HCs using GC-MS with a cooling trap and a liquescence procedure of the exhaust sample. Papa et al. [11] analysed C_1 to C_{12} hydrocarbons in automotive exhaust gas by a GC column heated from -60°C to 120°C. Black et al. [4] reported a measuring procedure for C_1 to C_{40} HCs in exhaust gas. The HCs from C_1 to C_{10} were collected in teflon film bags, while C_{10} to C_{40} HCs were collected either by porous polymer trap techniques (for gaseous compounds) or by teflon coated glass fiber filters (for particulate), which were them extracted with dichloromethane.

Particulate Measurement

The dilution tunnel used in this work is a mini tunnel, to which a part of the split raw exhaust is supplied.

A schematic diagram of the sampling system and the process of the analysis of particulate (SOF and Dry-Soot) and HCs is shown in Fig. 1. A part of the raw exhaust was introduced into the tunnel (1070×83.1 mm I. D.) via a tube (11 mm I. D.) connecting the exhaust pipe and tunnel, this tube is named the sampling tube (11 mm I. D.). When the dilution system reached equilibrium at a desired sampling condition, measurement was started by replacing the dummy filter in the particulate filter holder with a clean filter (Pallflex TX40HI20WW-70). The flow rate in the tunnel was approximately 100 Liters/min.

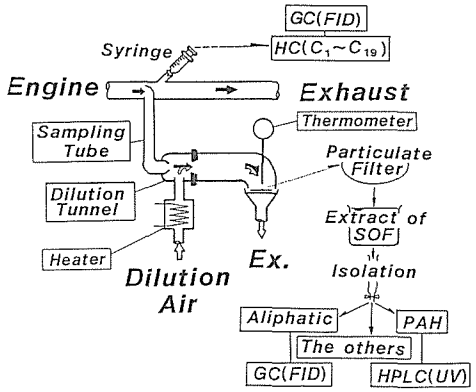


Fig. 1 Particulate and hydrocarbon measurement scheme

SOF Analysis

Extraction -The SOF (Soluble Organic Fraction) was soaked in dichloromethane to extract particulates trapped in the filter for specified extraction periods[12]. The amounts of SOF extracted by this method was compared with Soxhlet extraction.

Table 1 Column chromatography conditions

Column	Alumina		Silicagel	
Length (mm)	100	200	100	200
First eluant	TMP		Hexane	
Second eluant	Methanol		Hexane+Benzene (1 : 1 v/v)	
Exchange volume of eluant (ml)	20		5	14
Flow rate (sec/ml)	54.0	88.4	152	210

Separation of the SOF Extract -The concentrated SOF extract of the particulate samples was divided into aliphatic hydrocarbons (AHC), polynuclear aromatic hydrocarbons (PAH), and others by column chromatographic separation, as shown in Fig. 1.

The column chromatography was open column liquid chromatography on a 300 mm glass column with an inner diameter of 10 mm. The characteristics of phases and eluent solvents were investigated. Table 1 shows the parameters and analytical conditions.

Determination of PAHs -Components of PAHs were analyzed by the high-performance liquid chromatography (HPLC), which consisted of a degasser, a continuous-flow pump, a sample injector, a column heater, a octadecylsilan-bonded column, and a UV absorbance detector. Fig. 2 is a typical HPLC trace for a mixture of standard compounds obtained by this system. Analysis parameters and conditions were varied to determine resolution efficiency for PAHs, as shown in Table 2. On the chromatography, experiment was performed for three HPLC columns, two HITACHI GEL #3056 (150 or 250×4 mm I. D.) and an ERC-ODS (100×6 mm I. D.), and two types of moving phase, acetonitrile-water and methanol-water.

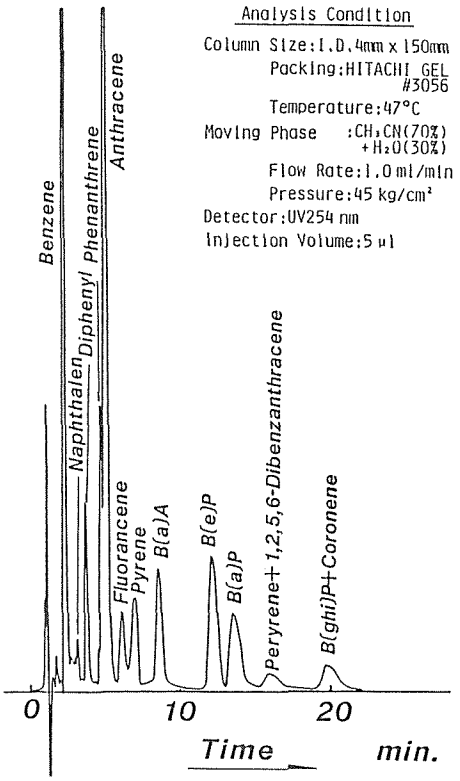


Fig. 2 Typical HPLC chromatogram of standard mixture of PAHs

Solvent and Standard Chemicals -Dichloromethane was used as extraction solvent for SOF in the particulates, and 2-2-4-Trimethylpentane, Hexane, Methanol, and Benzene were used as the effluent for column chromatography. Acetonitrile, Methanol, and distilled water

Table 2 HPLC chromatography conditions

Liquid chromatograph	HITACHI 655-0100
Detector UV wavelengt	HITACHI 638-41 195~350nm
Column (Reversed phase)	HITACHI GEL# 3056, 150 or 250 × 4mm I.D. ERC-ODS-1161, 100 × 6mm I.D.
Column temperature	20 °C~70°C
Mobile phase	Acetonitrile : Water (70 : 30 ordinarily) and Methanol : Water
Flow rate	0.3~1.8 ml/min
Sample volume	5 μl

Table 3 GC chromatography conditions

Gas chromatograph	HITACHI 663-50
Detector	FID
Column	Packed column, Silicone SF96 2m × 3mm I.D.
Column temperature	−30 °C (for 20min), −30~80 °C (3 °C/min) and 80~200 °C (5 °C/min)
Injection temp.	100 °C
Detector temp.	200 °C
Carrier gas	He (at 30 ml/min)
Hydrogen pressure	1.0 kg/cm^2
Air pressure	1.0 kg/cm^2
Sample volume	200cc (gas)

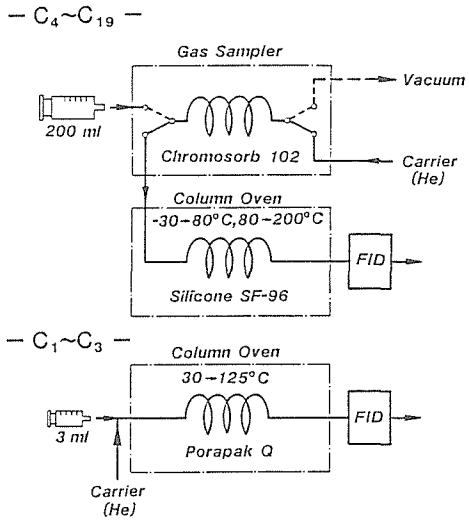


Fig. 3 Gas chromatography scheme for the determination of C_1 to C_{19}

were examined as the moving phase for HPLC.

To identify the chromatographic peaks of PAHs, pure chemicals were used as a standard species.

Gaseous Hydrocarbon Analysis

Gas-chromatography (GC) with a heated flame ionization detector (FID) has been used to determine hydrocarbon constituents in raw exhaust.

Hydrocarbon was analyzed by two chromatographic systems : one for the determination of hydrocarbons heavier than C_4, and another for the C_1 to C_3 hydrocarbons, which are not

separated by the first system.

Collection of Raw Exhaust -A raw exhaust sample was collected by a heated glass syringe, 200 cc was collected for the first GC system and 3 cc for the second.

The effect of the syringe temperature is discussed for the first GC system.

Chromatographic Procedure -The two systems are shown in Fig. 3, and chromatographic parameters and conditions in the first GC system are given in Table 3.

At room temperature a sample was injected into a stainless steel column (the gas sampler in Fig. 3), 1400×4 mm I. D., containing porous polymer, Chromosorb 102, to trap the organic compounds. The column was heated rapidly to 120°C or 200°C, and the ejected organic compounds were introduced into the Silicone SF96 containing column, 2000×3 mm I. D., maintained at −30°C. Measurement were conducted by increasing the temperature of the column from −30°C to 80°C at 3°C per minute and from 80°C to 200°C at 5°C per minute. With the second GC system, a sample was injected into the porapak Q containing column, 1000×2.5 mm I. D., at 30°C. The column was maintained at 30°C for 5 minutes, and then increased from 30°C to 125°C at 10°C per minute.

Test Engine

A 1425 cc four stroke single cylinder DI diesel engine was used. The engine has a 17.4 : 1 compression ratio and a rated power output of 7.36 kW at 1200 rpm. The combustion chamber was a deep dish type 44 mm in diameter, and the injection nozzle was a long hole type with 4 holes.

Result and Discussion

Extraction Method of SOF -Fig. 4 shows the relationship between the ratio of extracts (SOF/TPM) and the excess air ratio of engine with the Filter-soak method and the Soxhlet method. Both methods show similar results, and this indicates Filter-soak method is adequate for the extraction.

Fig. 5 shows the relationship between the extraction rate and extraction time of SOF by the Filter-soak method. The rate is unchanged above 3 hours, and the Filter-soak method may be considered adequate to extract SOF with reasonably short extraction times.

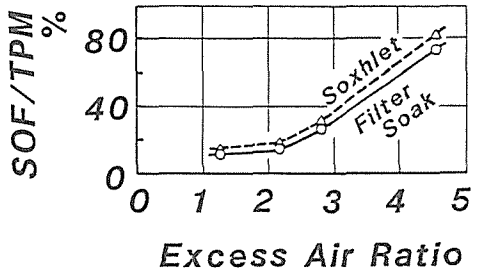


Fig. 4 Comparison of SOF extraction method
TPM : Total Particulate Mass
SOF : Soluble Organic Fraction

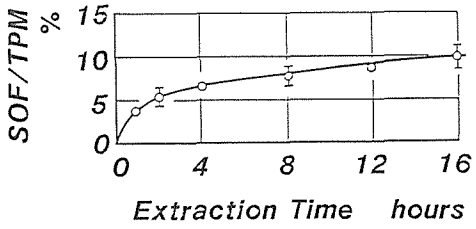
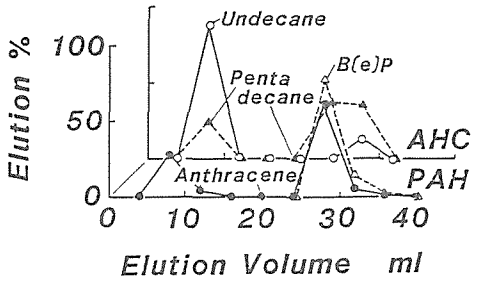
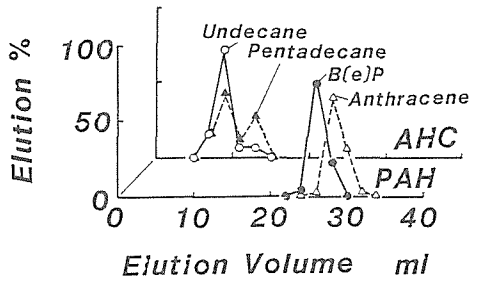


Fig. 5 Relation between extraction of SOF and extraction time with the filter soak method



(a) Alumina-gel column (200×10 mm I. D.)



(b) Silica-gel column (200×10 mm I. D.)

Fig. 6 Elution profiles of standard mixtures of aliphatic hydrocarbons (AHC) and polynuclear aromatic hydrocarbons (PAH) from column chromatography

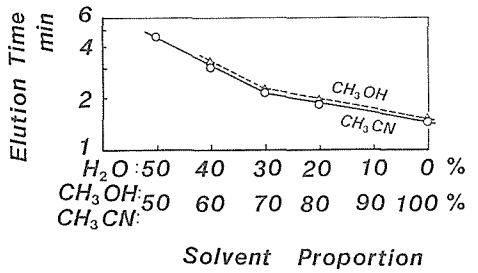


Fig. 9 Relationship between moving phase compositions and elution time of Benzene (Same analytical conditions with Fig. 2)

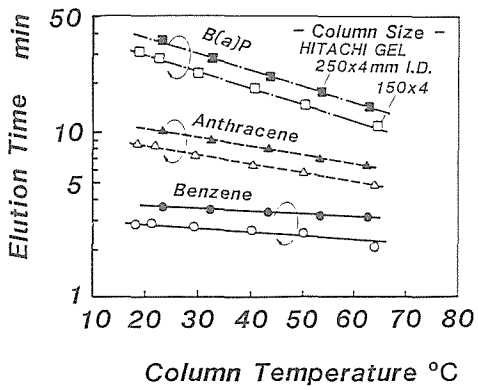


Fig. 7 An example of the relationship between elution time and column temperature for Benzene, Antracene, and B(a) P (Same analytical conditions with Fig. 2)

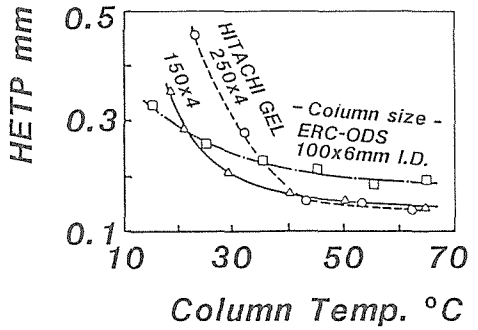


Fig. 8 Estimate of the height equivalent theoretical plate (HETP) for three types of HPLC column at different column temperatures (Same analytical conditions with Fig. 2)

Column Chromatographic Separation for SOF -Fig. 6(a) and (b) shows the elution profiles of aliphatic hydrocarbon (AHC) and polynuclear Aromatic hydrocarbon (PAH) from columns containing alumina-gel and silica-gel. It is clear that the separation efficiency for AHC and PAH by a silica-gel column is better than that with an alumina-gel column. The AHC is eluted by the first effluent (Hexane), and PAH by the second (Hexane : Benzene (1 : 1 v/v)).

The 200 mm long column results in higher resolution efficiency than the 100 mm column.

PAH Analysis by HPLC -The analytical parameters for HPLC are discussed on column size, moving-phase composition, maintaining column temperature, and UV-wave length of a

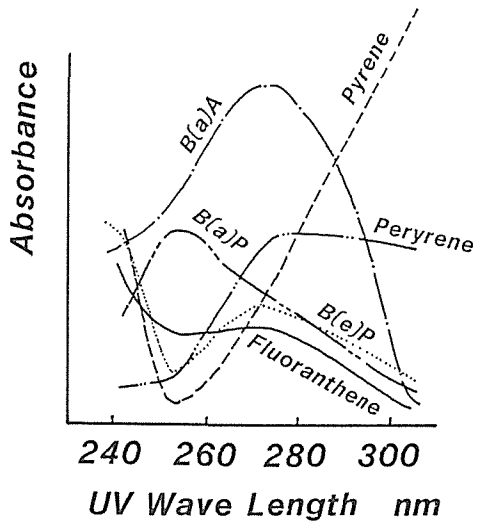


Fig. 10 Chracteristics of UV absorbance wave length as a PAH detector (Same analytical conditions with Fig. 2)

Table 4 Recovery of PAH compounds in the solvent by the concentration procedure

Compounds tested	Added (μg)	Recovered (μg)	Recovery (%)
Naphthalene	5.9	5.4	91.5
Phenanthrene	7.2	6.8	94.4
Fluoranthene	13.3	12.3	92.5
B (a) A	10.2	9.9	97.1
B (a) P	5.4	5.2	96.3

detector.

Fig. 7 shows an example of the relationship between elution time and column temperature for Benzene, Anthracene, and B(a)P by the two types of column in Table 2. Fig. 8 shows the results of estimated HETP of the columns, that is, the height equivalent theoretical plate for different column types and temperatures. Decreased HETP indicates the high column resolution efficiency. It shows that the 150×4 mm I. D. column is superior in maintaining column temperature.

Fig. 9 shows the relationship between the moving-phase composition and elution time of Benzene. Increases in the water portion of the moving-phase increases Benzene elution time, and the time difference between a peak and its neighbor peak on the chromatogram is lengthened, improving the compound separation.

As a result, separation for complex peaks can be performed by maintaining column temperature at a high level and using the watery moving-phase in HPLC.

Fig. 10 shows the characteristics of UV absorbance wave length on various PAH compounds. In this work, the 254 nm wavelength was generally used.

Quantitation and Recovery Efficiency -PAH components were quantified by a calibration curve obtained by HPLC.

Recovery efficiency of PAHs from dichloromethane extracts through to the HPLC analysis were confiremed to be better than 91 %, as indicated on Table. 4.

Gaseous Hydrocarbon Analysis by GC -Fig. 11 shows GC tracers for different temperatures of the sample syringe. It is apparent that the syringe temperature affects the high boiling point part of the gaseous hydrocarbons, especially above hydrocarbons of carbon number 6. This may be explained by the condensation of high boiling point component on the syringe wall. Therefore, to avoid such conditions, the temperature of the syringe should be kept

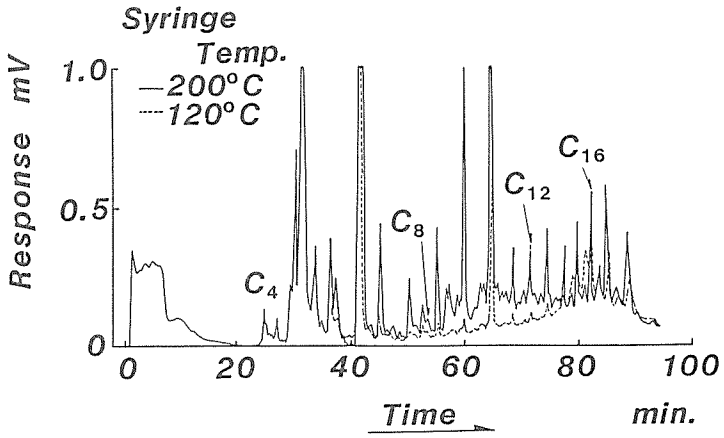


Fig. 11 Effect of sample syringe temperature on the determination of gaseous expired unburnt hydrocarbons with GC in the raw exhaust

higher than 200°C.

Conclusions

The results in this work may be summerized as follows :

1. SOF is adequately extracted into dichloromethane by Filter-soak method developed for this study.

2. PAHs are successfully determined by reversed-phase HPLC in a continuous series of column chromatographic separation of PAHs.

3. Silica-gel is superior to alumina-gel for column chromatographic separation of SOF extracts.

4. With HPLC, watery solvent as a moving-phase and high temperature gives high column efficiency for PAHs.

5. Heating the glass syringe collecting raw exhaust affects the determination of the high boiling point gaseous hydrocarbon component in the exhaust.

Acknowledgements

This work was supported by a Grant in Aid for Scientific Research (A) : "Studies on the particulate formation and emission mechanism of spray combustion", from the Japan Ministry of Education.

The authors wish to express their appreciation to T. Toma, graduate student of Hokkaido University, and S. Yamamoto, Japan Atomic Power Inc., for their cooperation in this work.

References

(1) J. S. MacDonald et al., SAE Transactions, 800185
(2) A. Obuchi et al., J. Chromatogr., 288 (1984) 187-194
(3) B. A. Petersen et al., CRC-APRAC Project No. CAPE-24-72 (1982. 6)
(4) F. Black et al., SAE Transactions, 790422
(5) G. E. Andrews et al., I. Mech. E, C73/83, 1983
(6) E. F. Funkenbush et al., SAE Transactions, 790418
(7) T. Tabata et al., Jpn. Soc. Air Pollut., 13, No. 2 (1978)
(8) B. A. Tomkins et al., Anal. Chem., 52 (1980) 85
(9) A. Obuchi et al., J. Chromatogr., 312 (1984) 247-259
(10) A. O'Donnel et al., National Air Pollution Administration and CRC Report No. IITRT C-6183-5
(11) L. J. Papa et al., J. Chromatogr., Vol. 5 (1968)
(12) T. Murayama et al., SAE Transactions, 861232