

JASO

Technical Paper

Investigation of Method for measuring
polycyclic aromatic hydrocarbon
in exhaust gas from gasoline/diesel engine

JASO TP-07004

Japanese Automobile Standards Organization
Society of Automotive Engineers of Japan, Inc.

1. Method for measuring polycyclic aromatic hydrocarbon in exhaust gas from automotive engine

1) Introduction

As for methods for measuring polycyclic aromatic hydrocarbons (PAHs), the analysis method of Environmental Protection Agency (EPA), test of drinking water such as tap water, and the manual for measuring hazardous air pollutant for the PAHs measurement in the atmosphere have been established in Japan. However, substantially no standard analysis method has been established to measure PAHs in exhaust gas from gasoline and diesel engines (hereinafter referred to as PAHs measurement method). Under such condition, however, measurements of PAHs in the automobile exhaust gas have taken place in various places and it is important to study and to be familiarized with the problems in measurement in order to ensure reliability of measurement values. Among various methods that are implemented for measuring PAHs, the filter sampling - high-performance liquid chromatography method (hereinafter referred to as the HPLC-FL method) is commonly and widely employed for automotive exhaust gas. This technical paper describes the result of the study on the HPLC-FC method.

This document summarizes the problems (notes) of the method for measuring PAHs based on "Method for measuring polycyclic aromatic hydrocarbon in exhaust gas from gasoline and diesel engines" which was created by Subcommittee for Non-regulated Substance, Committee for Exhaust Gas and Fuel Economy, Japan Automobile Manufacturers Association, Inc., based on the findings at Japan Automobile Research Institute. Note that the devices and analysis conditions described herein are merely an example, and the conditions that are appropriate for the individual devices need be set.

2) Purpose

To clarify the problems (notes) of and to standardize the PAHs measurement method using the HPLC-FL method.

3) Component to be studied

The components to be studied are the following 3 components. Benzo[a]anthracene (B[a]A) is prepared as a reference material.

- Benzo[a]pyrene (B[a]P)
- Benzo[k]fluoranthene (B[k]F)
- Benzo[ghi]perylene (B[ghi]P)
- (Benzo[a]anthracene) (B[a]A)

2. Problems of the study results of the PAHs Measurement Method

The following problems have been identified in the PAHs measurement method. At measurement, it is necessary to understand the impact of these problems and take countermeasures.

- Problem of PAHs generated from the devices

- Problem of collection rate
- Problem of interference components
- Problem of absorption and desorption of components
- Problem of a standard specimen
- Problem of analysis time

3. Precautions in measurement

1) Sampling method

Perform sampling for diluted exhaust gas.

After the humidity of a commercially available filter for particle sampling is controlled (TX40H120WW, PALLFLEX PRODUCT CORPORATION, 20 inch × 20 inch*, teflon coating filter) for 24 hours in a clean thermo-hygrostat environment (25 °C, 50 % RH), a scale with less than 0.1 mg reading limit shall be used for weighing. The filter shall be set in the particle sampling device (high volume sampler, etc.) supplied with the exhaust gas dilution device to collect particles. The vacuuming flow rate of the particle sampling device should be kept constant until the particle sampling volume aimed is obtained. Figure 1 shows an example of sampling method.

Weigh the filter after particle sampling under the same condition with before sampling. Until extraction operation after weighing, the filter shall be kept with the particle surface folded inside and sealed in a polyethylene bag to be stored in the dark cold place.

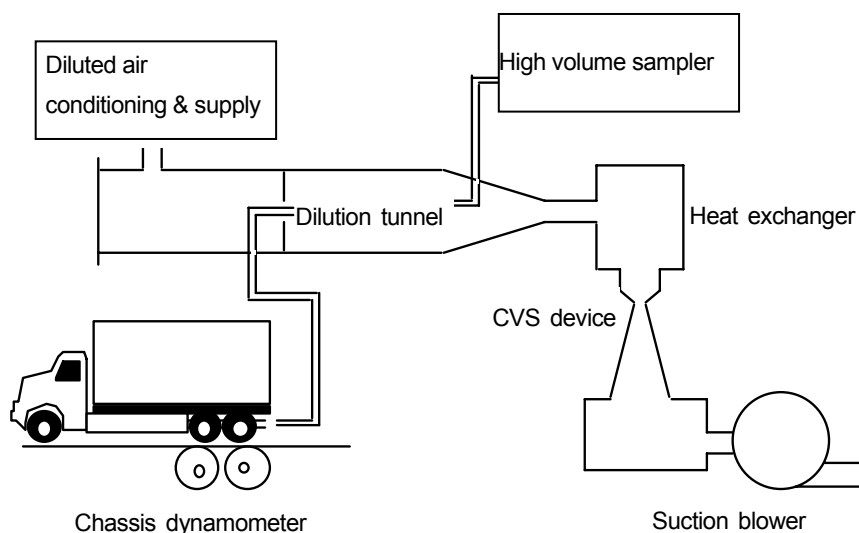


Figure 1 Example of Sampling Method

2) Pre-treatment method

Use dichloromethane (pesticide residue 1,000) to perform the Soxhlet extraction of the filter at a hot-water bath temperature of 60 °C for 24 hours. The solvent is removed from the obtained extracted solution under nitrogen gas stream using Kuderna-Danish Concentrator (26.6 kPa, 35 °C). Air-dry overnight the concentration liquid from which the solvent is removed until it is almost dried and

hardened and dissolve it in HPLC injection solvent (mainly acetonitrile is used) to make a specimen for analysis. When the extraction liquid after analysis is used for the Ames test, dymethylsulfoxide (DMSO) is used as injection solvent, however, be careful about the column lifetime be shortened.

3) Analysis method

3)-1 Analysis conditions

A commercially available HPLC analysis device was used. This device is composed of the following components and enables gradient analysis.

- System controller
- Feed pump (Feed flow rate range: 0.01 to 10 mL/min, discharge pressure: 980 to 39200 kPa)
- Fluorescence detector (detection wavelength range: 190 to 600 nm)
- Column oven (set temperature range: up to 80 °C)
- Auto-injector
- Data processor

Table 1 shows an example of HPLC analysis conditions. Detection wavelength in Table 1 is an example. Measure the excitation and fluorescent spectrum in advance and select the optimal wavelength that has little effect of interference components.

Table 1 Example of HPLC Analysis Conditions

Separation column	Wakosil-PAH 4.6 mm Ø × (100 mm+250 mm) 50 °C
Mobile phase	CH ₃ CN/H ₂ O 50 %/50 % ⇒ <u>95/5</u> ⇒ <u>95/5</u> 0 min 10-50 50-65
Detection wavelength	B[a]P Ex: 382 nm, Em: 407 nm B[a]A Ex: 293 nm, Em: 415 nm B[k]F Ex: 382 nm, Em: 407 nm B[ghi]P Ex: 382 nm, Em: 407 nm
Injection volume	1 ml/min
Specimen injection volume	10 µl

3)-2 Repeatability

Commercially available NIST standard substance, SRM1647d was used as an example.

Dilute the standard substance with acetonitrile 25 times to create solutions. Analysis was made using 1.0 mL of the obtained solution. Figure 2 shows the results.

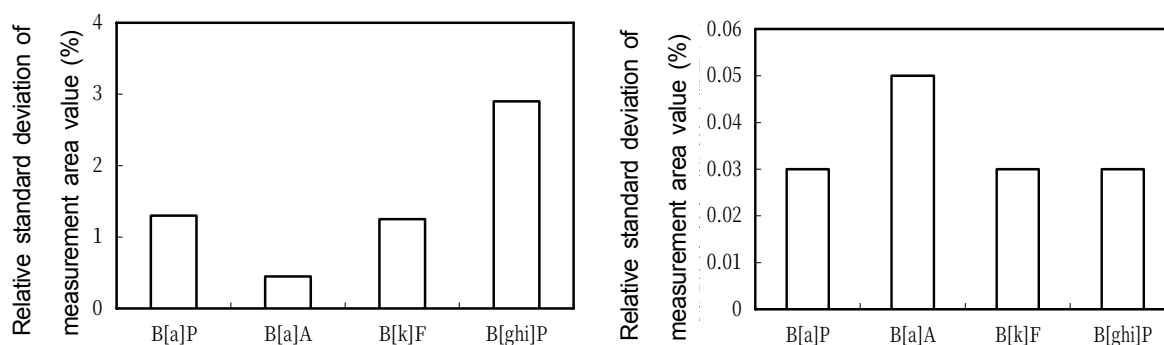


Figure 2 Repeatability of Area Value and Retention Time

3)-3 Creation of calibration curve

Dilute the standard substance with acetonitrile. Adjust the standard concentration series (approx. 5 steps including 0) and create the calibration curve. The 1-point calibration is utilized to determine PAH quantity in routine analysis.

The linearity and the detection limit of each substance is shown as below.

<Linearity range> B[a]P: 0.2 µg/ml, B[a]A: 0.4 µg/ml, B[k]F: 0.2 µg/ml, B[ghi]P: 0.4 µg/ml

< Detection limit value> B[a]P: 0.0005 µg/ml, B[a]A: 0.0004 µg/ml, B[k]F: 0.0005 µg/ml

B[ghi]P: 0.0015 µg/ml

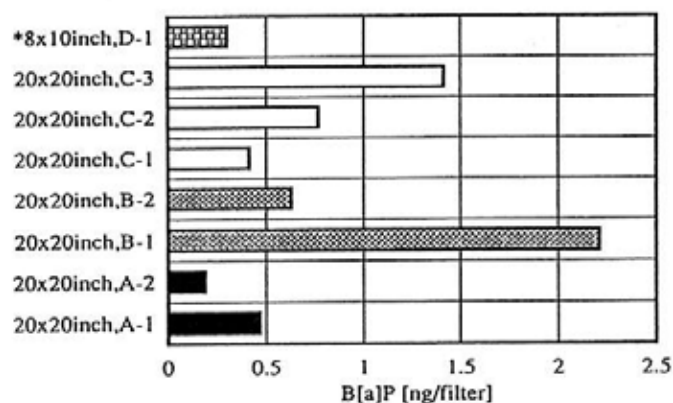
4) Problems in measurement

4)-1 Problem of generation from devices

Since only a small amount of PAH concentration exists in the exhaust gas, the background of the sampling filter and the separation from the device located at the sampling path may affect the quantitative value of PAH. Therefore, it is necessary to measure each PAH generation volume.

4)-1-1 Background of filter

Figure 3 shows an example of the background of the filter. PAH is detected from the uncollected filter itself and the generation volume varies even among the filters in the same lot. Therefore, confirm the background of the filter multiple times by lot. For the reduction of the background, heating treatment and pre-treatment method such as cleaning with the organic solvent have been suggested. These will be the issues to be studied in future.



* Filter size - Lot No. - Volume

Figure 3 Background of Filter (B[a]P Volume)