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Technical Paper

Investigation of Method for measuring hydrocarbons in exhaust gas from gasoline/diesel engine

JASO TP-06003

Japanese Automobile Standards Organization

Society of Automotive Engineers of Japan, Inc.

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1. Method for measuring hydrocarbons in exhaust gas from automotive engine

1) Introduction

There are several methods for measuring hydrocarbons as shown in Table 1.

Among these methods, the bag sampling-gas chromatography with a hydrogen flame ionization detector (FID) (hereinafter referred to as the GC-FID method) recommended by Japan Automobile Manufacturers Association, Inc. is the most common and time-proven method for measuring hydrocarbons in automotive exhaust gas. However, the method has not been standardized. To address this issue, we have summarized the result of the studies on the measurement method. As for the detector, although hydrogen flame ionization detectors are superior for analyzing hydrocarbons in terms of both detection range and reproducibility, we recommend combined use of FID and a quadrupole mass spectrometer (hereinafter referred to as MS) which should be used for identifying middle-grade components that contain a large number of components.

This document summarizes the problems (notes) of the methods for measuring hydrocarbons based on “Method for measuring hydrocarbons in exhaust gas from gasoline/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 (JARI). 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 method for measuring hydrocarbons in exhaust gas from gasoline/diesel engines using the bag sampling-GC-FID method.

3) Components to be studied

The following 5 components were studied.

- 1,3-Butadiene (C4H6)
- Benzene (C6H6)
- Toluene (C7H8)
- Xylenes (3 isomers: o-Xylene, m-Xylene, p-Xylene, C8H10)
- Ethylbenzene (Et-Benzene, C8H10)

2. Problems of the study results of the method for measuring hydrocarbons

The following problems have been identified even for the method for measuring hydrocarbons based on the bag sampling-GC-FID method. It is necessary to understand the impact of these

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problems and make countermeasures in making measurements.

- Problem of hydrocarbons generated from the devices
- Problem of collection rate
- Problem of interference components
- Problem of absorption and desorption of components onto sampling path
- Problem of availability of a standard specimen
- Problem of analysis time (temporal change after sampling)

Table 1 Major Methods for Measuring Hydrocarbons in Exhaust Gas

	Sampling method-Pre-treatment method	Analysis method	Gas to be measured
Method recommended by JAMA	Bag sampling-cooling concentration/heating absorption and desorption method	GC-FID (GC/MS)	▪ Automotive exhaust gas
MOE Manual[1]	Bag sampling method-(direct introduction method/cooling concentration method)	GC-FID GC-ECD or GC/MS	▪ Exhaust gas from gas duct, chimney and local ventilation, etc. ▪ Ambient air
	Vacuum bottle sampling method-(direct introduction method/condensate extraction and introduction method)		
	Canister sampling method-(direct introduction method/condensate extraction and introduction method)		
	Solid adsorption sampling method-solvent extraction method		
Others	Infrared spectroscopy (direct measurement)	FT-IR	▪ Gas in general

3. Precautions in measurement

1) Sampling method

The sampling method shall be the bag sampling method. A small-volume fluorine resin bag (5 L or 10 L) (Trade name: Tedlar® PVF Film manufactured by DuPont™ or equivalent) shall be used as a sampling bag.

In the actual sampling operation, diluted exhaust gas specimen and dilution air specimen emitted in the chassis dynamometer test as shown in Figure. 1 are sampled in a large-volume bag for the Constant Volume Sampler (CVS) device, and then transferred to a small-volume bag for GC analysis.

The specifications of the sampling equipment must be specified in the report since the length of the sampling line and whether or not to heat is treated affect the collection rate.

Keep in mind the following during the sampling operation.

(1) Carry out a blank test for unused bags for each lot. When the blank concentration is high, perform heat treatment before use. However, be careful of the heat treatment, since

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heat treatment may deteriorate storage stability.

(2) The bag shall have been covered with a light shielding cover before sampling exhaust gas from an actual vehicle in order to prevent photo-degradation (decrease in concentration) of hydrocarbon components.

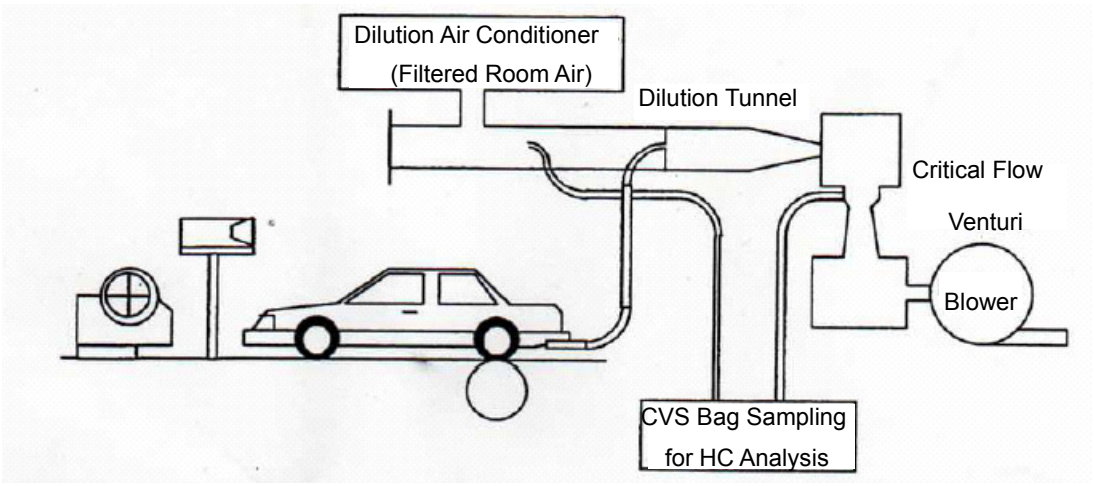

Figure 1 Chassis Dynamometer Test Devices and Exhaust Gas Sampling Path (JARI)

2) Pre-treatment method

In the CVS method, exhaust gas from an actual vehicle is diluted with a large amount of dilution air to prevent condensation of exhaust gas components caused by moisture, and as a result of this, the concentration of hydrocarbon components in the diluted exhaust gas is extremely low (several to several tens ppb level). Therefore, the specimen sampled in the bag need be concentrated before the GC analysis as shown in Table 2. The current GC analysis of hydrocarbons usually employs a method of concentrating and separating low grade components (C2 to C5) and middle grade (C6 to C12) components individually to measuring them separately.

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Table 2　Conditions of Concentrating Specimen Sampled in Bag (JARI)

Item \ Component	Low grade（C2 to C5）component		Middle grade（C6 to C12）component	
	Gasoline vehicle	Diesel vehicle	Gasoline vehicle	Diesel vehicle
Reagent addition amount	10 mL	5 mL	100 mL	5 mL
Pre-column	BX-10	UNIPAKS	-	OV-1
Concentration method	TCT (mega bore aluminum activated charcoal	TCT (mega bore aluminum activated charcoal	TCT (activated charcoal))	Empty column
Concentration method	-125 ˚C	-150 ˚C	20 ˚C	-150 ˚C
Temperature of thermal desorption	250 ˚C	250 ˚C	250 ˚C	250 ˚C
Focus trap	-	-	-125 ˚C	-
Temperature of thermal desorption	-	-	250 ˚C	-

3) Analysis method

3)-1 Use of exclusive analysis device

Since contamination of an analysis device with diesel exhaust gas is concerned, it is desirable that analysis devices that are exclusively used for gasoline vehicles and diesel vehicles respectively be used.

3)-2 Analysis conditions

Table 3 shows the GC analysis conditions.

Table 3　GC Analysis Conditions (JARI)

	Low grade（C2 to C5）component		Middle grade（C6 to C12）component	
	Gasoline vehicle	Diesel vehicle	Gasoline vehicle	Diesel vehicle
Column	GS-Alumina Mega bore column (ID 0.53 mm × 50 m)	Alumina-PLOT Mega bore column (ID 0.32 mm × 50 m)	DB-1 Capillary column (ID 0.25 mm× 60 m)	Petrocol DH Capillary column (ID 0.25 mm × 100 m)
Column temperature	40 to 180 ˚C	-60 to 200 ˚C	35 to 200 ˚C	-60 to 200 ˚C
Carrier gas	He	N_2	He	He
Detector	FID*	FID	FID, MSD**	FID

*FID: Hydrogen Flame Ionization Detector　**MSD: Mass Spectrometer

3)-3 Analysis completion time

Table 4 shows an example of a series of specimen analysis procedure.

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