JASO
Technical Paper

Investigation of Method for measuring 1-nitropyrene in exhaust gas from gasoline/diesel engine

JASO TP-07002

Japanese Automobile Standards Organization

Society of Automotive Engineers of Japan, Inc.

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1. Method for measuring 1-nitropyrene in exhaust gas from automobile engine

1) Introduction

Although various measurements have been carried out to measure 1-nytropyrene discharge volumes in exhaust gas of automobile, actual situation is that the standardized measurement has not been established yet.

This document summarizes the problems (notes) of the method for measuring 1-nytropyrene based on “Method for measuring 1-nytropyrene 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 method for measuring 1-nytropyrene in exhaust gas from gasoline and diesel engines.

3) Components to be studied

1-nytropyrene

2. Problems of the method for measuring 1-nytropyrene

- Blank
- Absorption and desorption of sampling path
- Artifact when sampling
- Extraction efficiency
- Interference component
- Storage stability of analysis specimen
- Standard substance
- Quantitative stability
- Analysis time
- Reduction column availability
- Analysis value difference depending on measurement institutions

3. Precautions on measurement

1) Outline of measurement

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In order to measure 1-nytropyrene in discharge volume of automobiles, three-step operation is required. This operation includes particle sampling, pre-treatment and analysis (Table 1).

Although fluorescent detection in high-speed liquid chromatograph provides high sensitivity as well as excellent detection selectivity, reduction to 1-aminopyrene is necessary since there is no fluorescence in 1-nytropyrene. In the method where reduction is performed in the pre-treatment process, the post-column reduction method in which reduction is performed inline is selected because of possible loss of unstable 1-aminopyrenes by degradation with light and the like as well as of complicated operation.

Table 1 Outline of 1-nytropyrene Measurement (Example)

Sampling method	Exhaust gas dilution - filter sampling
Pre-treatment method	Organic solvent (dichloromethane) extraction - concentration
Analysis method	High speed liquid chromatograph (HPLC) - post-column reduction fluorescent detection method[1)]

2) Sampling method

Perform sampling for diluted exhaust gas. After the humidity of a commercially available filter for particle sampling is controlled (e.g. PALLFLEX product, 20 inch × 20 inch, teflon coating filter) for 24 hours in a thermo-hygrostat chamber (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 vaccuming flow rate of the particle sampling device should be kept constant until the particle sampling volume aimed is obtained.

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 with light shielded and frozen.

3) 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 methanol to make a specimen for analysis.

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4) Analysis method[1)]

4)-1 Analysis conditions

Tables 2 and 3 show an example of analysis conditions and Figure 1 shows the flow path of the column switching. The specimen shall be injected under the flow path 1 in Figure 1. Change to the flow path 2 immediately before the outflow of 1-aminopyrene (AP) formed by the reduction of 1-nytropyrene using the reduction column and introduce only 1-aminopyrene fraction in the second column. Then, change to the flow path 3 before starting separation. The 1-aminopyrene (AP) that is introduced in the second column has stronger polar character compared to 1-nytropyrene of pre-deoxidizing and the retention is weakened in the opposite-direction column such as ODS and the isolation from other components improves. Finally, change to the flow path 1 and perform cleaning and leveling of the first column to prepare for the next analysis.

Table 2 1-nytropyrene Analysis Conditions (Example)[1)]

Analysis device	High speed liquid chromatography (Shimadzu: LC10AD)
Column	Guard column: Puresil C18 3.9 ϕ × 20 mm 1st column: Inertsil ODS-3 4.6 ϕ × 150 mm 2nd column: Puresil C18 4.6 ϕ × 250 mm Reduction column: Johnson Mathey Inc. Pt/Rh on 5 μm Al_2O_3
Column temperature	Analysis column: 50 °C Reduction column: 80 °C
Detector	Spectrofluorometric detector (Shimadzu: RF-540) Ex: 365 nm, Em: 430 nm
Mobile phase condition	Listed in continuous analysis program (Table 3)
Injection volume	20 μl
Standard substance	NIST standard substance SRM1587

* Manufacturing companies for analysis devices, columns, standard substances and the like are only examples.

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