

JASO

Technical Paper

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

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Index

1. Method for measuring aldehydes in exhaust gas from automotive engine-----	1
1) Introduction-----	1
2) Purpose-----	1
3) Components to be studied-----	1
2. Problems of the study results of the method for measuring aldehydes-----	1
3. Precautions in measurement-----	2
1) Sampling method-----	2
2) Pre-treatment method-----	3
3) Analysis method-----	3
4) Problems (notes) in measurement-----	5
5) Analysis accuracy assurance procedure guideline-----	7

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

1) Introduction

A method for analyzing aldehydes is specified in JIS K 0303 regarding formaldehyde. However, substantially no standard has been established for the methods for measuring aldehydes in exhaust gas from gasoline/diesel engines (hereinafter referred to as the method for measuring aldehydes). Meanwhile, since aldehydes emitted from automobiles including the substances applicable to PRTR are widely measured, it is important to study problems for the measurement in order to ensure reliability of the measured values. Among various methods that are implemented for measuring aldehydes, the 2,4-dinitrophenylhydrazine sampling - high-performance liquid chromatography method (hereinafter referred to as the DNPH-HPLC method) is commonly and widely employed for automotive exhaust gas. We have summarized the result of the study on the DNPH-HPLC method.

This document summarizes the problems (notes) of the methods for measuring aldehydes based on “Method for measuring aldehydes 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. 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 aldehydes in exhaust gas from engine/diesel engines using the DNPH-HPLC method.

3) Components to be studied

The components to be studied are the following 2 components specified as the important substances among the priority survey substances set by Ministry of Environment. The temporal change of acrolein is indicated as reference.

- Formaldehyde
- Acetaldehyde
- (Acrolein)

2. Problems in the result of study on the method for measuring aldehydes

The following problems have been identified for the method for measuring aldehydes from automotive exhaust gas. At measurement, therefore, it is necessary to understand the impact of such problems and make countermeasures.

- Problem of aldehydes 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

Direct exhaust gas and diluted exhaust gas shall be sampled. The impinger sampling method will be mainly described in this document. However, sampling with DNPH cartridges is also possible.

1)-1 Adjustment of absorbing solution

Commercially available DNPH (Reagents Grade) shall be dissolved in acetonitrile (for HPLC) to prepare a saturated solution, and shall be left to stand for several hours to recrystallize. The crystal shall be diluted with acetonitrile in accordance with the concentration of the exhaust gas to be measured, thereby preparing an absorbing solution. 20 mL of the absorbing solution shall be poured into a bubbler tube (absorption bulb), and mixed with 100 μ L of 3.8N perchloric acid to prepare an acidic perchloric DNPH acetonitrile solution. This acidic perchloric DNPH acetonitrile solution shall be used. Preferably, perchloric acid be added immediately before the use. A commercially available DNPH-Silica cartridge shall be normally used for sampling with cartridges. Cartridges of the same lot shall be used and they must have been kept at 5°C or less in a sealed state before use.

1)-2 Sampling of automotive exhaust gas

Figure 1 shows an example of the flow path of the sampling device which is used for sampling automotive exhaust gas. The absorption bulb shall be cooled with ice. An appropriate filter shall be provided to avoid contamination of soot or other substances in the specimen gas. Automotive exhaust gas shall be sucked by a bypass pump through a stainless steel pipe which has been heated to approx. 120 °C to replace gases in the sampling line thoroughly. Following that, the line shall be switched and the exhaust gas shall be sampled. The flow rate of the exhaust gas shall be adjusted to the flow rate 1L/min by a mass flow controller. The sum of the output values shall be the amount of the sampled gas. The target sampling time shall be 10 minutes when the engine is in the steady state, and a time corresponding to the applicable mode in a mode test. Number of impingers (or cartridges) shall be determined after checking the collection rate.