B-2.8 Methane and Nitrous Oxide Emission Characteristics from Automobiles

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Total Budget for FY1991-FY1994 21,106,000 Yen (FY1994 5,656,000 Yen)

Abstract Exhaust gases discharged from automobiles that are increasing rapidly in number are noticed as one of the reasons for a resent increase in atmospheric methane and nitrous oxide concentration, which have been considered as greenhouse effect gas.

In order to make an accurate estimation of methane and nitrous oxide contribution, measurement methods about them were studied and their discharged amount of various automobiles were evaluated under various driving conditions.

On the basis of those measurement results with taking statistics such as the number of automobiles, the total annual mileage, and the total annual fuel consumption into consideration, we attempted several methods for evaluating the annual global emissions. As a result, passenger vehicles were playing an important role in greenhouse effect and their annual emissions that were based on the global number of automobiles and the global amounts of fuel consumption were methane; 477.263 t/year and nitrous oxide; 313.472t/year, which was higher than what had been estimated.

Key Words Greenhouse Effect Gas, Automotive Exhaust Gas, Methane, Nitrous Oxide, Continuous Measuring Method, Three Way Catalyst)

1. Introduction

Automotive exhaust gas is suspected to be one of the main causes of the rapid increase in greenhouse effect gas such as methane and nitrous oxide concentrations in ambient air. Especially, a catalyst for NOx reduction may produces nitrous oxide and for the total evaluation of counter measure technique on greenhouse effect gas from automobiles, not only carbon dioxide(CO_2) but methane and nitrous oxide must be considered.

Table 1 Tested Vehicle Specification

Vehicle Type	Code on Figures and Tables	Emission Control Method	Engine Displacement (L)	Vehicle Weight (Kg)	Driving Mileage (Km)
Gasoline	TWC-OLD	Three Way Catalyst	1.99	1,390	26,000
CNG	TWC-CNG	Three Way Catalyst	1.27	975	38,000
Gasoline	OXI-NEW	Oxidation Catalyst	1.497	950	7,200
Gasoline	TWC-NEW	Three Way Catalyst	1.49	1,010	4,600
Gasoline	CONVEN	None	1.487	990	87,000
Gasoline	OXI-OLD	Oxidation Catalyst	1.81	1,240	96,000
Diesel	DIESEL	EGR	2.47	1,830	49,000

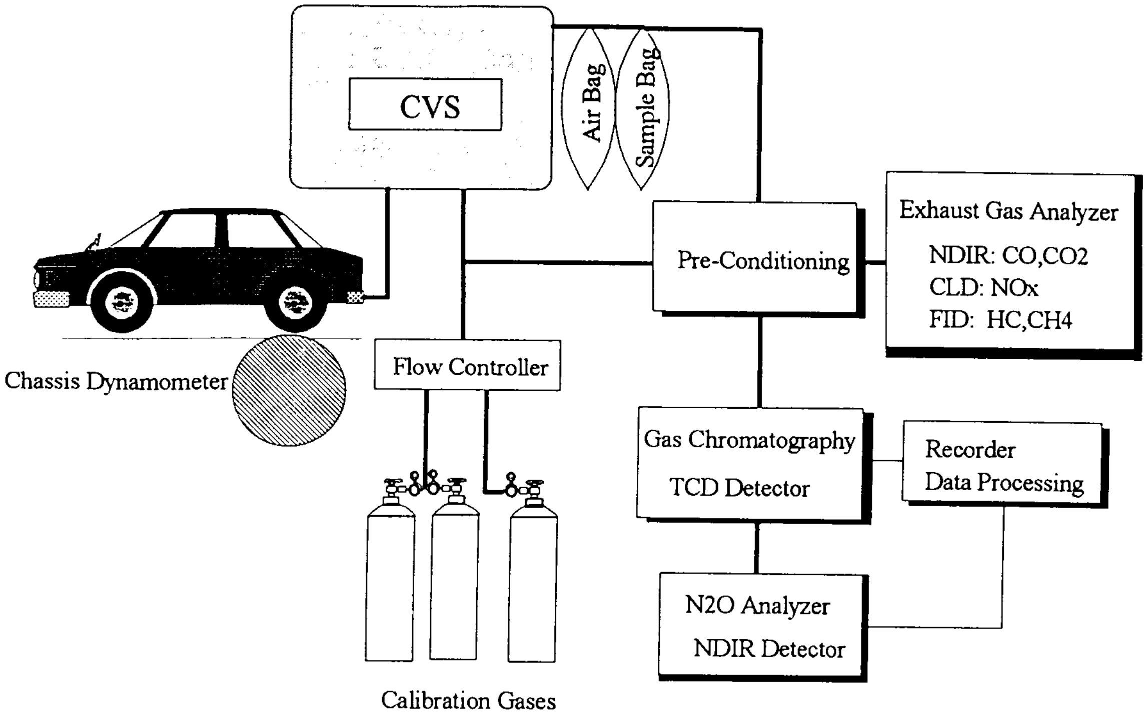


Fig. 1 Schematic of Experiment System

The objective of this study is to clarify the exhaust emission characteristics of these two components discharged from automobiles and based on these results, to estimate global emissions of methane and nitrous oxide from automobiles.

2. Experiment Apparatus and Method

(1) Measurement Method and Procedure of calculating the Emission Index

Total global emission of methane and nitrous oxide emitted from automobiles can be obtained by multiplying the total number of vehicles and the mass emission from one vehicle per year. However, the types of vehicles, annual driving mileage, percentage of fuel type used and driving pattern etc. are varied among every countries and thereby the mass emission may differ also.

Then, by measuring methane and nitrous oxide mass emissions of several kinds of vehicles under various driving conditions, the emission index required for estimating the total global emission was considered. In this study, we have chosen test vehicles listed in table 1. For typical type of vehicles for the global emission estimation, we have interested mainly three way catalyst equipped vehicles which is considered to have high nitrous oxide emission and a natural gas fueled vehicle which has high methane emission characteristics.

For the measurement of these two components, chassis dynamometer based exhaust emission measurement system shown in Fig.1 was used and several driving modes based on typical test driving modes used in each country were selected and methane and nitrous oxide emissions of the each vehicle were measured under these driving modes.

Finally, with statistical data concerning transportation energy, total fuel consumed or numbers of vehicles in each country , methane and nitrous oxide mass emission of unit driving distance or unit fuel consumption were calculated for the emission index. The index based on relations of other exhaust gas component (NOx for nitrous oxide, HC for methane) was also considered.

(2) Gas Analyzing Method

To observe methane and nitrous oxide emission behaviors under each driving conditions, a continuous measuring with high response is necessary. However, the concentration of these components in automotive exhaust is very low and high level carbon monoxide and carbon dioxide coexist simultaneously and consequently, the measurement was very difficult with conventional measuring methods. So, we developed a non dispersive infrared analyzer (NDIR) combined with oxidation catalyst for pre-conditioning of the sample gas for nitrous oxide measurement and have used for direct exhaust gas measurement from the exhaust pipe[1),2)]. Methane concentration has been measured by deducting the non methane hydro-carbon concentration value from the total hydro-carbon concentration value.

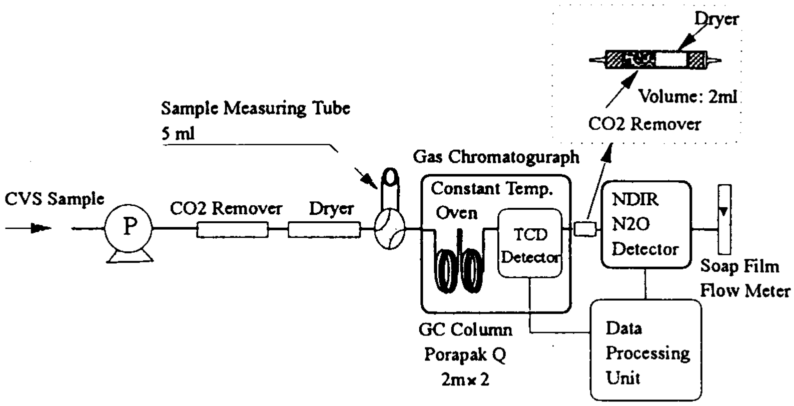


Fig.2 Sample Flow Diagram of GC-NDIR Method

When measuring mass emission of nitrous oxide by CVS method, the effect of coexisting interfering components in sample gas became not negligible because high sensitivity measurement is required. Then, combining NDIR detector and a gas chromatography, new measuring method (GC-NDIR) where coexisting interfering components are removed first then only nitrous oxide is measured by NDIR detector connected with TCD detector was developed[3)]. Fig.2 shows the principle.

3. Test Results and Discussion

(1) Methane and Nitrous Oxide Emission Characteristics of the Tested Vehicles

The emission characteristics of methane and nitrous oxide of gasoline fueled vehicles (no catalyst, with oxidation catalyst, with three way catalyst), a compressed natural gas

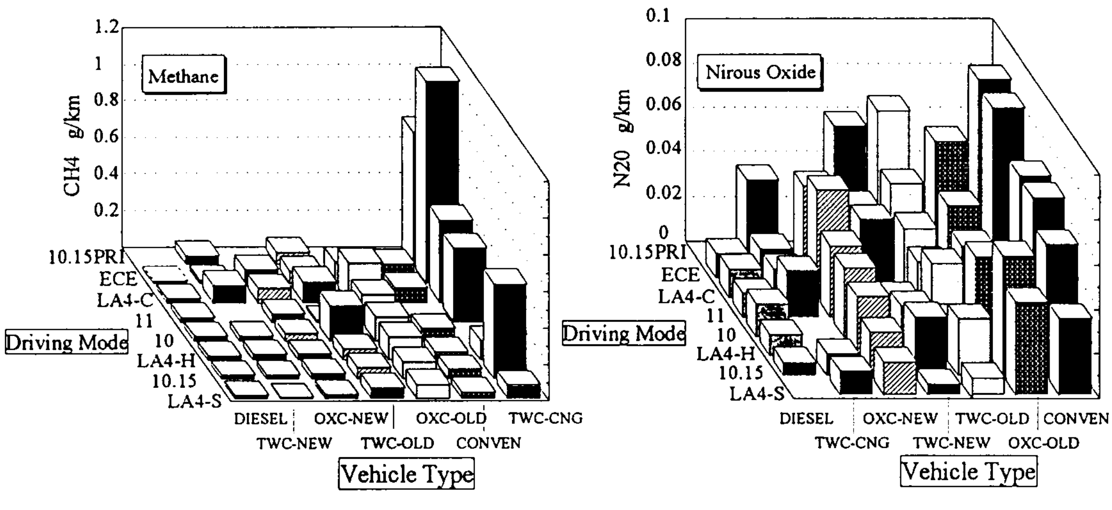
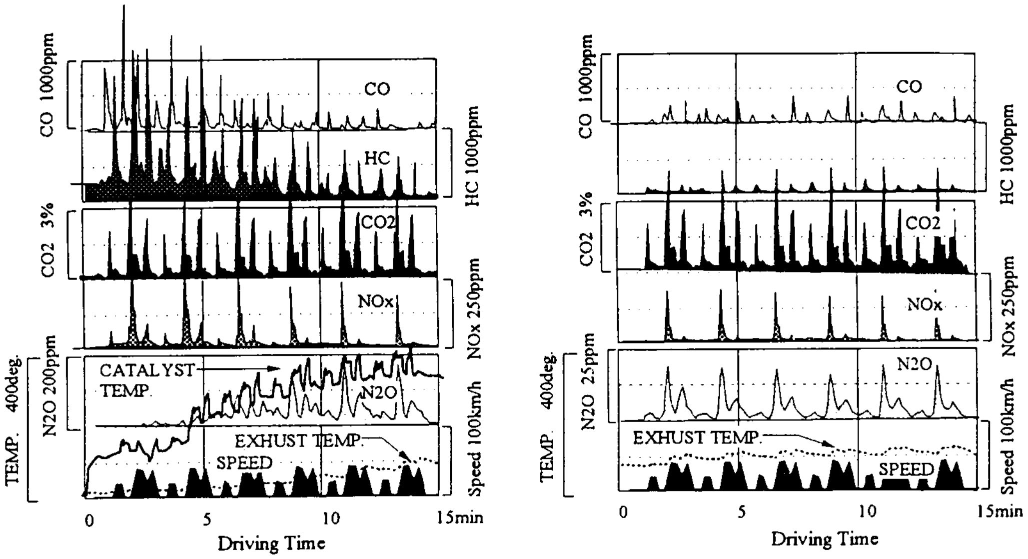


Fig.3 Methane and Nitrous Oxide Emission Characteristics of Tested Vehicles Under Various Driving Modes



(a) Cold Start Condition

(b) After Warm up

Fig.4 Emission and Temperature Behaviours of a TWC vehicle

(CNG) fueled vehicle and a diesel vehicle are shown in Fig.3. At the case of the diesel vehicle, both emissions are low. At the case of gasoline fueled vehicles, nitrous oxide emissions are highest at the old three way catalyst equipped vehicle and the lowest is the new three way catalyst vehicle. This difference in nitrous oxide emission between the new and the old three way catalyst vehicle is over 10 times. On the contrary, difference in methane was less than 3 times.

Table 2 Emission Index of Each Type of Vehicle

Vehicle Type	Emission Index (g/Km)	
	CH4	N2O
Average of TWC	**0.0625**	**0.048**
TWC-OLD	0.0730	0.144
TWC-CNG	0.3690	0.016
OXI-NEW	0.0400	0.027
OXI-OLD	0.1740	0.058
DIESEL	0.0280	0.011
CONVEN	0.0730	0.075

Over 1 million CNG fueled vehicles are used at present in the world and it is said that CNG fueled vehicles have an advantage for green house effect due to their low CO_2 emission and considered to increase in numbers near future. Although the tested vehicle was equipped with three way catalyst and regulated exhaust emissions are satisfactory low, exhaust hydro-carbon components are almost methane and thereby it is important to consider not only CO_2 emission but also methane emissions for evaluating its advantage to global worming effect.

(2) Methane and Nitrous Oxide Emission Characteristics under Various Driving Conditions

According to the result of the emission measurement under various driving conditions, methane and nitrous oxide emissions are deeply affected by warm up conditions rather than driving mode patterns. Generally nitrous oxide is higher at cold starting modes and decreases as average speed goes up. Nitrous oxide emissions under steady-state driving conditions have also decreased according to the speed increase.

Table 3 Estimation of Methane and Nitrous Oxide Global Emission Calculated with Mileage and Numbers of Vehicles

ITEM	Local Example			WORLD
	JAPAN	USA	FRANCE	
N2O Emission Index g/km Passenger vehicle	0.0480	0.0480	0.0480	0.048
CH4 Emission Index g/km Passenger vehicle	0.0625	0.0625	0.0625	0.063
N2O Emission Index g/km Commercial Vehicle	0.0110	0.0110	0.0110	0.011
CH4 Emission Index g/km Commercial Vehicle	0.0280	0.0280	0.0280	0.028
Annual Mileage km Passenger Vehicle	9,861	16,985	13,700	13,000
Annual Mileage km Commercial Vehicle	11,278	22,314	22,000	20,000
N2O Mass Emission g/year/Passenger Vehicle	473	815	657	624
CH4 Mass Emission g/year/Passenger Vehicle	616	1,061	856	812
N2O Mass Emission g/year/Commercial Vehicle	124	245	242	220
CH4 Mass Emission g/year/Commercial Vehicle	315	624	616	560
Numbers of Passenger Vehicle	37,076,015	145,043,000	23,380,000	453,000,000
Numbers of Commercial Vehicle	22,838,608	45,698,000	31,773,500	140,000,000
N2O Mass Emission ton/year Passenger Vehicle	17,549	118,251	15,375	282,672
CH4 Mass Emission ton/year Passenger Vehicle	22,850	153,972	20,019	368,063
N2O Mass Emission ton/year Commercial Vehicle	2,833	11,217	7,689	30,800
CH4 Mass Emission ton/year Commercial Vehicle	7,212	28,552	19,572	78,400
Total N2O Mass Emission ton/year	20,382	129,467	23,064	313,472
(Percentage)	(7%)	(41%)	(7%)	(100%)
Total CH4 Mass Emission ton/year	30,062	182,524	39,592	446,463
(Percentage)	(7%)	(41%)	(9%)	(100%)

Therefore the test driving mode used for methane and nitrous oxide emission evaluation should be urban driving mode with relatively low average speed and need not to change the test mode correspondingly countries or regions since there is no significant difference among tested urban modes at warmed up conditions. However, in case of three way catalyst vehicles as shown in Fig.4, the catalyst temperature due to the engine warm up conditions affects greatly on methane and nitrous oxide emission behaviors, the test driving mode for methane and nitrous oxide measurement must reflect not only warmed up but also cold starting conditions. Thereby the emission indexes used in this report were calculated by combining cold starting and warmed up data.

Table 2 shows the emission index of each type of vehicle. The CNG vehicle has extremely high methane emission index and catalyst equipped vehicles have high nitrous oxide emission index. Vehicles with high mileage tend to increase both methane and nitrous oxide emissions.

4. Estimation of Global Mass Emissions

By using Emission index gained by the described method at the previous chapter, annual global mass emission of methane and nitrous oxide was estimated with the following three kinds of basis.

(1) Estimation based on Global Number of Vehicles

The global number of vehicles is approximately 600 million and most of them are concentrated in Northern Hemisphere countries such as the United States, European countries and Japan where exhaust gas regulations are stringent. 75% of the total are passenger vehicles and considered to be equipped with a catalyst. The annual mileage of these passenger vehicles in advanced nations is about 13,000km/year in average[4)], which is much longer than that of buses and trucks and does not defer meaningfully among the countries. According to these fact, it is considered that no significant error in the estimation will occur if the estimation is held only by passenger vehicle basis. So the following estimations were held only with passenger vehicle basis.

Table 3 shows the estimation results. In that table, we also shows the total local emissions in Japan, the United States and France, which is the typical example of European countries. The estimated global mass emissions of methane from automobiles is 446.463 ton/year and that of nitrous oxide is 313.472 ton/year by global numbers of vehicles basis.

Table 4 Estimated Mass Emission by Global Fuel Consumption

Global Total Mass Emission	
Nitrous Oxide	352,364ton/year
Methane	578,808ton/year

(2) Estimation based on Global Fuel Consumption

Total amount of gasoline and light oil annually consumed in the world are mostly used for automobiles and consequently, annual global emission of methane and nitrous oxide can be estimated from statistical global fuel consumption data if the emission index of these two component per unit fuel is clarified. Table 4 shows the estimation results based on global fuel consumption[5]. The results are slightly higher than that of global number of vehicles basis.

(3) Estimation based on Correlation with Other Gas Components

CO, HC and NOx in automotive exhaust are the regulated components in most countries and thereby their emissions in each countries could be easily obtained. Supposing that the main cause of methane is remainder of the total HC after catalyst oxidation and that of nitrous oxide is mostly by-product formed during reduction process of NOx with catalyst, there may be relations between total HC and methane emissions and between NOx and nitrous oxide emissions. Then an estimation of the emission index based on these relations was

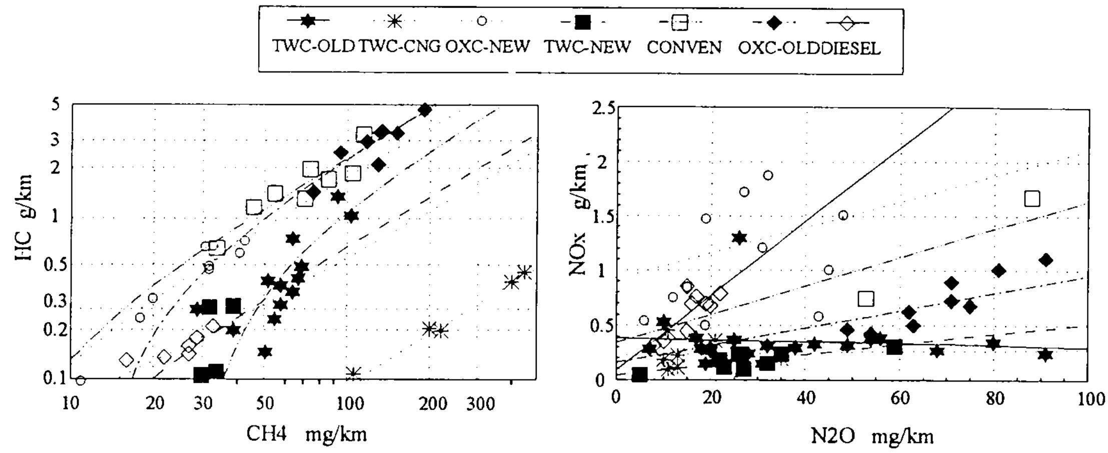


Fig.5 Correlations between HC and CH4 and Correlations between NOx and N2O

considered. The advantage of this method is to calculate the mass emissions easily with officially announced HC or NOx mass emission data or the emission regulation limit if the correlation coefficient is clear.

Fig.5 shows the correlation between total HC mass emissions and methane mass emissions and that of NOx and nitrous oxide. Both figure shows the correlation between the two components are varied among types of vehicles and thereby the accuracy of the estimation may not be enough unless a correlation coefficient of each type of vehicle is used. Then, we selected typical correlation coefficient for gasoline and diesel vehicles and calculated methane and nitrous oxide emission index based on these coefficients. The result is shown in Table 5. Since actual HC and NOx emission data in each country were not clear, we used the

Table 5 Emission Index Estimated from Other Gas Component

Country	Gas Component	Regulation limit	Correlation Coefficient	Emission Index N2O	Emission Index CH4
		g/km		g/km	g/km
USA	NOx	0.62	0.200	0.1240	
	HC	0.25	0.160		0.0400
ECE	NOx	3.50	0.200	0.7000	
	HC+NOx	6.50	0.160		0.4800
JAPAN (GASOLINE)	NOx	0.25	0.200	0.0500	
	HC	0.25	0.160		0.0400
JAPAN (DIESEL)	NOx	0.60	0.037	0.0222	
	HC	0.40	0.185		0.0740

Table 6 Comparison of Estimation Results

Base of Estimation	Methane (ton/year)	Nitrous Oxide (ton/year)
Numbers of Vehicles	477,263	313,472
Fuel Consumption	578,808	352,363
Correlation of other gas	804,000	308,000

regulation limit in each country for the base of estimation. Nitrous oxide emission index gained by this method agreed with that gained by other two methods in case in Japan. However, in case in the United States or in Europe, the estimated values are much higher than that gained by other two methods. This may be caused by the difference of the test methods. Although the emission test is held after warm up in Japan, in Europe and the United States, the test is held under cold start conditions and HC and NOx emissions may be higher than Japanese test results. This may has caused the differences.

Since these regulation limits are to be adopted for newly make vehicles and the catalyst may deteriorate and its nitrous oxide emission will increase as mileage accumulated, the estimation by the regulation limit may be under-estimated than the actual emissions.

However, more accurate estimation may be possible with this method by applying actual HC and NOx emission data in each country.

Table 6 shows the global methane and nitrous oxide mass emissions calculated from these emission index with the comparison of the other estimation results. Although only the emission indexes of Japan in Table 5 were applied for the global estimation, methane value is much higher than that gained with the other method.

6. Conclusion

Emission characteristics of methane and nitrous oxide from automobiles were experimentally analyzed and the global emissions of these two components were estimated by 3 method with the emission index gained from the measurement results.

Total annual mass emissions from automobiles are 0.477Tg/year for methane and 0.313Tg/year for nitrous oxide by numbers of vehicle basis and similar results were obtained by the other two methods.

Although the amount of methane from automobiles in total global emission is less than 1%, that of nitrous oxide is almost equal to have estimated in combustion field and it is suggested that the percentage of global nitrous oxide mass emission from automobiles in combustion field is higher than what had been estimated..

By forecasts of the growth of catalyst equipped vehicles due to tighter exhaust emission regulations in Europe or rapid increase in vehicles in Asia, the importance of methane and nitrous oxide from automobiles will increase here after and we will need to continue further research of these components in automotive field.

References

1) N.Koike, M.Odaka: "Nitrous Oxide in Automotive Exhaust Gases"
Proceedings of 23rd meeting of Traffic Safety & Nuisance Research Institute

2) N.Koike, M.Odaka: "Nitrous Oxide Emission Characteristics from Automobiles"
Proceedings of JSAE 1993 Autumn meeting October 1993

3) N.Koike, M.Odaka: "Nitrous Oxide Emission Characteristics from Three Way Catalyst Equipped Vehicles"
Proceedings of 24th meeting of Traffic Safety & Nuisance Research Institute

4) Automotive Industry Handbook 1994 Daily Automobile Journal Co.Ltd

5) Transportation Energy Handbook 1994
Transportation Policy Bureau, Ministry of Transport