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NO₂ LEVELS IN DIESEL EXHAUST

By

W. F. Marshall

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TABLE OF CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	1
Test procedures and results.....	2
Summary and conclusions.....	6

ILLUSTRATIONS

<u>Fig.</u>		
1.	NO ₂ fraction of total NO _x vs engine load--Engine No. 2.....	3
2.	NO ₂ fraction of total NO _x vs exhaust temperature--Engine No. 2.....	3
3.	NO ₂ fraction of total NO _x vs engine load--Engine No. 3.....	4
4.	NO ₂ fraction of total NO _x vs engine load--Engine No. 4.....	4
5.	NO ₂ fraction of total NO _x vs engine load--Engine No. 5.....	4
6.	Effect of exhaust treatment on NO ₂ fraction--Engine No. 1, rated speed.....	4
7.	Comparison of NO ₂ results: ambient temperature CL vs heated CL.....	5
8.	NO ₂ fraction of total NO _x vs exhaust temperature--heated and ambient temperature CL's.....	5
9.	NO _x levels obtained with two analyzers: ambient temperature CL versus heated CL.....	6

TABLES

1.	Engine specifications.....	2
2.	Ventilation rates for dilution of toxicants to TLV's, cfm/rated hp.....	5

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ABSTRACT

The safe operation of diesel-powered equipment in underground mines is predicated on there being sufficient ventilation to dilute the exhaust such that none of the toxicants in the dilute mixture exceed allowable levels. In order to determine the ventilation requirement for an engine, it is necessary to measure levels of the various toxicants in the exhaust. Measurements in the past typically either have excluded nitrogen dioxide or have not provided information on nitrogen dioxide specifically. Primarily this exclusion has resulted from lack of a fast, on-line analytical method.

Development of the chemiluminescence analyzer appears now to provide the requisite capability; this instrument has been demonstrated to yield valid information for nitrogen dioxide levels and has been applied in a series of experiments conducted at the Department of Energy's Bartlesville (Okla.) Energy Research Center (BERC).

Measurements of nitrogen dioxide in the exhaust from several diesel engines operated over wide ranges in speed and load were made as part of BERC's cooperative program with the U.S. Bureau of Mines. Results of these experiments indicate that nitrogen dioxide concentrations vary from less than 10 pct to approximately 30 pct of the total oxides of nitrogen. The nitrogen dioxide fraction was maximum at light load and decreased with increasing engine power. This trend was consistent for all five engines tested.

INTRODUCTION

Although data on oxides of nitrogen (NO_x) emissions from diesel engines are widely available, information on nitrogen dioxide (NO₂) emissions is rather sparse. This lack of information on NO₂ specifically has resulted both from (1) difficulties in measuring the material, and (2) from a presumption that all (or nearly all) of the NO_x discharged from engines is eventually oxidized to NO₂ in the atmosphere and that, therefore, information on NO₂ level in the exhaust was of little interest. However, NO₂ is much more hazardous than nitric oxide (NO); consequently, in underground mines the levels of NO₂ in the exhaust could be an important factor in assessment of hazard due to presence of diesel exhaust in the working environment. The oxidation of NO to NO₂ in a mine should, ordinarily, not be of major importance because this is a rather slow reaction in dilute mixtures of exhaust in air. For example, if the exhaust products were diluted such that the initial level of NO was 25 ppm [its threshold limit value (TLV)], the time

¹Mechanical engineer.

required to attain levels of 5 ppm (TLV of NO₂) is approximately 36 minutes. An adequate ventilation system would ensure that the residence time would be much less than this. Moreover, if the ventilation were sufficient to dilute the exhaust to a level of 12.5 ppm NO, the time required to reach 5 ppm NO₂ is greatly increased--ca. 3 hours. Thus, ventilation appears to be a means of reducing the potential for level of NO₂ to approach hazardous concentrations. If, however, the level of NO₂ in the exhaust is significant, then the addition of the directly-generated NO₂ to that produced by oxidation of NO in the mine air could yield a total above that considered "safe" or satisfactory.

In its cooperative program with the Bureau of Mines, BERC has collected (via experiment) data on the composition of diesel exhaust from a variety of engines. In several of the engine tests, NO₂ levels were determined.

TEST PROCEDURES AND RESULTS

Tests were conducted with five engines covering several variations in design. Engine specifications are given in table 1. The engines were mounted on test stands and coupled to eddy-current dynamometers. The test modes included (but were not limited to) those specified in the 13-mode cycle test procedure.

TABLE 1. - Engine specifications

Engine	Max. power, bhp	Features
1	140	2-Stroke cycle, direct-injection
2	50	4-Stroke cycle, direct-injection
3	100	4-Stroke cycle, precombustion chamber
4	125	4-Stroke cycle, precombustion chamber
5	150	4-Stroke cycle, precombustion chamber

Additional tests with engine 1 included use of two exhaust treatment systems (catalyst and water scrubber).

Measurement of NO_x levels was made with a commercial chemiluminescence (CL) analyzer. The principle of CL is based on the reaction of NO and ozone to form an excited NO₂ molecule which subsequently relaxes to the ground state. In relaxing, the NO₂ molecule emits a photon which is detected by a photomultiplier tube or a photodiode. The amount of radiation detected is then proportional to the concentration of NO₂ formed and to the level of NO in the original sample. In order to measure total NO_x (including any NO₂ in the sample) by this technique, any NO₂ present must be reduced to NO prior to its introduction into the detection chamber. A thermal converter or catalytic converter is ordinarily used for this reduction process. The level of NO₂ is simply the difference between the two measurements (NO_x minus NO).

Results of tests with an engine have been examined for a relationship between load and the distribution--or ratio--of NO₂ to total NO_x in the exhaust.

The results (figure 1) show the highest values for the NO_2 fraction (30 to 40 pct) occurring at light-load conditions decreasing to about 10 pct at heavy loads. Plotting the NO_2 fraction versus exhaust temperature eliminates much of the scatter in the data (figure 2). Equilibrium values for NO_2/NO_x are included in figure 2; note that equilibrium is approached at the higher temperatures. All of the other engines exhibited similar dependence of NO_2/NO_x on load (figures 3 through 6).

The results of the tests in which catalytic reactors or water scrubber were incorporated into the exhaust system showed only minor differences in the ratio of NO_2 to NO_x (figure 6). Neither of the exhaust treatment systems had a significant effect on total NO_x level.

In order to assess the significance of the NO_2 emission rates in relation to those of the other toxicants, the data were examined to determine ventilation rates required for dilution of exhaust to acceptable levels. Results of these computations, based on maximum emission rate of each toxicant, are given in table 2. These results indicate that the ventilation necessary for dilution of the other toxicants is also adequate to reduce the level of NO_2 to less than 5 ppm, the present TLV for NO_2 .

From the data in the following table it can be shown that, on the basis of present values for allowable level of NO_2 , this toxicant does not play a highly significant role in the assessment of health hazards associated

FIGURE 1. - NO_2 fraction of total NO_x vs engine load
--Engine No. 2--

FIGURE 2. - NO_2 fraction of total NO_x vs exhaust temperature--Engine No. 2

FIGURE 3. - NO_2 fraction of total NO_x vs engine load
--Engine No. 3--

FIGURE 4. - NO_2 fraction of total NO_x vs engine load
--Engine No. 4--

FIGURE 5. - NO_2 fraction of total NO_x vs engine load
--Engine No. 5--

FIGURE 6. - Effect of exhaust treatment on NO_2 fraction
--Engine No. 1, rated speed--

TABLE 2. - Ventilation rates for dilution of toxicants to TLV's, cfm/rated hp

Engine	CO ₂ , (TLV=0.5 pct)	CO, (50 ppm)	NO, (25 ppm)	NO ₂ , (5 ppm)
1	36	70	133	45
2	40	150	100	52
3	44	112	44	14
4	50	22	65	25
5	42	13	43	12

with operation of diesel engines in underground mines. Moreover, recent data suggest that the sampling/analytical method employed for measurement of NO₂ might overestimate the amount of NO₂ actually present in the exhaust.

The data presented thus far in the report were based on measurements obtained with an ambient temperature CL instrument. In order to prevent condensation of water in the reaction chamber, a water trap was installed in the sample line upstream of the analyzer. Recently a CL instrument has been introduced which can accommodate wet, untreated exhaust obviating the need for the water trap. Results from a limited number of tests using this heated CL analyzer show NO₂ levels approximately two-thirds of those determined with the system which incorporates a water trap (figure 7). The effect of exhaust gas temperature on NO₂ fraction as measured by the two methods is shown in figure 8. Results obtained by both methods show similar dependence of NO₂ fraction on exhaust gas temperature and comparable values at the higher temperatures.

FIGURE 7. - Comparison of NO₂ results: ambient temperature CL vs heated CL

FIGURE 8. - NO₂ fraction of total NO_x vs exhaust temperature--heated and ambient temperature CL's

The two instruments showed good agreement with respect to total NO_x (figure 9). This indicates that losses of NO_x in the two sampling/analysis methods are not significantly different. The higher levels of NO_2 associated with the "cold" system indicate an enhancement of oxidation of NO or reduction of NO_2 in the heated system. Additional experiments are being planned in order to determine the causes of the apparent differences in NO_2 , and to determine which of the two methods yields more valid data.

SUMMARY AND CONCLUSIONS

1. Ventilation rate requirements for dilution of NO_2 to its TLV were typically much lower than requirements for other toxicants.

2. The NO_2 fraction of total NO_x in diesel exhaust varies from about one-third at low power to about one-tenth at high power modes.

3. The exhaust treatment systems (water scrubber, catalytic reactor) had a relatively small effect on NO_2 level.

4. Nitrogen dioxide concentration as measured with a heated sampling/analysis system was about two-thirds of that determined with a system which incorporated a water trap. Inasmuch as the latter system has been used for collection of much of the data that are reported to this point in time, it is reasonable to assume that those data may overestimate both the amount of NO_2 actually present in exhaust as discharged and the ventilation required to dilute the ambient level of NO_2 to its TLV.

FIGURE 9. - NO_x levels obtained with two analyzers: ambient temperature CL versus heated CL