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Ammonia Emissions from the EPA's Light Duty Test Vehicle

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ABSTRACT

Ammonia (NH_3) emissions were measured from the EPA's Light Duty Test Vehicle while operated on a chassis dynamometer. The vehicle's (1993 Chevrolet equipped with a three-way catalyst) emissions were measured for three transient (urban driving, highway fuel economy, and hard acceleration) cycles and steady state operation. Previous research[1,2] has shown that NH_3 is predominately emitted from vehicles with a catalyst (three-way or dual-bed). The vehicle's catalyst is designed to reduce nitrogen oxides (NO_x) to nitrogen (N_2) and oxygen (O_2) during normal operation. The reduction of NO_x to NH_3 occurs during periods of reducing conditions when insufficient O_2 is available. NH_3 emissions were measured during fuel-rich/reduced-O_2 conditions (open-loop control scheme). The results demonstrate that NH_3 production is correlated to combustion conditions[3]. The results also show that the amount of NH_3 produced correlates with the amount of time that the vehicle remains in the open-loop control scheme. The significance of this finding is that NH_3 production can be predicted for a fleet based on the frequency of enrichment of vehicles equipped with a three-way catalyst. The results also provide a means of determining the location of roadway links and/or specific locations where NH_3 production can be anticipated based on predicted engine power.

INTRODUCTION

North Carolina and other states have been studying[4] the overloading of nitrogen compounds that has occurred in rivers and waterways, resulting in algae plumes and fish kills. Traditionally these sources of nitrogen compounds have been blamed on runoff and overflow from agricultural operations. Acid rain monitoring networks, such the National Acid Deposition Program/National Trends Network (NADP/NTN), have indicated a continuous increase in ammonium (NH_4^+) concentration within the rain samples collected[5]. If these samples are considered as a surrogate for air concentrations, nitrogen compounds in the atmosphere are also increasing. In 1989, 85 percent of the on-road vehicles were equipped with a three-way catalyst. Remote sensing data collected in 1999 in Raleigh, NC, indicated that 97 percent of the on-road vehicles were equipped with a three-way catalyst. From 1989 to 1999, there was an 11.3 percent increase[6,7,8] in vehicles operated on North Carolina roads. The combination of a greater percentage of the on-road vehicle fleet being equipped with a three-way catalyst and an increase in vehicle fleet size resulted in a 20 percent increase of vehicles with three-way catalysts being operated on North Carolina roads. The chemistry required to generate NH_3 is a fuel-rich/reduced-O_2 condition at the catalyst. These conditions are controlled by the engine's computer and exist for power demand and start-up operation.

For example, n-octane (a common component of gasoline) could be reduced to NH_3 by reactions such as:

$$2NO + C_8H_{10} + 4O_2 \rightarrow 2NH_3 + 8CO + 2H_2O \quad (1)$$

When an excess of O_2 is available, the catalyst would function as designed to destroy the nitric oxide (NO), and the following reaction would predominate:

$$2NO + C_8H_{10} + 9.5O_2 \rightarrow 8CO_2 + 5H_2O + N_2 \quad (2)$$

To date, NH_3 emissions have been calculated based upon a mass emission for a distance traveled, resulting in evenly distributed emissions across the modeled region. Geographical information systems (GIS)-based modeling efforts allow modal and temporal distribution of emissions onto a road network rather than over a region. The resultant data of GIS-based modeling provide emissions data with better spatial resolution to support ambient air deposition and exposure assessments for populations affected by mobile emissions.

EXPERIMENTAL METHODS

The EPA's light duty test vehicle. A 1993 Chevrolet Lumina was purchased by EPA's Air Pollution Prevention and Control Division in 1998. The vehicle has a computer-controlled, fuel-injected 3.1-liter 6-cylinder engine and a three-way catalyst. The vehicle's engine control, engine, and exhaust system have not been modified and are as they were when manufactured.

The purpose of this test vehicle was to determine the functional relationship between the vehicle's engine and control system and the emissions produced. The engine and emissions control system in this test vehicle, and in most light duty vehicles now in service, are computer controlled. Emissions were measured while the vehicle was operated on a chassis dynamometer under a variety of operating conditions. The inputs to the computer from the sensors for O_2, mass air flow, engine revolutions per minute, and other parameters were monitored to determine when the computer commanded a shift from closed-loop to open-loop, fuel-enrichment operation. Under closed-loop operation, the catalyst functions as designed to produce effective emissions control. Under short periods of open-loop operation, primarily to boost the power ouput of the engine, the catalyst operating conditions are drastically affected and the emissions are greatly increased.

Vehicles are generally designed to minimize open-loop operation when being tested on a chassis dynamometer in accordance with the federal certification test cycle procedure. The test procedure was revised to include more high-speed operation, and manufacturers are thereby limited in the programmed use of open-loop operation in vehicle control schemes. However, use of fuel enrichment in vehicle control schemes is not entirely eliminated for a variety of customer satisfaction and technical (e.g., catalyst cooling) reasons. These new Supplemental Federal Test Procedures are being phased in between 2001 and 2004 model years. However, vehicles can have significant periods of open-loop operation when high power demands (e.g., heavy acceleration) are commanded by the vehicle operator, especially in vehicles built in earlier model years.

In this study, the vehicle engineering parameters correlated with the NH_3 emissions are recorded and analyzed with an instrumented vehicle. The instrumented vehicle was tested on a number of commonly used dynamometer test cycles as well as evaluated on the roadway. These data will be useful in assessing the emissions impact at specific roadway segments where fuel enrichment is prevalent.

An additional purpose of this test vehicle was to establish a relationship between emissions measured on the road and on the dynamometer.[9] This is important because the majority of emissions data to date have been collected while the vehicles were operated on dynamometers, yet the emissions are modeled for vehicles operated on the road.

The vehicle contains four deep-cycle 12-volt batteries and a true sinusoidal inverter to power instrumentation and operate data-recording computers. The vehicle is equipped with a receiver type hitch and a lightweight trailer rated for 204 kilograms.

Measurement methods. Gaseous measurements are made for carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbons (HCs), nitrogen

oxides (NO_x), and NH_3. The exhaust gas is sampled at three ports. The gas sampled from the first port is cooled to remove water and delivered to the CO, CO_2, HC, and NO_x monitors under a slight pressure [~12 centimeters water (H_2O)]. Gas sampled from the second port is diluted, cooled with conditioned ambient air, and delivered to the NH_3 and CO_2 monitors. The conditioned ambient air has been dried and cleaned using silica gel, charcoal, and a mol sieve. The second CO_2 monitor measures the diluted sample concentrations to ensure that a dilution ratio of ~15:1 is being maintained. The dilution ratio was measured to prevent moisture condensation in the sample lines and to calculate the true exhaust gas NH_3 concentration. The third port is used for direct exhaust gas sampling. The vehicle is also equipped with hardware and software to record the engine computer data stream [i.e., revolutions per minute (RPM), fuel flow, and commanded enrichment]. This data stream, along with a wide-range O_2 sensor mounted in the exhaust system, is used to determine if the vehicle is operating in a fuel-rich/O_2-reduced condition. Exhaust gas concentrations, engine computer data, and other data of interest are recorded using a personal computer (PC).

Two techniques were used to measure NH_3: (1) analysis of NH_4^+ ions from impingers containing dilute sulfuric acid (H_2SO_4),[10,11] and (2) chemiluminescence analyzer [12] determination of NH_3 as NO. The acid impinger or gas washing technique represents an average concentration over a period of time, usually 10-20 minutes. Gas was sampled from the third port, pulled through a gas-washing vessel, equipped with a diffusing cylinder and filled with ~0.01 N H_2SO_4, at a rate of approximately 1 liter per minute. Gaseous NH_3 in the sample is absorbed into solution as bubbles from the gas sample ascend through the liquid column. The concentration of NH_3 in solution is then determined (as NH_4^+) by colorimetric flow injection analysis or by ion chromatography using a Lachat Quikchem Model 8000 FIA Auto-analyzer with three channels [ortho-P, NH_4^+, and nitrate (NO_3^-)]. The method is based on sodium salicylate (not alkaline phenol) and has a 10 ppb detection limit for NH_4^+.

The TECO Model 17C chemiluminescence NH_3 analyzer is designed to sample at intervals of no less than 40 seconds. This is reasonable because, when operated in the automatic mode, the analyzer has to sample NO, NO_2, NO_x, and total nitrogen (N_t) before there is enough information to calculate an NH_3^+ concentration. To overcome this sampling time problem, two chemiluminescence analyzers were operated in the manual mode, one indicating total nitrogen (N_t= NO + NO_2+ NH_3) continuously and the other indicating NO_x [NO + nitrogen dioxide (NO_2)] continuously. The difference between these two analyzers represented the NH_3 diluted concentration. The manually operated analyzers updated the indicated concentrations every 0.5 second and operated in a range of 0-100 ppm. True NH_3 gas concentration was determined based upon the CO_2 dilution ratio.

Validation of ammonia measurements. Sampling from NH_3 gas cylinders analyzed by Scott Technologies validated the gas washing technique. Cylinder gas was diluted with humidified zero air and sampled using the gas washing technique. Dilution flow rates were regulated using rotameters and measured using a DryCal flow measurement device. The comparison between the gas washing technique and diluted cylinder gas concentrations indicated a correlation coefficient of 0.93 (r^2) and Equation (3).

$$\text{Gas Washing Technique, ppm} = 1.7515 + 0.8561\,(\text{Diluted } NH_3 \text{ Cylinder Gas, ppm}) \quad (3)$$

Diluted cylinder gas concentrations ranged from 2 to 28 ppm, and 36 individual tests were conducted. Figure 1 provides a graphical representation of this comparison.

The dual analyzer technique was calibrated using NO and NH_3 gas. The N_t calibration data exhibited a correlation coefficient of 0.9993 (r^2) and Equation (4).

$$\text{Analyzer Response [Nt], ppm} = 0.6999 + 0.9844\,(\text{Cylinder Gas [Nt], ppm}) \quad (4)$$

Calibration concentrations ranged from 0 to 85.6 ppm, and the analyzer response was characterized before and after data collection. Equation (4) is the result of all input concentrations regressed onto all response concentrations. Converter efficiency was evaluated with both NO and NH_3 present. Converter efficiency exhibited a correlation coefficient of 0.9995 (r^2) and Equation (5).

Analyzer Response [Nt], ppm = -1.2973 + 0.9808 (Cylinder Gas [Nt], ppm) (5)

During calibrations, analyzer response was adjusted to ensure that the concentrations recorded were accurate. Figure 2 compares these response data and is considered to represent an estimate of precision and accuracy of the concentrations recorded. These data include the calibration responses, converter efficiency, and calibration checks conducted between tests. Figure 2 also shows that the analyzers remained stable throughout the testing.

The gas washing technique is an accepted method, whereas the dual chemiluminescence analyzer technique is an unconventional technique. The gas washing technique was used to validate the dual analyzer technique. Automotive exhaust gas samples were collected simultaneously using the gas washing and dual analyzer techniques. Average concentrations were calculated for each of the collected samples for both the gas washing and dual analyzer techniques. The comparison between gas washing and dual analyzer techniques indicated an average difference of 1.6 ppm, a correlation coefficient of 0.8604 (r^2), and Equation (6).

Gas Washing Technique, ppm = 1.6528 + 0.9630 (Dual Analyzer Technique, ppm) (6)

Average concentrations ranged from 0 to 71 ppm, and there were 14 tests. Figure 3 provides a representation of this comparison, and Table 1 provides the average concentrations determined for each of the 14 tests.

Air flow rate calculations. A significant source of error for mobile source emission rate calculations is associated with the volumetric flow rate through the engine. Dynamometer testing facilities provide the opportunity to compare the total exhaust gas volume measured by the test facility to the total exhaust gas volume calculated for the test vehicle. Test vehicle volumes are the summation of second-by-second flow rate calculations. These total exhaust gas volume calculations contain numerous sources of error including sensor response times, changing volumetric efficiency, temperature and pressure changes, and changing chemistry within the exhaust gas. Test vehicle flow rates were calculated using three methods. The first took advantage of the mass airflow rate data included in the engine computer data stream. The second method used RPM, the internal combustion volume of the motor, and appropriate corrections for temperature and pressure. The third method used the volume of fuel injected and the engine-computer-data-stream-commanded air/fuel ratio. The first method used the engine computer data channel, and mass air flow (MAF) rate and was calculated using Equation (7).

$$MAF_{AIR} = (AFR)(Vol_E)(Pi/Ps)(Ts/Ti)(M/28.9)(C_1) \quad (7)$$

where:

MAF_{AIR} = Mass air flow, liters/sec.

AFR= Engine computer flow rate, g/sec.

Vol_E = Volumetric efficiency, used 75%.

Pi= Intake manifold pressure, mmHg.

Ps= Pressure, standard (760 mmHg).

Ts= Temperature, standard (298 K).

Ti= Intake manifold temperature, K.

M= Moles at 28.9 grams/mole.

C_1 = Constant, 24.45 liters/mole.

The second method used the known volume of the engine, the RPM, and the intake air manifold conditions. RPM airflow rate through the engine was calculated using Equation (8).

$$RPM_{AIR}=(REV)(E_{vol})(1/2)(Vol_E)(Pi/Ps)(Ts/Ti) \quad (8)$$

where:

RPM_{AIR} = RPM air flow rate, liters/sec.

REV = Revolutions per second,RPM/60.

E_{vol} = Engine internal volume, 3.1 liters.

½ = 2 revolutions for engine volume.

Vol_E = Volumetric efficiency, used 75%.

Pi= Intake manifold pressure, mmHg.

Ps= Ambient pressure, mmHg.

Ts= Ambient temperature, K.

Ti= Intake manifold temperature, K.

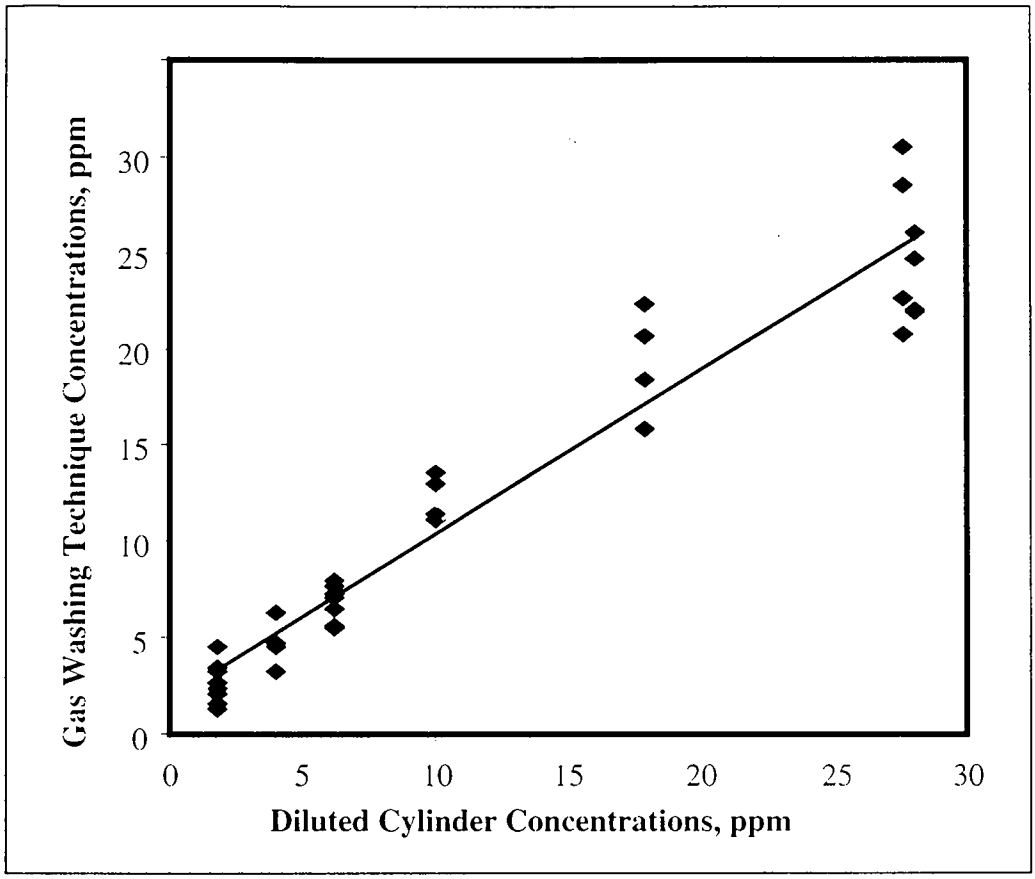

Figure 1. Comparison of the gas washing technique measured concentrations to the ammonia gas standard diluted concentrations.

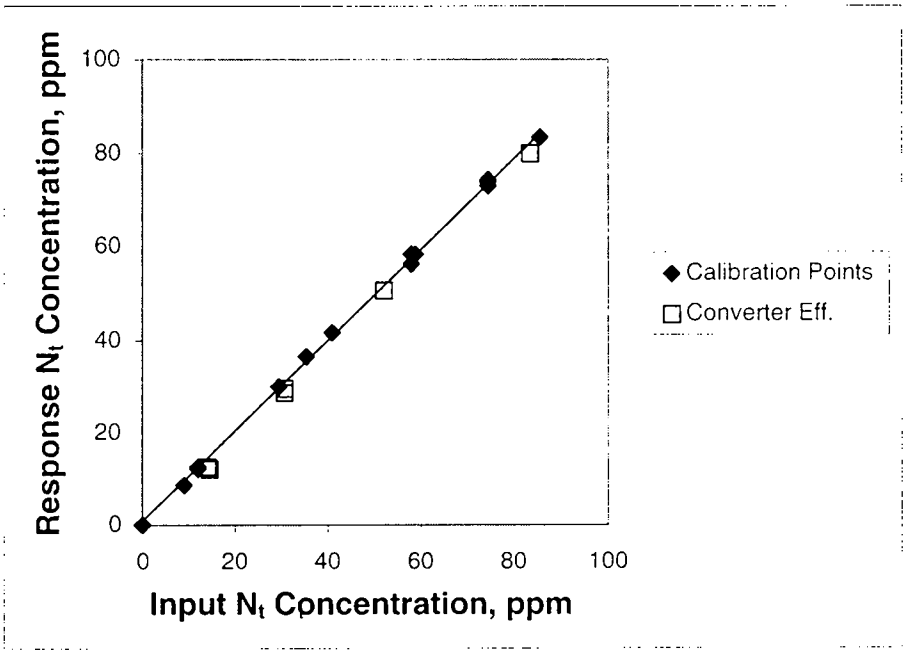

Figure 2. Comparison of the Scott Specialty Gases calibration standards and the Teco analyzer response. These data include the calibration responses, converter efficiency checks, and calibration checks conducted between tests.

Test Conducted	Gas Washing, ppm	Dual Analyzer, ppm	Average MAP, mmHg	Dyno Test Volume, m^3	Engine Computer Air Flow, m^3	RPM Technique Volume, m^3	Injector PW Technique Volume, m^3
FTP	18.6	23	352.00	12.46	12.22	14.198	13.48
FTP	12.8	17.4	351.85	13.39	13.85	14.888	13.98
505	8.9	15.3	367.31	6.24	7.10	6.344	5.82
Steady State	5.7	10	300.54	7.97	6.11	8.881	5.78
Hwy Fuel	16	38.8	394.08	10.90	11.30	12.212	8.80
FTP	4.7	3	352.97	13.38	14.02	15.226	14.35
505	0	7	369.53	5.63	6.34	6.009	5.33
Steady State	1.6	12.2	302.44	8.03	5.84	8.568	5.58
Hwy Fuel	2.4	5.7	392.89	11.04	12.24	12.337	12.35
Hwy Fuel	6	11.4	395.24	10.54	12.03	12.168	11.55
Hard Acceleration	51.1	52.6	425.48	11.12	13.24	8.205	8.11
Hard Acceleration	70.7	68.8	434.56	11.10	13.22	8.355	7.80
Hard Acceleration	40.3	61.8	432.80	10.38	13.28	8.388	8.17
Hard Acceleration	52.7	37.9	439.50	10.72	13.78	8.346	8.33

MAP: Manifold absolute pressure.
FTP: Federal test procedure, 40 CFR, Part 86, Urban Driving Cycle.
505: Represents the third sample bag (505 seconds) of the FTP, urban driving cycle, referred to as the "hot 505."
Hwy Fuel: Federal Test Procedure, 40 CFR, Part 86, Highway Fuel Driving Cycle.
Hard Acceleration: Driving cycle included with the Clayton dynamometer software package, described in Figure 4.

Table 1. Comparison of average ammonia concentrations, manifold pressures, and test cycle volumes calculated using the three flow method calculation techniques.

The third method used the injector pulse width data channel provided by the vehicle's computer. Dependent upon commanded power, the engine control strategy changes the ratio of pulse width frequency to MAP sensor voltage. This makes an accurate calibration (using total fuel volume) of the fuel injectors nearly impossible. This response is shown in Figure 5. Figure 5 also demonstrates how the calibration between injector pulse width and MAP sensor volts changes during commanded fuel enrichment. The volume of gas injected per pulse width was determined by recording the total fuel volume combusted and the total number of pulse widths over the same period of time. Fuel density and carbon content values were taken from References 12, 13, and 14, and no actual fuel analysis was conducted. Injector-pulse-width-calculated airflow rate through the engine was calculated using Equation (9).

$$Inj_{AIR} = [(PW)(A/F) + (PW)](C_2) \quad (9)$$

where:

Inj_{AIR} = Airflow rate, liters/sec.

PW = Injector pulse width, g/sec.

A/F = Engine computer air-to-fuel ratio.

C_2 = Constant, 0.84602 liter/g.

The greatest contribution to the uncertainties of flow rate is the constantly changing volumetric efficiency of the engine. Volumetric efficiencies ranged from 89 to 66 percent, respectively, for low to high engine flow rates with a correlation coefficient of 0.77(r^2). An average volumetric efficiency of 75 percent was chosen for the calculations to provide a reasonable median of

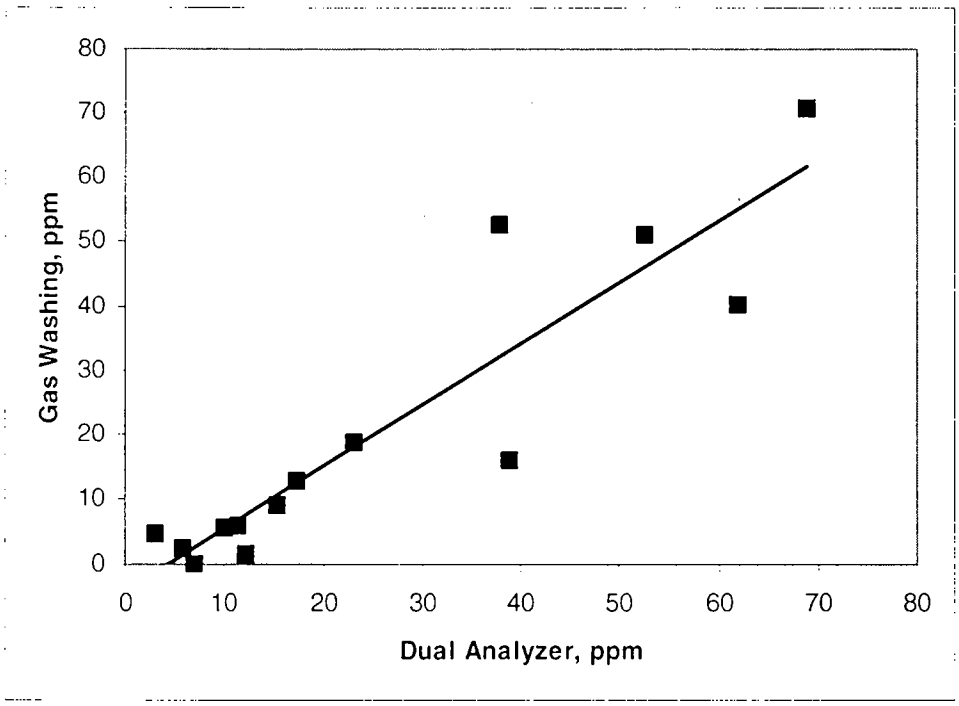

Figure 3. Comparison of the dual analyzer technique measured ammonia concentrations to the gas washing technique measured ammonia concentrations.

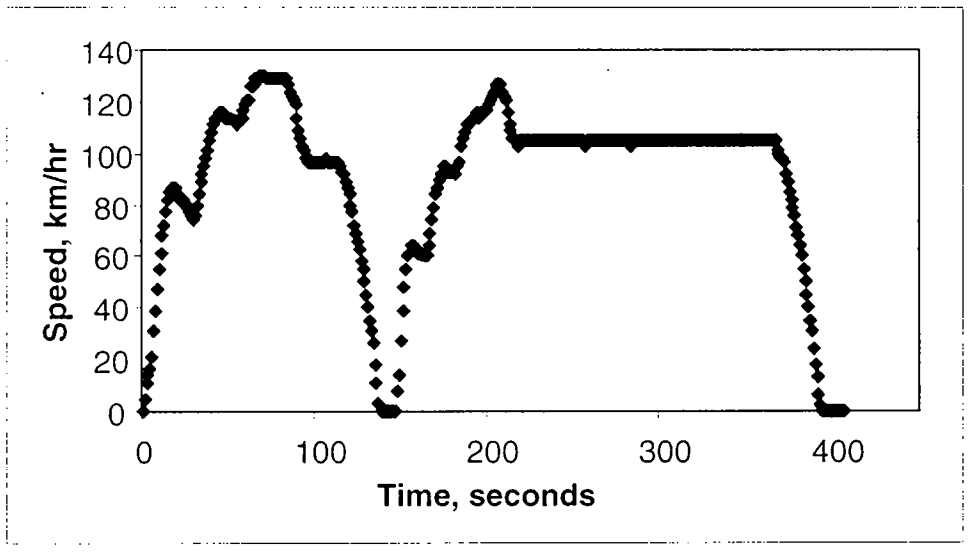

Figure 4. Speed versus time trace for the hard acceleration cycle.

differences across the three flow method techniques. This data collection effort included significant loads on the engine, resulting in enrichment events. Volumetric efficiency is a function of load, and the results can be seen in Figure 6. Figure 6 shows how the total test volume calculated by each of the three methods compares to the volume of exhaust gas determined by the Georgia Institute of Technology dynamometer facility. Figure 6 also shows how the repeated tests exhibited very similar differences from the dynamometer facility (i.e., data points are clustered

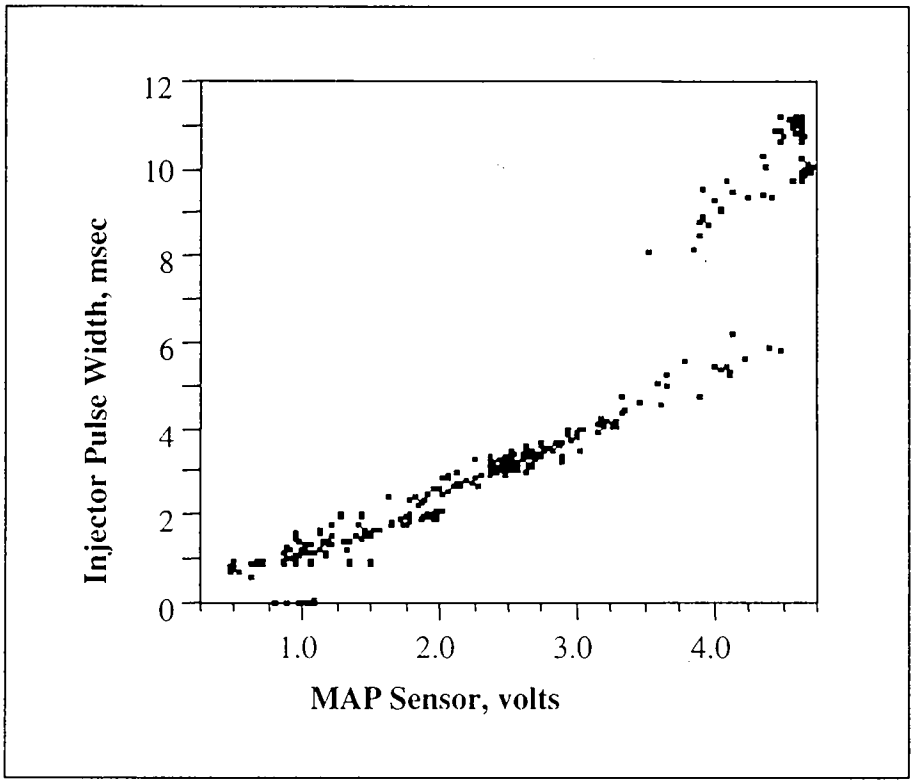

Figure 5. The relationship between injector pulse width and the intake manifold absolute pressure. The break in the graph is where enrichment combustion conditions were being commanded by the engine computer.

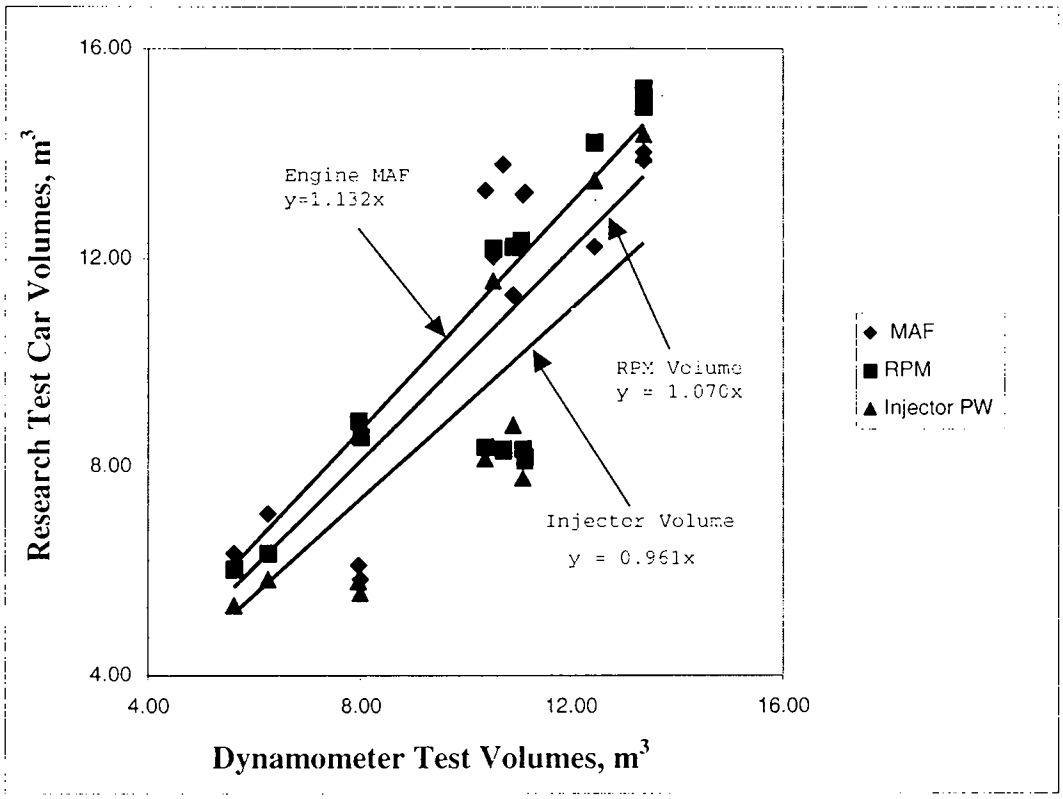

Figure 6. Comparison of the air volumes determined using the instrumented vehicle and the air volumes determined by the dynamometer facility.

together by the test cycle operated). Table 1 contains the total volume of exhaust gas as determined by the dynamometer facility and each of the three flow rate calculation techniques used for the test vehicle engine.

Ammonia mass emissions. NH_3 mass emissions are the product of NH_3 measurements (concentrations) and the air flow rate (volume/time) calculations. The concentrations for these dynamometer tests are determined using the dual analyzer technique, and the mass air flow rate was obtained from the engine computer data stream (MAF_{AIR}) on a second-by-second basis, as shown in Equation (10).

$$NH_3 \text{ Emission} = (N_{tAnalyzer1} - NO_{xAnalyzer2})(DR)(MAF_{AIR})(C_3) \quad (10)$$

where:

NH_3 Emission = Ammonia emission, g/sec.

$N_{tAnalyzer1} - NO_{xAnalyzer2}$ = Ammonia concentration, ppm.

DR = Dilution ratio as indicated by two CO_2 analyzers.

MAF_{AIR} = Mass air flow, mole/sec.

C_3 = Constant, 28.9 g/mole.

The total grams per test value was calculated by summing the grams per second values for each test, and the grams per mile was calculated by dividing the total grams per test by the total distance traveled during the test. The signal-to-noise ratio for the calculated NH_3 concentrations was a concern. The N_t and NO_x data were smoothed using rolling averages, a macro was used to resolve differences when NO_x was greater than N_t and additional smoothing functions were applied to the final NH_3 concentrations. Dilution ratio is the ratio between the CO_2 analyzer (concentrations) sampling the raw exhaust gas and the CO_2 analyzer (concentrations) sampling the gas being delivered to the NH_3 analyzers.

Test matrix. The hypothesis was that the test vehicle would produce NH_3 only when the exhaust gas O_2 concentrations were low enough to facilitate reduction chemistry within the catalyst.

Dynamometer test cycles were chosen based upon two criteria. The first criterion was to collect data using a test cycle frequently used by other testing laboratories. The FTP is the most common test, providing a large data set for comparison, and this comparison might also provide some insight as to why NH_3 has only recently become recognized as a significant mobile emission. The second criterion was to collect data using a test cycle that included significant enrichment opportunities. The goal of this work was to demonstrate the NH_3 emission potential for the test vehicle (passenger light duty vehicle) and develop a relationship between the load (percent of time in enrichment) and the amount of NH_3 produced. The test vehicle was used to collect these data while operating through three transient dynamometer cycles and one steady state (72 km/hr) cycle. The transient cycles included the FTP, highway fuel economy, and hard acceleration. The FTP consists of a cold-start urban driving cycle, a 10-minute soak, and a hot-start repeat of the initial 505 seconds. The steady state data collection began after engine temperature and emissions had stabilized. The highway fuel economy cycle is conducted at higher speeds and less acceleration modes than FTP. The FTP and highway fuel economy cycles are EPA test cycles described in 40 CFR. The hard acceleration cycle was included with the Clayton dynamometer software package. The ability of the catalyst to form NH_3 was also considered to be an age factor. The testing included the original catalyst (with ~ 120k kilometers) and a new General Motors - Original Equipment Manufacturer (GM-OEM) catalyst (with ~ 800 kilometers).

RESULTS AND DISCUSSION

The results have shown a correlation between NH_3 emissions and enrichment events. Table 2 provides the percentage of time that the test vehicle was operating in enrichment conditions and the average emissions for each of the test cycles and catalyst. Average values reported in Table 2 have been calculated by combining the old and new catalyst test results for each of the cycles tested. Although emissions of NH_3 were typically higher with the old catalyst, not enough tests were made to define a difference.

Data indicating fuel-rich/reduced-O_2 conditions were analyzed for correlation to average

Cycle	GM OEM O_2 Sensor Enrichment Time, %	EPA O_2 Sensor Enrichment Time, %	Test Emissions, g/km	Predicted Emissions [GM/EPA], g/km
FTP[A]	6.8	2.5	0.040	0.052 / 0.030
FTP[A]	6.3	3.7	0.037	0.047 / 0.040
505[A]	11.3	6.3	0.035	0.090 / 0.062
Steady State[A]	0	0	0.009	0.000 / 0.009
Hwy Fuel[A]	4.8	2.3	0.050	0.034 / 0.029
FTP[B]	6.1	3.4	0.007	0.045 / 0.037
505[B]	6.6	2.4	0.027	0.050 / 0.029
Steady State[B]	0	0	0.011	0.000 / 0.009
Hwy Fuel[B]	3.0	0.7	0.008	0.019 / 0.015
Hwy Fuel[B]	3.4	2.0	0.015	0.022 / 0.025
Hard Acceleration[B]	22.9	22.4	0.145	0.189 / 0.197
Hard Acceleration[B]	18.7	21.7	0.204	0.153 / 0.191
Hard Acceleration[B]	11.6	13.1	0.186	0.093 / 0.119
Hard Acceleration[B]	16	13.1	0.135	0.130 / 0.119
Average Values				
Steady State	0	0	0.010	0.000 / 0.009
505	9.0	4.4	0.031	0.070 / 0.046
FTP	6.4	3.2	0.028	0.048 / 0.035
Hwy Fuel	3.7	1.7	0.024	0.025 / 0.021
Hard Acceleration	17.3	17.6	0.168	0.141 / 0.157

"A" denotes the use of the original catalyst with 120k km and "B" denotes the use of a new catalyst.

Table 2. The relationship between percent enrichment and ammonia emissions.

dynamometer emissions and modal (second by second) emissions. The average dynamometer emission analysis was to verify that the production of on-road NH_3 emissions could be predicted, and modal analysis was to develop a method of predicting on-road NH_3 emissions. NH_3 average emission rate (g/km) per test cycle was regressed onto the percentage of cycle time that enrichment conditions existed. Enrichment indicators included the engine computer data stream, the GM-OEM sensor volts, and the EPA-installed wide-range O_2 sensor.

The engine computer data stream included an indicator of either "rich or lean" conditions as calculated by the engine computer using the GM-OEM O_2 sensor. Engine combustion control is dithered between rich and lean conditions for drivability and catalyst operation. Hesitation-free acceleration requires a slightly rich combustion mixture, and complete oxidation requires a slightly lean combustion mixture. The rich and lean indicator reflected this dithered operation with a range of 43.8 to 57.4 percent of the time indicating rich operation. The engine computer did maintain an indication of rich conditions during the short periods of significant NH_3 production, but the percentage of time indicating rich conditions was not sufficient to establish a correlation to average NH_3 emissions.

The second engine computer indicator of enrichment was the GM-OEM O_2 sensor voltage. The sensor voltage ranged between 0 and 1 volt, with 0 indicating lean conditions and 1 indicating rich conditions. A graphically determined voltage was derived and used as an indicator of enrichment. Any values greater than 0.85 volt were considered to be rich combustion mixtures. Figure 7 provides an indication of this sensor's performance while NH_3 concentrations were being measured for one of the hard acceleration test cycles. Figure 7 shows a direct correlation between the O_2 sensor's maximum voltage reading and NH_3 production. A regression analysis of percent enrichment and

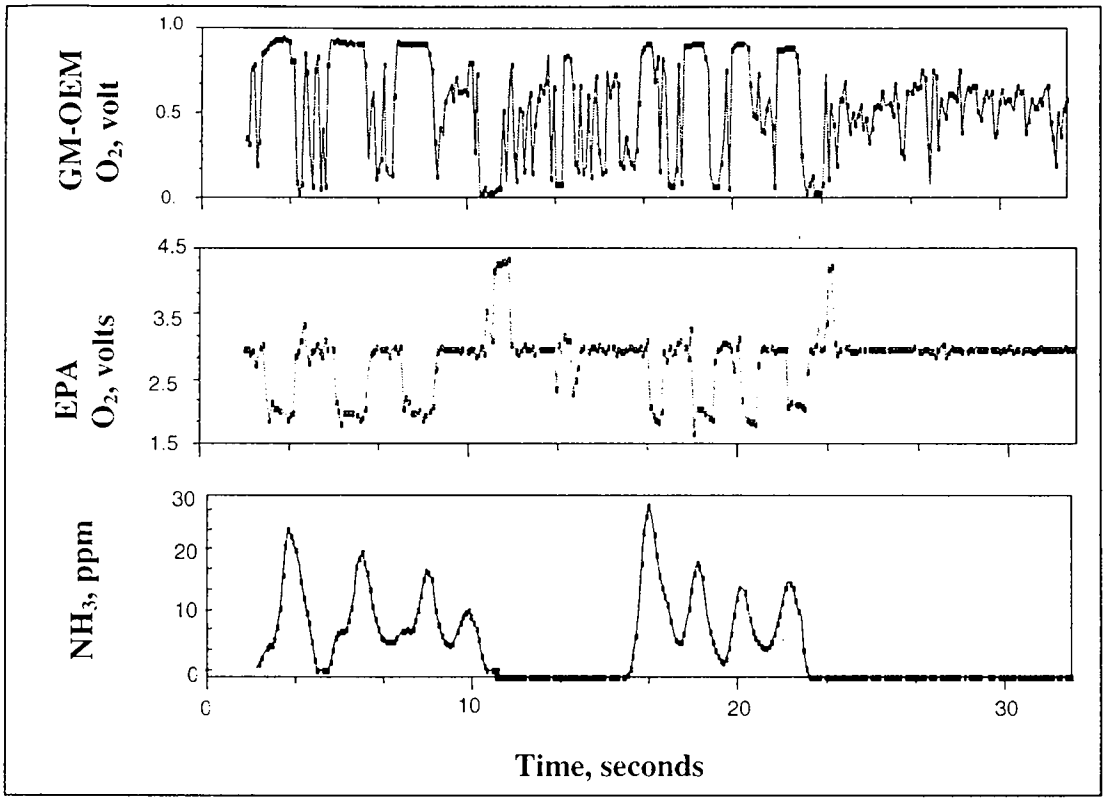

Figure 7. Change in oxygen concentration in relationship to the production of ammonia. Also an indication of the signal-to-noise ratio between the original GM-OEM oxygen sensor and the EPA-installed oxygen sensors.

average cycle (g/km) emissions indicated a correlation coefficient (r^2) of 0.835.

The third indication of enrichment was the EPA-installed wide-range O_2 sensor mounted between the engine and the catalyst. Again, a graphically determined voltage was derived and used as an indicator of enrichment. The sensor ranged between 1.5 and 4.5 volts with 4.5 indicating lean conditions and 1.5 indicating rich conditions. Any values less than 2.8 volts were considered to be rich combustion mixtures. Figure 7 provides an indication of this sensor's performance while NH_3 concentrations were being measured for one of the hard accelerations test cycles. Figure 7 also provides a graphical indication of the signal-to-noise ratio and response rate for the two O_2 sensors. The GM-OEM sensor was faster to respond to changes in O_2 concentrations and the signal-to-noise ratio was significantly greater than the EPA-installed wide-range O_2 sensor.

Figure 8 shows the average test cycle percent enrichment regressed onto average cycle NH_3 emissions (g/km). These results show a correlation coefficient (r^2) of 0.919 and also show that the emissions with no enrichment are 0.009 g/km when averaging across both the GM-OEM and the EPA-installed percent enrichment data. Table 2 contains the predicted emissions for both the EPA and GM-OEM O_2 sensors. These predicted emissions show that NH_3 production is inversely proportional to O_2 concentration. When evaluating data that contain both enrichment and no enrichment, the emissions were found to be bimodally distributed for O_2 concentration. Figures 9 and 10 show this bimodal distribution for all of the tests and one of the hard acceleration cycles, respectively. These graphs represent average test cycle percent enrichment of 2.4 and 13.1, respectively. Modal emissions were analyzed using the EPA-installed wide-range O_2 sensor as the indicator of rich combustion mixtures.

Modal NH_3 emission analysis required time alignment for sample system volumes, analyzer analysis, and the response time of the different channels within the chemiluminescent analyzers. Even after taking these delays into account, the

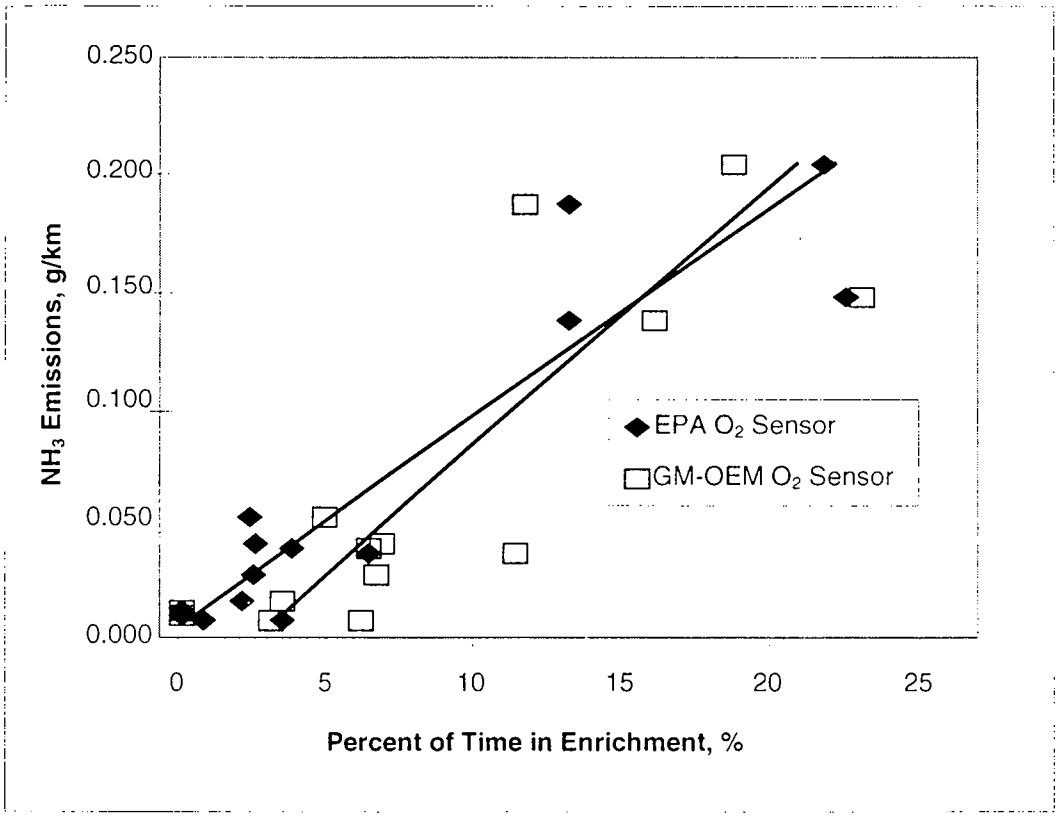

Figure 8. Percentage of time that the engine was operated in an enrichment mode as indicated by both the EPA and GM-OEM oxygen sensors.

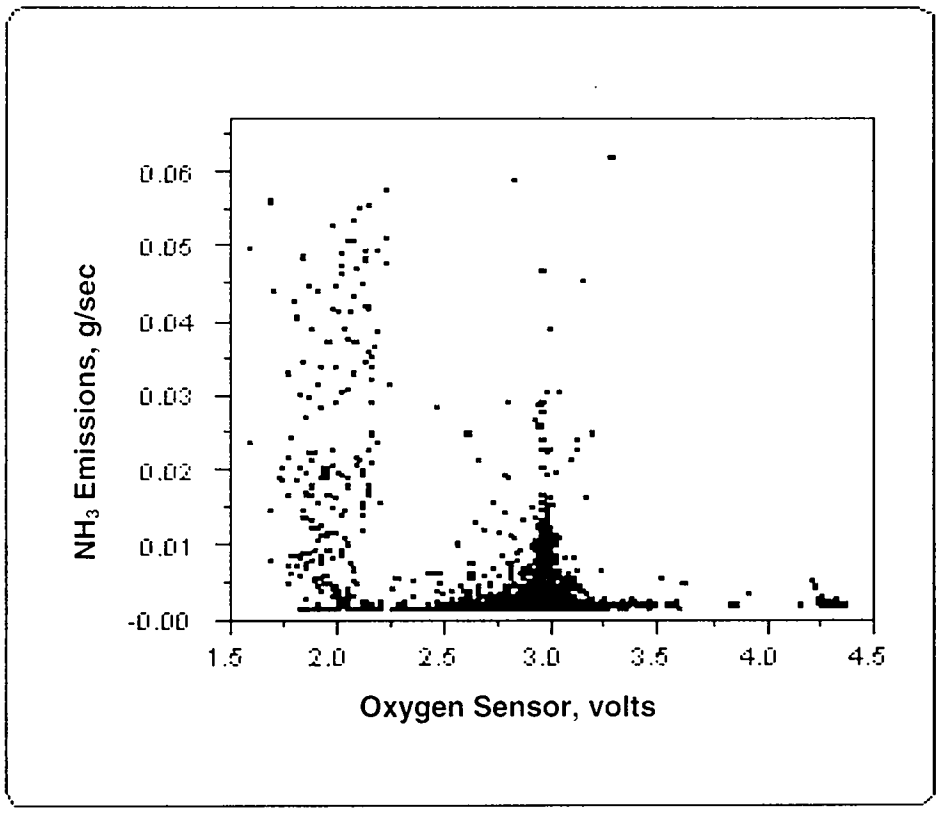

Figure 9. The relationship of ammonia emisions for oxygen concentration, reflecting results from all 14 cycles tested.

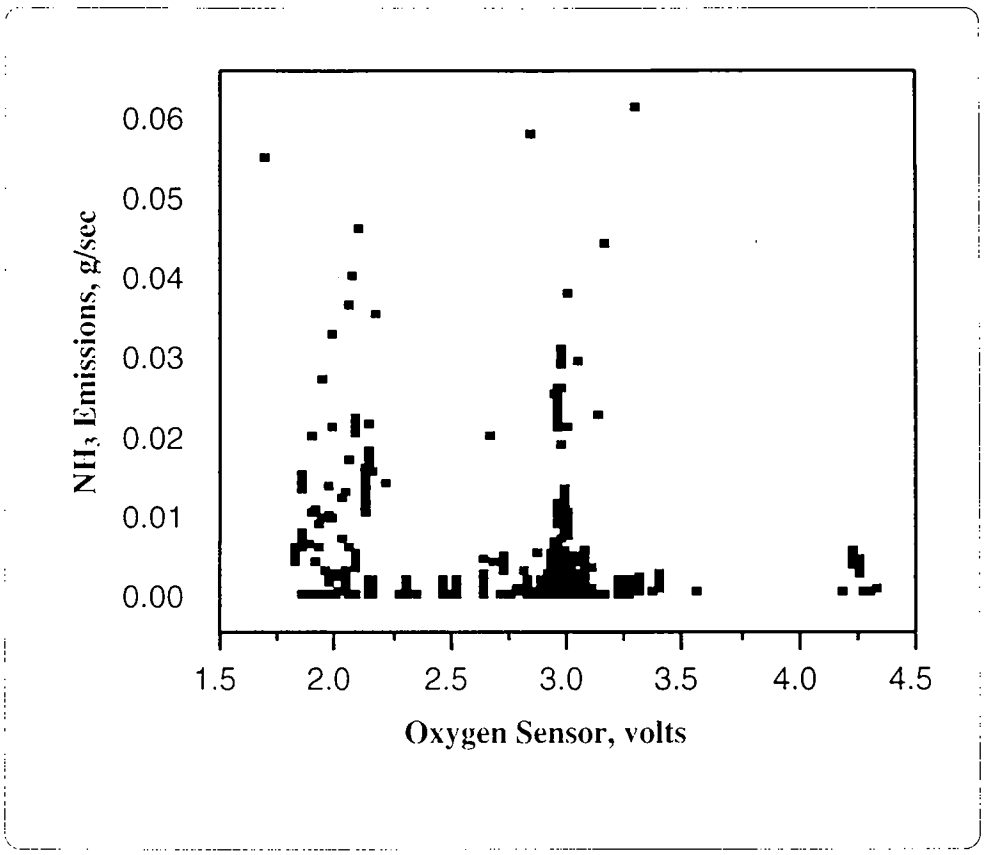

Figure 10. The relationship of ammonia emissions for oxygen concentration, reflecting data from only one of the hard acceleration cycles tested.

modal analysis indicated a third delay that is thought to be associated with the reduction chemistry reactions within the catalyst. The delay between rich combustion conditions within the engine and NH_3 emissions is estimated to be 14 seconds or 0.4 km later at 96 km/hr. Second-by-second analysis of NH_3 emissions shows that NH_3 emissions are well correlated to reduction in O_2 concentrations. Figure 11 shows the percent enrichment regressed onto total NH_3 (grams) measured for each of the 14 cycles tested for both the EPA-installed and the GM-OEM O_2 sensors. Previous instrumented vehicle emissions analysis has shown acceptable correlation to mass air flow rate (MAF) through the engine. Regression equations were developed for both all data and hard acceleration test cycles, and sorted for enrichment and non-enrichment events. Neither analysis provided acceptable confidence, but on average the enrichment data showed base line emissions at 0.006 g/km and a slope of 0.00074[MAF (mole/sec)]. These results have shown that predicting NH_3 emissions must include the prediction of enrichment events and that O_2 concentration is a direct indication of when enrichment is in effect.

CONCLUSIONS

An automotive exhaust gas NH_3 measurement technique was demonstrated, and significant NH_3 emissions have been shown to correlate to fuel enrichment events. This supports the original hypothesis that significant NH_3 emissions will occur only when insufficient oxygen at the catalyst allows reduction chemistry to predominate within the catalyst.

The dual chemiluminescent analyzer technique showed acceptable agreement with the exhaust gas concentrations measured by the gas washing technique. The total NH_3 mass emissions for the standard FTP cycle agreed with work completed by other researchers. Modal data analysis shows that

be predicted using percentage of time of enrichment. Predicting the percentage of time of enrichment is the subject of on-going EPA research.

The average base line emissions with no work-induced enrichment events (e.g., steady state) are not significantly different from previous data and on average range from 0.009 to 0.011 g/km. Fuel enrichment events resulted in NH_3 emissions that on average ranged from 0.135 to 0.204 g/km. Two tests of emissions from tunnels have been performed to address fleetwide NH_3 emissions from vehicles. The San Francisco Bay area tunnel[16] results indicated an adjusted NH_3 emission factor of 0.05 g/km. The Sherman Way tunnel study[1] indicated an adjusted NH_3 emission factor of 0.06 g/km. Tunnel studies measure the change in air concentrations, and these results have been adjusted to g/km units by estimating a fleet economy of 23 miles per gallon. The vehicle reported in this paper gets 30 miles per gallon. Given the uncertainty in fuel consumption and the percent enrichment of the tunnel study fleet, these results are in reasonable agreement with the results reported in this paper. Data presented here were collected using only one test vehicle, but the engine control strategy and catalyst design are consistent for a large percentage of on-road vehicles. It is therefore reasonable to believe that the results presented here can be applied to many of the on-road vehicles today.

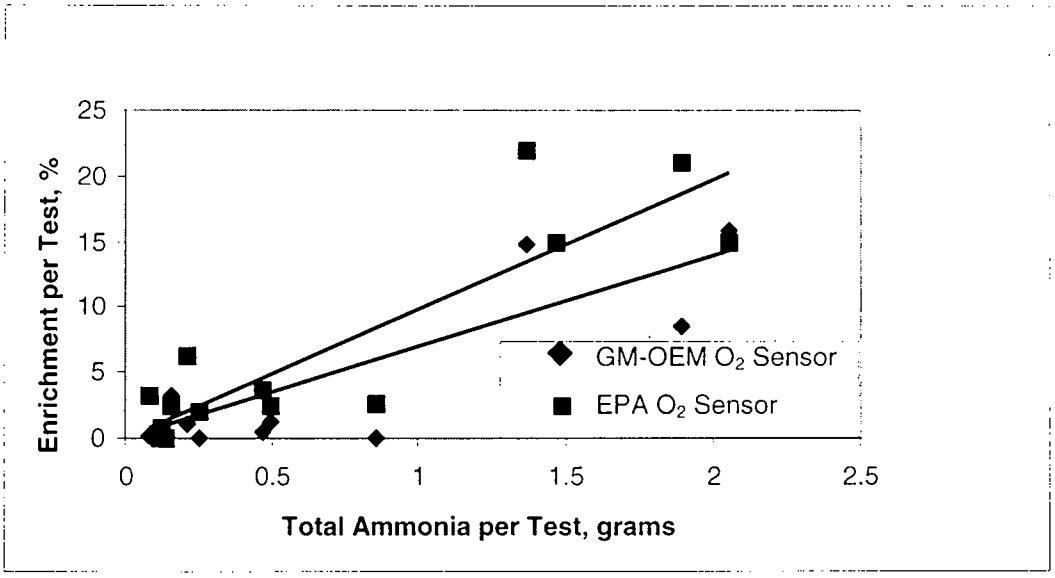

Figure 11. Percentage of enrichment per test and the total grams of ammonia produced.

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16. ABSTRACT The paper discusses measurements of ammonia (NH3) emissions from EPA's light-duty test vehicle while operated on a dynamometer. The vehicle's (1993 Chevrolet equipped with a three-way catalyst) emissions were measured for three transient (urban driving, highway fuel economy, and hard acceleration) cycles and steady state operation. Previous research showed that NH3 is predominantly emitted from vehicles with a catalyst (three-way or dual-bed). The normal operation of the vehicle's catalyst is to reduce nitrogen oxides (NOx) to nitrogen (N2) and oxygen (O2). The reduction of NOx to NH3 would have to occur during periods of operation when insufficient O2 is available. NH3 emissions were measured during fuel-rich/reduced-O2 conditions (open-loop control scheme), and the results indicated that NH3 production is correlated to combustion conditions. The results also indicated that the amount of NH3 produced correlates with the amount of time that the vehicle remains in the open-loop control scheme. The significance of this finding is that NH3 production can be predicted for a fleet based on the frequency of enrichment of vehicles equipped with a three-way catalyst. The results also provide a way to determine the location of roadway links and/or specific locations where NH3 production can be anticipated based on predicted engine power.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Mobile Equipment	Test Vehicles	15E
Ammonia		07B
Dynamometers		14B
Catalytic Converters		07A, 13I
Internal Combustion Engines		21K

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