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Enhancement of Remote Sensing for Mobile Source Nitric Oxide

Yi Zhang, Donald H. Stedman, Gary A. Bishop, Stuart P. Beaton, Paul L. Guenther, and Iain F. McVey
Department of Chemistry, University of Denver, Denver, Colorado

ABSTRACT

A nitric oxide (NO) detector was developed and integrated into the original carbon monoxide (CO) and hydrocarbon (HC) remote sensing system developed by the University of Denver. The system is capable of measuring the CO, HC, and NO exhaust emissions of thousands of on-road vehicles per day. Analysis of a typical field measurement in Denver shows CO, HC, and NO emissions have similar statistics which can be well represented by a gamma distribution. The fraction of NO high emitters tends to increase with age, apparently arising from deterioration of the emissions control system. This paper presents the inverse relationship between NO and either CO or HC emission.

INTRODUCTION

Emissions of hydrocarbons (HCs), oxides of nitrogen (NO_x, which denotes the sum of NO and NO_2), and carbon monoxide (CO) from mobile sources play a central role in major urban air pollution problems, including photochemical smog, acid deposition, and violation of CO standards. In the presence of solar radiation, NO_x reacts with HCs and their oxidation products, through a series of reactions involving hydroxyl radicals, to produce strongly oxidizing compounds and to increase the concentration of ozone.[1] The air quality standard for CO is violated as a result of direct CO emission under conditions of persistent meteorological stagnation. Measurements of these constituents in in-use motor vehicle exhaust are therefore essential for understanding these problems and controlling urban air quality.[2]

The development of remote sensing technology capable of accurately measuring the CO and HC exhaust emissions of many thousands of vehicles per day provides a practical approach for routinely characterizing on-road vehicle CO and HC exhaust emissions. Previous remote sensing studies of on-road CO and HC emissions revealed that most vehicles emit less than 1% CO and 0.1% HC (propane equivalent), while most of the measured on-road emissions are from vehicles with the highest emissions (10% for CO and 1.5% for HC).[3,4] Most of those high emitters have been shown in pullover and repair studies to have mechanical malfunctions due to improper or inadequate maintenance, damage, or owner/mechanic tampering.[5,6] The remote sensing technique has also been applied successfully to measure vehicle emissions in a tunnel environment.[7]

Combustion and exhaust chemistry depend upon many factors, but the dominant factor is the air/fuel ratio. Fuel-rich combustion results in elevated CO and HC emissions due to incomplete combustion.[8] Lean combustion results in the highest expected NO emissions since NO is formed from N_2 and O_2 during combustion in the hot gas at high compression in and behind the flame front.[8] Total vehicle load affects %CO emission relatively little, while %HC emission is elevated at low load,[9] and %NO emission is elevated at high load.[10]

This paper describes the use of a newly developed dual capability IR-UV remote sensing system for measuring vehicle CO, HC, and NO emissions in real time, with an emphasis on NO detection. The results of a typical field measurement are presented.

IMPLICATIONS

Enhancements to remote sensing technology for on-road vehicle emissions by the addition of NO detection provides a practical approach to simultaneously measure the primary exhaust emission components of concern—CO, HC, and NO—in real time. It expands the potential contribution of remote sensing technology to understanding and control of mobile source pollution.

INSTRUMENTATION

IR Photometry for Determining CO and HC

Remote sensing for CO and HC is based on non-dispersive infrared (NDIR) spectroscopy. An infrared beam is directed across a single lane of traffic to a detector. The IR absorption bands produced by CO, HC, and CO_2 in the exhaust plume are isolated by separate bandpass filters at 4.6 mm, 3.4 mm, and 4.3 mm, respectively. The measured absorptions are then ratioed to the reference absorption at 3.9 mm, where vehicle exhaust gases do not absorb, to eliminate the effect of dust and smoke behind the vehicle. The data are digitized and compiled by a computer system. Since the size of the exhaust plume through which the infrared radiation passes is unknown, the absolute amount of CO, HC, and CO_2 cannot be directly determined. Thus, the ratios of CO/CO_2 and HC/CO_2 are calculated and then converted to the CO, HC, and CO_2 fractions present in the dry exhaust plume through the combustion equations.[8] This conversion assumes a

known carbon-to-hydrogen ratio in the fuel, and rejects any excess air which may be present but that does not participate in the combustion process. The HC is calibrated with and reported as an equivalent concentration of propane. The measured results can also be quantitatively converted into instantaneous mass emissions in grams of emission per gallon of fuel burned.[5] When desired, a video camera can be added to the system for the purpose of vehicle identification. The details of the instrument are described elsewhere.[11,12]

In studies sponsored by the California Air Resources Board (CARB) and General Motors Research Laboratories,[13] the CO and HC measurements have been shown to accurately reflect instantaneous exhaust emissions in blind comparisons with vehicles of known on-road emissions. More recent studies by CARB show that the remote sensing CO readings are correct within ±5% of the values reported by an on-board gas analyzer (NDIR), and within ±15% for HC.[14]

Addition of UV Photometry for NO determination

Remote sensing of NO has been added to the system by integrating an ultraviolet source[15] and detector. The doublet UV absorption peak of NO at 227 nm wavelength was selected to avoid infrared interference from water vapor in the exhaust plume. Since most of the NO_x emitted in vehicle exhaust is NO,[8] this is effectively a NO_x detector.

A schematic diagram of the optical components of the remote sensing system with the NO detector is shown in Figure 1. The UV beam from a deuterium lamp is combined with the IR beam by a beam-splitter to produce the collimated IR-UV beam. After crossing the road, the parallel IR and UV light is focused onto the twelve-faceted mirror, which spins at 12,000 rpm and produces a chopping rate of 2400 Hz. The spinning polygonal mirror sweeps the light sequentially across the four IR channels (not shown) and the two UV channels (signal and reference), allowing each detector to receive a full strength signal for a fraction of the time. The light to be swept towards the UV channel is reflected by a dichroic mirror (Acton Research, Inc.) which reflects UV light at 227 nm and transmits IR light, thereby separating the UV light from the IR. The UV light is then directed via a mirror so that some of the beam passes through a 3.2 mm-path sealed quartz reference cell and some of the beam bypasses the cell. Therefore, a reference signal and a measurement signal for NO are obtained. The reference cell contains a known concentration of NO that is much higher than the possible concentration in the vehicle exhaust. The purpose of the reference cell is not only to reduce the noise caused by UV light source instability and instrument vibration, but also to eliminate interferences from exhaust aromatic hydrocarbons absorbed in wavelengths near 227 nm that would otherwise be picked up by the detector due to the wide bandpass of the filter. The light then passes through an interference filter onto the photomultiplier tube (PMT).

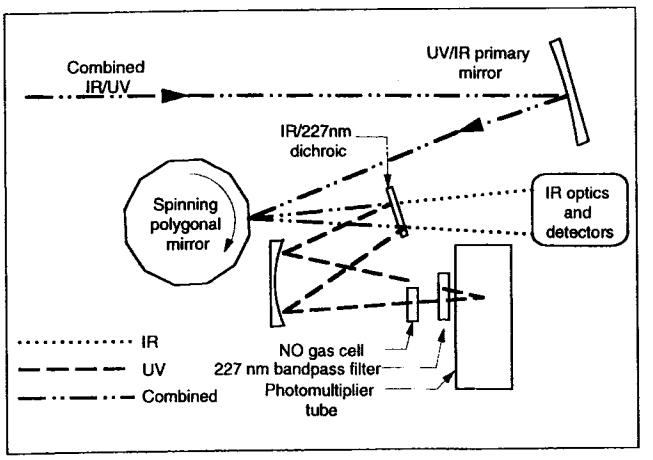

Figure 1. Schematic diagram of the optical path of the NO remote sensor.

The software used for NO detection converts the measured signal to NO optical depth by means of a laboratory calibration equation. Correlation between the NO and CO_2 optical depth as a function of time allows the NO/CO_2 ratio to be determined. The ratio is then converted to the exhaust NO concentration, corrected for water and any excess air, by the same combustion equations used for CO and HC.

The NO calibration equation used by the software algorithm was determined by measuring the NO absorption signal as a function of NO concentration in a flow cell 8 cm long by 5 cm in diameter. The NO and N_2 diluent flow were regulated by a mass flow controller. The equation is linear over the 1 to 5,000 ppm range typical of vehicle exhaust. On-site calibration can be conducted with a sealed cell or a certified gas cylinder containing known concentrations of CO, CO_2, propane, and NO.

Detection Limit and Repeatability of the NO Detector

A cylinder containing pure CO_2 was measured 16 successive times as a blank test to determine the variability of a blank in regard to detection of NO. The average %NO reading for the blanks was 0.000 with a standard error of the mean of 0.003.

Four vehicles were tested under similar conditions; i.e., they were warmed up and driven at a constant speed of 20 mph in a large circular parking lot. A 1989 Honda Civic was measured 10 times by the remote sensor and gave a mean NO concentration of 80 ppm with a standard error of the mean of 44 ppm. A 1993 Ford Escort was measured 10 times and gave a mean NO concentration of 160 ppm, with a standard error of the mean of 57 ppm. A 1985 Chevy Celebrity was measured 51 times and gave a mean NO concentration of 560 ppm, with a standard error of the mean of 88 ppm. A 1975 Porsche (with neither a catalyst nor exhaust gas recirculation equipment) was measured 24 times and gave a mean NO concentration of 1940 ppm, with a standard error of the mean of 237 ppm. The measurement variability increases

with increasing NO concentration. To estimate the repeatability, the differences between every two successive data points were calculated, resulting in a statistical distribution of the differences for each tested vehicle. The difference distribution was determined to be a Gaussian distribution by a χ^2 = test. At the significance level of $\alpha = 0.05$, the confidence interval on the mean of each set of the differences was $-90 \leq \mu_{Ford} \leq 170$, $-140 \leq \mu_{Honda} \leq 120$, $-190 \leq \mu_{Chevy} \leq 210$, and $-240 \leq \mu_{Porsche} \leq 440$. The upper limit of the confidence interval may be used as the degree of repeatability (i.e., for the Porsche, the difference between any two repeat NO measurements was less than 440 ppm when the measured mean was 1940 ppm). The estimate of repeatability increases with the increase in NO concentration. The regression line is

$$\text{Repeatability} = 0.16 \times [\text{NO}] + 123 \quad (R^2 = 0.99)$$

The repeatability for any NO ppm level can be estimated by using the regression equation. Note that this is a very conservative estimate of the instrument noise, because in each case, some of the observed variation is caused by the vehicle.

FIELD MEASUREMENTS

A remote sensor for on-road CO, HC, and NO exhaust emissions was used to measure the emissions of more than 50,000 vehicles at several locations in the U.S. and Europe. This study used the results of a typical data set collected from Denver in January 1994. The measurements were carried out at the off-ramp from southbound I-25 to southbound Speer Boulevard, close to downtown Denver. The intersection is tightly curved, with an uphill 6% grade, so that the vehicles were traveling under load, but (in view of the heavy traffic and tight curve) were not strongly accelerating. Tailpipe CO, HC, and NO exhaust emissions of passing vehicles were measured by the remote sensing system. Error checking routines in the computer eliminated invalid data caused by an inadequate amount of exhaust or by noise exceeding preset bounds. The license plates of passing vehicles were recorded on videotapes which were read later for license plate information. The license plate numbers for in-state vehicles were forwarded to the Department of Motor Vehicles of the State of Colorado to determine vehicle make and model year information.

Since the results of the CO and HC data were similar to data from previous studies done at the same location,[9,16] this paper only presents the results of NO and related data.

Overall Results

The mean NO emission of the data set was 500 ppm, with a standard deviation of 800 ppm, while the median was 300 ppm. Half of the NO emissions came from about 11% of the total vehicles with emissions in excess of 1500 ppm NO. These vehicles are referred to as "NO gross polluters." Figure 2 shows the distribution of the fleet by NO emission category: 60% of the fleet emitted less than 500 ppm NO. The skewed nature of the distribution is similar to CO and HC distributions in previous studies.[17] As with CO and HC emission distributions, the NO distribution can be fitted to a gamma distribution by the method of moments. The clear bars in Figure 2 show the gamma fit to the measured distribution.

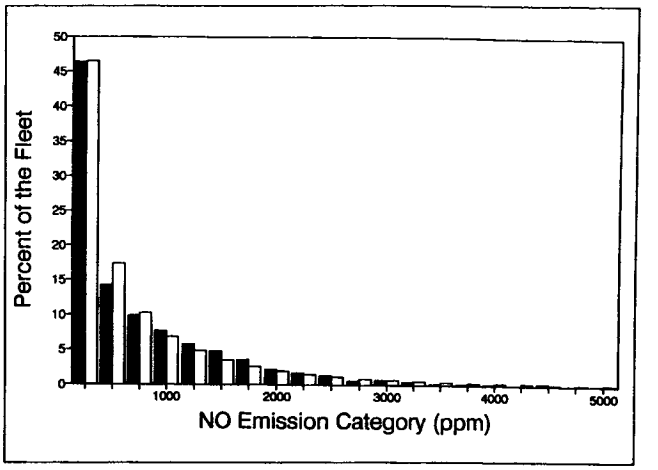

Figure 2. Normalized distribution of the fleet by NO emission category shown as black bars and a gamma distribution fitting the data shown as clear bars. Each 1000 ppm category is divided into four intervals of 250 ppm.

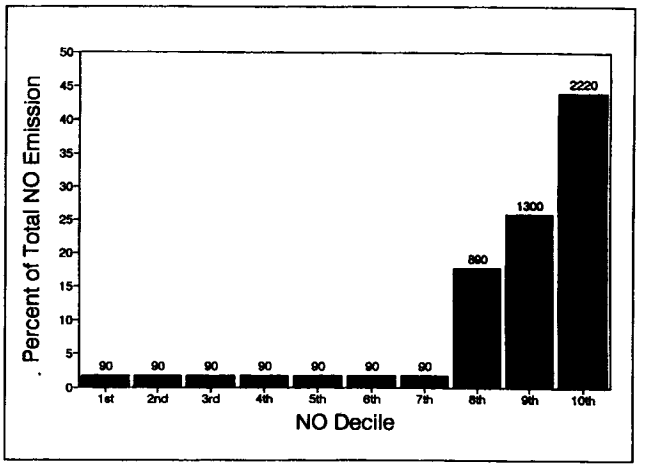

Figure 3. Fractional NO contribution organized into deciles. The lowest seven deciles are given the average of all seven since the differences between them are negligible. Over each bar is the mean NO emission for that decile expressed in ppm.

For Figure 3, the data were sorted by NO emission level, from the lowest to the highest, and then divided into 10 equal groups (deciles). Each bar corresponds to the percentage contribution to the total NO emissions of one-tenth (a decile) of the fleet. The number over each bar is the average NO emission for that decile. The lowest emitting seven bars have been averaged together, because the small distinctions which would arise from one to the next are not significant, and they correspond to a small portion of the total emissions. In contrast, the highest emitting decile, with a mean of 2200 ppm, contributes almost half of the emissions.

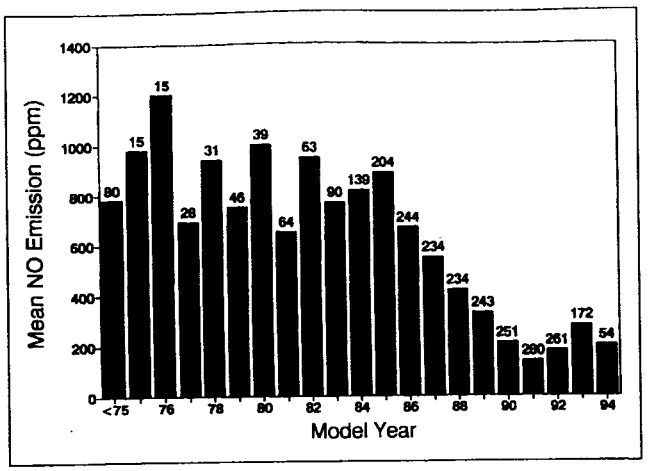

Figure 4. Mean NO emission as a function of vehicle model year. Over each bar is the number of vehicles measured in that model year.

As illustrated by Figures 2 and 3, motor vehicle NO emissions have a highly skewed distribution. The overall average of the NO distribution is dominated by the small fraction of high emitters. This is the same result that was obtained for on-road CO and HC emission distributions.

NO Emissions vs Model Year

Figure 4 shows the average NO emissions as a function of the vehicle model year. Over each bar is the number of vehicles measured in that model year. The average model year for the fleet is 1987 (vehicles were about 7 years old when measured in January 1994). Note that the remote sensing data and the video license plate data are independent from each other; i.e., if a statistically significant year-to-year smooth variation in emissions was observed, that observation could only be made if the average data were in fact more precise than the observed year-to-year variation. The following aspects appeared upon analysis:

1) The vehicles in the five most recent model years gave average NO emissions of about 200 ppm and showed no evidence of detectable deterioration. This observation reflects the high performance of modern, computer controlled, three-way catalyst and closed-loop emission control systems.
2) The mean NO emission rose smoothly as the vehicle model aged from 1989 back to 1985, which was expected to be the result of catalyst and/or exhaust gas recirculation (EGR) system deterioration, breakage, and tampering.
3) The NO emission levels of vehicles older than the 1985 model year appeared to cease to deteriorate and vary around 1000 ppm. Older vehicles probably tend to lose compression with increasing age, thus lowering average NO emission. For the same vehicles, the average CO and HC emissions continue to increase for model years before 1985, as shown in previous studies.[9,16] This observation implies increasingly rich operation and lower temperature combustion, which also result in lower NO emissions. Both processes would counteract any tendency for poor maintenance to further increase NO emission with age.

Correlation of NO with CO and HC

At a fixed site one would expect some degree of inverse correlation between average NO and average CO or HC emissions. In order to investigate this phenomenon, the data were grouped based on the NO emission level. The average CO and HC emissions for each NO interval were calculated and then plotted as shown in Figures 5 and 6, respectively.

Both CO and HC emissions are highest when NO emission is below 250 ppm. This is expected, since CO and HC emissions are significant and NO emission is minimized when the engine is operated under fuel-rich conditions, that is, when the oxygen in the fuel-air mixture that enters the engine is consumed without converting all the fuel carbon to carbon dioxide. The measured CO emissions, and to a lesser extent HC emissions, tend to decrease as NO

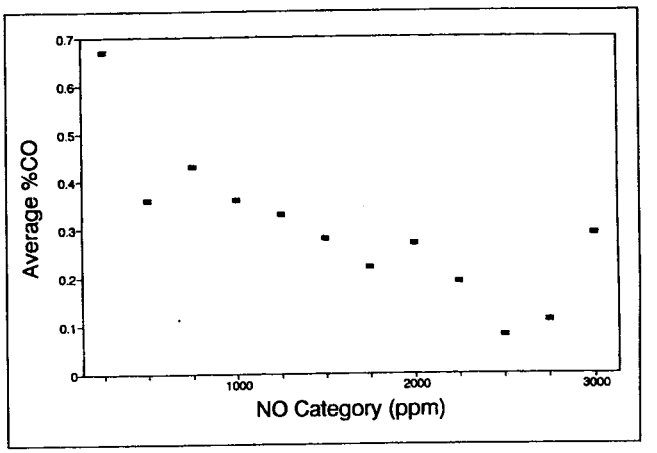

Figure 5. A plot showing average CO emission as a function of NO emission category. Each 1000 ppm NO category is divided into four intervals of 250 ppm.

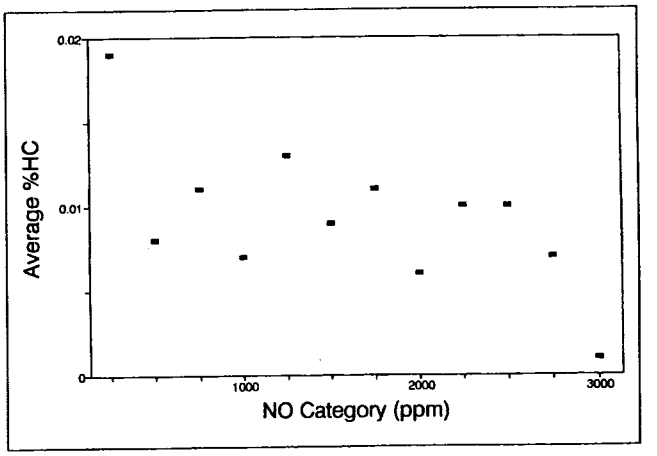

Figure 6. A plot showing average HC emission as a function of NO emission category. Each 1000 ppm NO category is divided into four intervals of 250 ppm.

emission increases. This observation agrees with the expected emissions effect of the air/fuel ratio at which the engine is operating. The highest NO bins contain relatively few vehicles (see Figure 2), thus statistical noise increases towards those categories. The CO and HC data are not highly correlated with the NO data because NO and HC are independently variable based on vehicle load.

CONCLUSIONS

A remote sensing NO detector was successfully developed and integrated into the original CO and HC measuring system developed by the University of Denver. The system provides a practical approach to monitor simultaneously on-road motor vehicle CO, HC, and NO emissions. The NO detector has sufficient sensitivity and precision to separate the high emitting vehicles (above 2000 ppm NO) from the low emitting vehicles (under 1000 ppm NO). The results of a typical field study show that only about 10% of the vehicles are high NO emitters, contributing almost half of the total NO emissions. The distribution of the NO emissions is highly skewed and can be accurately represented by a gamma distribution similar to the previously observed distributions of CO and HC emissions. When measured in 1994, vehicles between four to ten years of age showed a rapid increase in average NO concentration, apparently reflecting deterioration of their emission control systems. Measured average CO and HC emissions decrease with increasing average NO emissions, which would be expected based on their combustion chemistry relationship.

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About the Authors

Yi Zhang is a recent Ph.D. recipient; Dr. Donald H. Stedman (corresponding author) is the Brainerd Phillipson Professor of Chemistry; Dr. Gary A. Bishop is a research scientist; and Dr. Stuart P. Beaton and Paul L. Guenther are research associates at the University of Denver, Chemistry Department, Denver, Colorado 80208. Iain F. McVey is currently a graduate student at Kent State University, Kent, Ohio.