*Environ. Sci. Technol.* **2000**, *34,* 897−899

# Motor Vehicle Fleet Emissions by OP-FTIR

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Using open-path Fourier transform infrared spectroscopy (OP-FTIR) we have measured the variations in ambient concentrations of carbon monoxide (CO), carbon dioxide ($CO_2$), and nitrous oxide ($N_2O$) caused by emissions from motor vehicles at a high traffic site in the Denver metropolitan area. Comparison of the OP-FTIR data to average emissions results obtained from on-road exhaust analysis using individual vehicle remote sensing revealed reasonable agreement, with a CO emission ratio ($CO/CO_2$) of 0.050 ± 0.004 (100 ± 8 g CO/kg fuel) from OP-FTIR and 0.059 (118 g CO/kg fuel) from the on-road measurements. We also report a $N_2O$ emission ratio of $(1.87 \pm 0.13) \times 10^{-4}$ (0.59 ± 0.04 g $N_2O$/kg fuel) from OP-FTIR and outline the potential of OP-FTIR for on-road measurements of several important exhaust components.

## Introduction

Direct measurement of pollutant emissions from on-road vehicles poses an interesting challenge due to their spatial and temporal variations as well as their variations from vehicle to vehicle. One common approach to measuring these emissions is by making use of on-road sensors (*1*−*4*). These instruments must be fast-response in order to make direct measurements of the concentration of pollutants in the exhaust of vehicles. Fuel based mass emissions information can be obtained directly and emissions per mile calculated from these exhaust concentration data if an estimate of fuel economy is available. Another method used to determine vehicle emissions involves the use of tunnels (*5*, *6*). In tunnel studies, the concentrations of the pollutant at the tunnel inlet and outlet are combined with air flow information to calculate average fleet emission rates. The major disadvantages of this technique are that there are few suitable tunnels in which to make such measurements, and both the fleets and driving habits in tunnels may differ significantly from those outside tunnels. Open road emission ratio measurements have been made in the past using an $SF_6$ tracer release, for instance studies by Zweidinger et al. (*7*) and McLaren et al. (*8*).

In this study, we investigate the potential use of open-path Fourier transform infrared (OP-FTIR) spectroscopy to combine the tunnel and tracer methods by measuring a fleet average fuel based emission ratio. In effect this technique makes use of $CO_2$, and the other usually minor carbon-containing gases, as a fuel mass tracer.

## Experimental Section

Measurements were obtained on July 10, 1997, in central Denver, north of the interchange between I-25 and 6th Avenue. These roadways have a daytime traffic load of approximately 16 000 vehicles per hour. The OP-FTIR data were collected between the hours of 5:45 AM and 9:45 AM, bracketing the morning rush hour. In addition, FEAT (Fuel Efficiency Automotive Test) (*1*−*3*) data were collected between the hours of 11:12 AM and 1:40 PM on the adjacent exit ramp. Previous studies at this ramp have shown $CO/CO_2$ ratios to be constant to within ±4% during the course of a day (*9*). This ramp is a tightly curved connector ramp with an uphill grade of approximately 8% and has previously been documented as a high-volume site where vehicles are under moderate load (*9*). FEAT measures emissions from a single interchange ramp. The OP-FTIR is measuring air from the same ramp and 12 lanes of nearby upwind freeway.

The OP-FTIR measurements used a commercially available spectrometer (Midac model M-2500-C), a Michelson interferometer with gold coated, flat mirrors, and a Ge/KBr beam splitter. The IR beam was produced by a silicon carbide source and detected with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The OP-FTIR was set up in a monostatic arrangement, making use of a retroreflector array positioned 81.6 m away from the spectrometer, resulting in an optical path of 163.2 m. One hundred transmission spectra were coadded at a spectral resolution of 0.5 $cm^{-1}$. Typical averaging times were 85 s, during which time an average of about 300 motor vehicles pass upwind of the beam path.

The raw transmission spectra were truncated to the region 2020−2270 $cm^{-1}$ and then converted to absorbance spectra through Beer's law. These absorbance spectra were analyzed for component concentrations using a method for quantitative analysis that has been described fully by Griffith (*10*). In this method, multicomponent calibration spectra are calculated using the program MALT (*M*ultiple *A*tmospheric *L*ayer *T*ransmission) and information from the 1996 HITRAN (*Hi*gh Resolution *Tran*smission Molecular Absorption Database) database of spectral line parameters (*11*). The MALT-generated spectra are then used as synthetic calibration spectra in a conventional Classical Least Squares (CLS or K-matrix) procedure (*12*, *13*), using the regions 2040−2223 $cm^{-1}$ for CO and 2145−2250 $cm^{-1}$ for $CO_2$ and $N_2O$. The MALT/CLS method of obtaining component concentrations has been shown to provide sensitive, precise, and accurate quantitative analyses of spectra obtained in the field (*10*, *14*). Typical uncertainties for the absolute concentration of each component (measured in ppm or ppb) in the 150 spectra reported were 0.7% for $CO_2$, 1.6% for CO, and 1.8% for $N_2O$.

The FEAT instrument developed at the University of Denver has been described in detail elsewhere (*1*−*3*). FEAT is an on-road testing system based on nondispersive infrared spectroscopy for the measurement of $CO_2$, CO, and hydrocarbons (HC) and on high-speed ultraviolet absorption spectroscopy at 226 nm for the measurement of nitric oxide (NO) (*15*). The FEAT instrument was set up across the adjacent single-lane exit ramp and measured the $CO/CO_2$, $HC/CO_2$, and $NO/CO_2$ ratios in the exhaust of individual vehicles passing through its beam. These ratios are then used along with the combustion equations to determine the $\%CO_2$, %CO, %HC, and %NO that would be read by a tailpipe probe. During this study, the 3148 vehicle average $\%CO_2$ and average %CO measured by FEAT were 14.44 and 0.85, respectively, with an expected error of ±3% (*9*).

## Results and Discussion

To compare information obtained by OP-FTIR to that obtained using FEAT, we consider an emission ratio for CO

10.1021/es9909226 CCC: $19.00 
Published on Web 01/22/2000

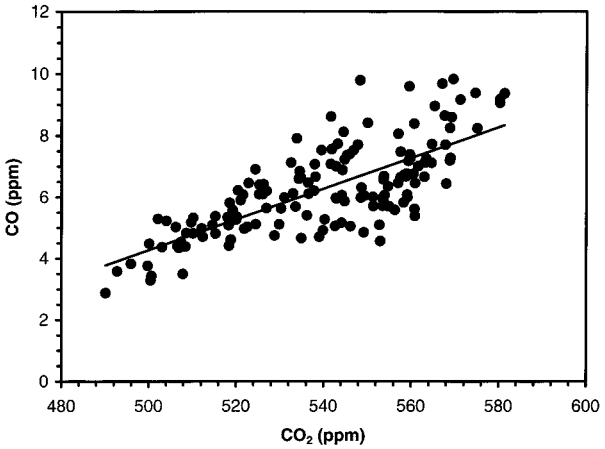


**FIGURE 1. CO concentration (ppm) versus $CO_2$ concentration (ppm) measured by OP-FTIR between 5:45 AM and 9:45 AM on July 10, 1997, in central Denver. The line represents a least-squares linear fit to the data, with slope = 0.050 ± 0.004 and $r = 0.748$.**

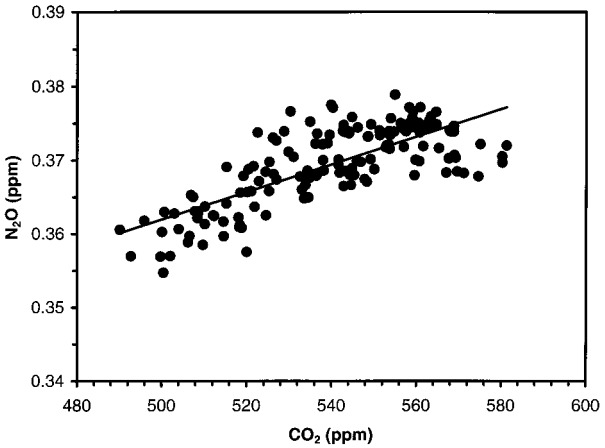


**FIGURE 2. $N_2O$ concentration (ppm) versus $CO_2$ concentration (ppm) measured by OP-FTIR between 5:45 AM and 9:45 AM on July 10, 1997, in central Denver. The line represents a least-squares linear fit to the data, with slope = (1.87 ± 0.13) × $10^{-4}$ and $r = 0.753$.**

in the form of the molar $CO/CO_2$ ratio. The emission ratio is determined from the correlation of the variation in ambient concentration of CO to the variation in ambient concentration of $CO_2$, and it is useful in determining quantities of interest to emission inventories.

Figure 1 shows a plot of the concentration of CO versus the concentration of $CO_2$ measured by OP-FTIR as well as a line representing the results of a least-squares linear fit to the data (correlation coefficient, $r = 0.748$). Using the slope of this line, the CO emission ratio and its standard error, measured by OP-FTIR, is 0.050 ± 0.004 (100 ± 8 g CO/kg fuel). This result is close to the CO emission ratio calculated from FEAT data (0.85/14.44), which is 0.059 (118 g CO/kg fuel). Due to the large number of vehicles sampled by FEAT, the reported error of the mean measurements is very small in comparison to those obtained by OP-FTIR, for which the apparent "noise" is dominated by the fact that the upwind fleet for any given 85 s averaging period is not expected to have a constant emission ratio. Certainly the error induced by the comparison of different ensembles of vehicles at slightly different times is larger than the error in FEAT measurements. Furthermore, FEAT measures the average $CO/CO_2$ ratio of passing cars, while the OP-FTIR measures the overall average of the fleet. Although these measurements are independent of fuel economy, because of the skewed nature of motor vehicle emissions, the average of the ratio of $CO/CO_2$ measured by the FEAT unit is bound to overestimate the ratio of the averages, even from the same fleet.

The quality of the comparison between the CO emission ratios obtained via OP-FTIR and FEAT provides encouraging evidence for the utility of the OP-FTIR method in measuring emission ratios for other vehicle pollutants. As an example, Figure 2 shows a plot of the concentration of $N_2O$ versus the concentration of $CO_2$ measured by OP-FTIR as well as a line representing the results of a least-squares linear fit to the data ($r = 0.753$). The $N_2O$ emission ratio obtained from this plot is (1.87 ± 0.13) × $10^{-4}$ (0.59 ± 0.04 g $N_2O$/kg fuel). This result is close to the U.S. EPA's estimated emission rate of 0.41 ± 0.04 g $N_2O$/kg fuel (*16*). Knowledge of $N_2O$ emissions from vehicles is important because automotive exhaust is thought to be one of the main anthropogenic sources contributing to the increase of this greenhouse gas (*17*). It has been shown that catalytic converters can produce $N_2O$ (*18*, *19*), and with the increase of catalyst-equipped vehicles over the past 2 decades, it is necessary to gather as much data about $N_2O$ emissions from vehicles as possible. As this study has shown, OP-FTIR provides a viable option for such measurements. Other emissions potentially measurable by this and related (e.g. long-path UV) techniques include $NH_3$, NO, $NO_2$, aromatics, aldehydes, etc.

## Acknowledgments

This work has been supported by NSF Grant No. ATM-9417061 and the Camille and Henry Dreyfus Postdoctoral Program in Environmental Chemistry. The authors thank Prof. D. W. T. Griffith and I. M. Jamie for their assistance with the MALT/CLS programs.

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*Received for review August 10, 1999. Revised manuscript received November 18, 1999. Accepted December 6, 1999.*

ES9909226