AEDC-TR-93-18

UV Absorption Technique for Monitoring Mobile Source NO Emissions

R. P. Howard and W. J. Phillips
Sverdrup Technology, Inc., AEDC Group

November 1993

Final Report for Period October 1992 – September 1993

Approved for public release; distribution is unlimited.

ARNOLD ENGINEERING DEVELOPMENT CENTER
ARNOLD AIR FORCE BASE, TENNESSEE
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE

NOTICES

When U. S. Government drawings, specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise, or in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

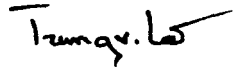
Qualified users may obtain copies of this report from the Defense Technical Information Center.

References to named commercial products in this report are not to be considered in any sense as an endorsement of the product by the United States Air Force or the Government.

This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

APPROVAL STATEMENT

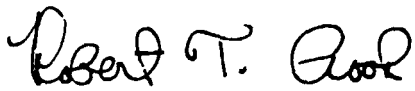
This report has been reviewed and approved.



TRUNG V. LE
Project Manager
Technology Division
Test Operations Directorate

Approved for publication:

FOR THE COMMANDER



ROBERT T. CROOK
Chief, Technical Management Flight
Technology Division
Test Operations Directorate

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	November 1993	Final -- Oct. 1, 1992 - Sept. 30, 1993

4. TITLE AND SUBTITLE

UV Absorption Technique for Monitoring Mobile Source NO Emissions

5. FUNDING NUMBERS

PE - 65807F

6. AUTHOR(S)

Howard, R. P. and Phillips, W. J., Sverdrup Technology, Inc., AEDC Group

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Arnold Engineering Development Center/DOT
Air Force Materiel Command
Arnold Air Force Base, TN 37389-9011

8. PERFORMING ORGANIZATION REPORT NUMBER

AEDC-TR-93-18

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

Arnold Engineering Development Center/DOT
Air Force Materiel Command
Arnold Air Force Base, TN 37389-9011

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Available in Defense Technical Information Center (DTIC).

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Ultraviolet (UV) absorption techniques developed and used by the Arnold Engineering Development Center (AEDC) for measurements of nitric oxide (NO) in exhaust flows of turbine and liquid-propellant rocket engines have been adapted for measurements of NO in the exhausts of automobiles. Measurements were performed across a roadway with a 10-percent mixture of NO being released into the exhaust stream of a small truck traveling at speeds ranging from 6 to 30 mph. Emission factors for these simulated exhausts ranged from 0.92 to 23.05 gm/mi. Nitric oxide was detected in measurements using NO-resonance lamp radiation passed twice across the roadway for emission factors as low as 1.78 gm/mi. Nitric oxide absorption was not detected on exhaust measurements of automobiles traveling (coasting) at constant speeds. Nitric oxide was detected at measurable levels on automobiles forced to stop and then accelerate through the measurement station.

14. SUBJECT TERMS	15. NUMBER OF PAGES
mobile source emissions, nitric oxide, NO, automobile exhaust, UV absorption	22
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAME AS REPORT

PREFACE

The work reported herein was conducted at the Arnold Engineering Development Center (AEDC), Air Force Materiel Command (AFMC), under Program Element 65807F, at the request of AEDC/DOT, Arnold Air Force Base, TN. The AEDC/DOT Project Manager was Mr. T. V. Le. Management for this project was performed by Sverdrup Technology, Inc., AEDC Group, support contractor for the propulsion test facilities, AEDC, AFMC, Arnold Air Force Base, TN, under Air Force Project No. 0099. The Sverdrup Project Manager was W. J. Phillips.

CONTENTS

ILLUSTRATIONS

1.0 INTRODUCTION

Environmental concern over pollution levels in nonattainment areas has prompted interest in roadside monitoring of gaseous pollutants from vehicles. Enforcement requires a measurement capability to identify and quantify emissions regulated by state and federal control acts. In a technology project sponsored by AEDC, optical techniques developed at AEDC for the measurements of nitric oxide (NO) have been evaluated to determine their sensitivity to detect and quantify NO densities in automobile exhaust. These nonintrusive optical techniques, developed and used at AEDC for quantitative measurements of NO in arc-heated air sources (Ref. 1) and rocket and turbine engine exhaust plumes (Refs. 2 and 3) could play an important role in roadside pollution level monitoring and enforcement. This report documents efforts conducted at AEDC to evaluate nitric oxide-ultraviolet (NO-UV) absorption techniques for roadside monitoring of automobile exhausts.

Two UV-absorption techniques are in use at AEDC for measuring the path-averaged number density of NO molecules over a line-of-sight (LOS) measurement volume. Using these techniques, radiation passing through the medium is partially absorbed at particular spectral absorption features of the NO molecule. The (0,0) absorption band of the $X^2\Pi$-$A^2\Sigma$ electronic transition of NO is the absorption feature of interest. This electronic transition is centered spectrally at 226.5 nm. Both UV-absorption techniques ratio lamp radiation transmitted through the medium to a reference measurement (without NO) to determine measured transmittance (τ). At a particular wavelength, the transmittance is related to the product of NO number density and media path length through the radiative transfer equation (Ref. 2). One technique, referred to as resonance absorption, uses a discharge lamp containing NO to produce resonance radiation. The lamp emits radiation from excited NO molecules primarily at spectral positions coincident with the molecular absorption features of the test media, thus allowing better measurement sensitivity than continuum radiation sources. The other technique, referred to as continuum absorption, uses a deuterium lamp that emits a spectral continuum of radiation. Although the inherent sensitivity to number density is less, the lamp is smaller, easier to operate, and the sensitivity can be greatly increased, owing to the greater intensity of the lamp radiation which allows multiple passes of the source radiation through the test gas.

For specific test media conditions, the NO density-path length product can be determined by matching the test data to laboratory measurements performed through a sample cell at simulated test media conditions. However, because of the varied applications of these techniques at AEDC, a physics-based computer model was developed to determine the number densities from measurements for the wide range of test conditions in applications previously mentioned. The reader is referred to Refs. 1 and 4 for a detailed discussion of the physics and model. However, it should be understood that a reliable model must include instrumentation effects on the measurements and should be verified according to laboratory measurements performed at conditions similar to the test measurement conditions.

To assess the sensitivity of these techniques, measurements were performed through simulated automobile exhausts containing controlled amounts of NO. Additional measurements were performed on biased and random selections of automobiles passing through the measurement station. Representative measurements and conclusions are presented in this report.

2.0 EXPERIMENTAL SETUP

The NO measurement system, illustrated schematically in Fig. 1, consists of a radiation source (lamp), a shutter with an electronic controller, collimating and focusing optics, and a detector system controlled by a personal computer. Measurements were performed with two types of lamps. The resonance lamp, a source of NO radiation, was a DC-excited capillary flow-discharge tube operated at 10-torr static pressure. The spectral-continuum lamp was a 40-W DC-excited deuterium lamp which emits continuum radiation within the spectral region of these measurements. The detector system was a 0.32-m Czerny Turner spectrograph with a 0.025-mm entrance slit width, a 2,400-groove/mm grating, and a 1,024-element, UV-enhanced, intensified, linear silicon-diode array detector mounted at the exit focal plane of the spectrograph. This configuration allowed spectral measurements from 216 to 245 nm. A typical instrument response function (equivalent slit function) measured for an individual detector element is given in Fig. 2. The spectral resolution, full-width-half-maximum of the response was about 0.16 nm.

The measurements were performed across a roadway on the Arnold Air Force Base, as illustrated in Fig. 1. The NO measurement system instrumentation components (source and receiver) were mounted on one side of the roadway, except for a mirror on the opposite side which was used to reflect the lamp radiation back to the spectrometer. For measurements using the resonance lamp, the total optical path between the lamp and spectrometer was about 60 ft, with the collimated beam parallel to and approximately 18 in. above the roadway. For measurements using the deuterium lamp, an additional mirror was added to give a 4-pass system with an optical path of 120 ft. The interaction of the collimated beam with the exhaust gas defines the line-of-sight measurement volume. Since the exhaust gas does not fill the entire optical path between the lamp and spectrometer, the path length of the measurement volume, L, is the summation of these interaction distances from the multiple passes of the beam.

A truck was configured with a cylinder of gas, a flow transducer, and a gas handling system to control the amount of NO released during the sensitivity assessment measurements. The gas mixture was released through a stainless steel tube into the normal exhaust gas stream of the truck. The stainless steel tube was mounted along the tailpipe of the vehicle which was about 18 in. above the roadway and pointed toward the passenger side of the truck. The calibration gas was a 10-percent mixture of NO using N_2 as the balance gas. The gas

mixture was released at flow rates between 3.45 and 17.2 standard liters per minute (slpm) with the truck speed varied from 6 to 30 mph. The effective emission factor (grams of pollutant per vehicle mile) can be obtained from the flow rates of the gas mixture and the vehicle speed from the relationship:

$$\epsilon = \frac{2.68 f M_\omega X}{v}$$

where:

ϵ = emission factor, gm/mile

f = flow rate (slpm)

M_ω = molecular weight

X = mole fraction of pollutant

v = vehicle speed, mph

This yields effective NO emission factors between 0.92 and 23.0 gm/mile for the controlled measurements reported.

All vehicles, including the truck used for controlled measurements, were monitored by a radar gun to measure vehicle speed. Xybion® gated video cameras recorded license plate numbers for later identification of the vehicle types.

3.0 DATA ACQUISITION

A set of 30 raw data spectra were acquired continually over a 15-sec interval per vehicle exhaust measurement. The toal integration time for each spectrum was 0.5 sec. Data acquisition was manually triggered about 7 sec before a vehicle passed through the optical beam. The first two spectra were acquired with the lamp shuttered to quantify background levels, $I_B(\lambda_i)$, which were primarily due to internal detector noise. The shutter was then opened to measure the raw data lamp signal, $I_0(\lambda_i)$, in the absence of exhaust gases. This was followed by a momentary beam interruption by the vehicle, and then measurements of the lamp, $I_T(\lambda_i)$, transmitted through the trailing exhaust. Spectral transmittances were determined from the raw data measurements according to

$$\tau_i = \frac{I_T(\lambda_i) - I_B(\lambda_i)}{I_0(\lambda_i) - I_B(\lambda_i)} \quad (2)$$

where λ_i denotes the center frequency of radiation falling onto the i^{th} detector element of the linear array. The denominator of Eq. (2) is a reference lamp spectra acquired without NO in the optical path. The numerator is a measure of the lamp radiation passed through a medium containing NO.

Spectra, acquired with and without NO in the optical path, are presented in Figs. 3a and 4a for the resonance and continuum lamps, respectively. Several vibrational bands of the NO gamma system emitted from the resonance lamp (labeled in Fig. 3a) illustrate molecular features of the NO molecule within the spectral range of the measurement system. However, due to the low temperatures, NO in the automobile exhaust absorbs only at the (0,0) band, as observed in the lower curves of Figs. 3a and 4a. The (0,0) band absorption is seen more distinctly in the spectral transmittances, Figs. 3b and 4b. Note that spectral regions of low lamp intensity produce greater noise levels on the spectral transmittances, as would be expected from signal-to-noise considerations.

Continual spectral coverage allows identification and correction for attenuation effects not attributable to NO gamma absorption. This is illustrated in Figs. 4 and 5 where particulates (possibly dust or water droplets) scattered radiation from the collimated beam. A good estimate of transmittance at the absorbing wavelengths can be determined as illustrated in Fig. 5. A linear (or polynomial) fit to transmittance values at wavelengths just above and below the spectral region absorbed by NO becomes the reference baseline for the NO absorption feature. The corrected transmittance is determined by dividing the measured transmittance by the fitted curve.

4.0 RESULTS

Controlled measurements were performed using the resonance source lamp for a constant 30-mph truck speed and NO/N_2 flow rates of 3.45, 6.63, 12.84, and 17.2 slpm. The equivalent emission factors are 0.92, 1.78, 3.44, and 4.61 gm/mile, respectively. Neither absorption nor anomalous spectral effects were observed on data acquired as the truck passed the measurement station without flowing the gas mixture. Also, absorption for the lowest NO/N_2 flow rate was not discernible from the noise level. However, molecular NO absorption was apparent for the 6.63 slpm flow rate and increased significantly at higher flow rates. Transmittance spectra with maximum absorption are given in Figs. 6 and 7 for release flow rates of 12.84 and 17.2 slpm, respectively.

A reconfiguration of the measurement system allowed the deuterium lamp radiation to cross the roadway four times, thus increasing the effective measurement volume path length by a factor of two. Using this lamp as the radiation source, measurements were performed with a gas mixture flow rate of 17.2 slpm and truck speeds from 6 to 30 mph, giving a range

of emission factors from 23.0 to 4.61 gm/mile, respectively. A spectral transmittance representative of the measurements is given in Fig. 8 for a truck speed of 30 mph (ϵ = 4.61 gm/mile). As the truck speed was increased, the measured transmittance increased from about 0.65 (ϵ = 23.0 gm/mile) to approximately 0.9 (ϵ = 4.61 gm/mile). Also, less absorption was observed as the truck traveled in the direction of the gusty 5 mph winds than in the opposite direction for the same flow rates. The temperature of the tailpipe (monitored with a thermocouple gage) increased from 145 to 500°F during this series of measurements.

Spectral transmittances of Figs. 7 and 8 were acquired at the same simulated exhaust conditions but with different types of lamps. As stated in the introduction, the NO resonance lamp radiation is usually more readily absorbed due to the spectral coincidence of the lamp radiation and absorbing transitions. However, two factors account for more absorption of the deuterium lamp radiation in these measurements. First, the absorbing transitions of NO in the exhaust gas are pressure broadened, making the absorbing linewidths much wider than the Doppler-broadened resonance lamp radiation linewidths. But more importantly, the path of the deuterium lamp radiation through the exhaust was twice that for the resonance lamp radiation measurements. Doubling the path length should approximately square the transmittance at a particular wavelength. Thus, the use of a deuterium lamp in a 4-pass configuration was more sensitive to NO number density in these measurements than a resonance lamp configured for only 2-pass measurements.

Strong spectral absorption features not attributable to NO gamma band absorption, shown in Fig. 9, were observed in one data set acquired during the simulated exhaust measurements. Although the NO absorption centered at 226.5 nm was present as usual, additional features primarily at lower wavelengths indicate absorption due to another chemical species (not discussed in this report). These features have neither been identified nor observed in later measurements aimed at duplicating the measurement conditions. Possibly, unique weather conditions or a coincidental anomalous emission from the truck (engine at idle) could have been responsible for the presence of the species. During the measurements, both the NO/N_2 mixture and an 18-percent concentration of CO in a CO/N_2 mixture (not discussed in this report) were released at flow rates of 17.2 and 83.8 slpm, respectively, with the truck coasting at 30 mph. The tailpipe was about 500°F. A slight drizzle of rain had just stopped, and the air temperature was about 80°F.

A biased set of data was collected on a selection of large older vehicles with large engines using the NO resonance lamp with a 2-pass beam. Data were acquired as these automobiles accelerated through the measurement station from a stopped position 150 ft away. Most of the data showed distinctive absorption in the NO gamma (0,0) band ranging from 80- to 95-percent transmittance. This is illustrated in Fig. 10 where the transmittances for several NO gamma bands (labeled in Fig. 3a) are plotted in time (scan number) for several vehicles.

There were several seconds between measurements for different vehicles which are separated by vertical dotted lines in the figure. Considering data for each automobile as a test, the first data points are pretest transmittances. A sudden drop in transmittance occurred as the vehicle blocked the optical path, immediately followed by a rise in transmittance to about 1.0 at spectral regions other than the (0,0). Transmittance at the (0,0) band slowly increased (absorption decreased) in time as the exhaust dispersed.

Finally, measurements were performed on automobiles selected at random as they passed the measurement station. Most vehicles either coasted or slowed down while passing through the measurement station and therefore were not operating under load conditions. Absorption was not observed on these automobiles. The same was true for the reconfigured 4-pass measurement system using the deuterium lamp. However, when cars at random were made to stop about 100 ft from the measurement station, NO absorption was observed as the vehicle accelerated through the measurement station.

A theoretical modeling code (Refs. 1, 2, and 4) was used to calculate transmittances through a homogeneous medium while varying the NO number density and assuming a pressure or 1 atm, a temperature of 300 K, and a path length of 6 m. The transmittances, corresponding to the primary bandhead of the (0,0) band (226.28 nm), are plotted in Fig. 11 as a function of NO concentration (ppm) times the path length (m) for both NO resonance and continuum source lamps. Although the code was not calibrated exclusively for the range of present measurement conditions, the calculation will give a fair estimate of the amounts of NO for measured transmittances.

The determination of exhaust number density from the theoretical code calculations requires assumptions about the dispersion of the exhaust gases trailing the vehicle. For example, the data shown in Fig. 8 were acquired using the deuterium lamp. The NO emission factor was 4.61 gm/mile, which is equivalent to 5.8×10^{17} molecules/cm. Assuming that during the measurement the exhaust gases were entrained behind the vehicle within a volume with a cross-sectional area 1 meter high by 2 meters along the width of the truck, this emission factor equates to an NO density of 2.9×10^{13} molecules/cm^3, or a measurement path column density of 9.4 ppm-meter, assuming a total number density at ambient conditions of 1-atm pressure and 300 K temperature. Note that the deuterium lamp beam was passed four times across the road giving an equivalent beam-exhaust interaction distance of 8 m. The measured transmittance at the (0,0) bandhead was approxiamtely 0.85, which relates to an NO column density of 26 ppm-meter in Fig. 11 for the continuum lamp calculations. However, the measured transmittance for the vehicle traversing the measurement station in the opposite direction was about 0.92, or about 10 ppm-meter, a number which agrees closely with the density inferred from the emission factor. Similar results were observed for other sets of data acquired using the deuterium lamp and controlled flow-rate conditions.

5.0 SUMMARY AND CONCLUSIONS

The purpose of this study was to determine the feasibility of monitoring NO emissions from automobiles using UV-absorption techniques, with present emphasis on determining the detectability of NO for emission rates comparable to automobile emissions and increasing the measurement sensitivity. Measurements were performed across a roadway using simulated exhausts and automobile exhausts to determine lower limit detectability and feasibility, respectively. Measurement sensitivity was increased by multipassing the source radiation across the roadway. NO-resonance lamp radiation was passed twice across the road (through the test media), and the higher-intensity deuterium lamp radiation was passed 4 times across the road.

Lower detectable limits were determined from measurements through simulated exhausts produced by flowing a 10-percent NO/N_2 gas mixture along the exhaust pipe of a small truck. The 2-pass NO-resonance technique detected NO for emission rates as low as 1.78 gm/mile. Measurements with the deuterium lamp were more sensitive because the beam was passed through the test medium 4 times, increasing the effective path length by a factor of 2 over measurements with the resonance lamp.

Nitric oxide absorption was not detected using either lamp on exhaust measurements of automobiles passing through the measurement station at constant speeds. The typical driver response was to coast or deaccelerate through the measurement station, actions which may account for null measurements. However, NO absorption was observed each time an automobile was forced to stop before reaching the measurement station, and then accelerate through the measurement station as the data were acquired.

The continuum absorption technique, although inherently less sensitive than the NO-resonance technique for equal path lengths, is preferred due to the availability of high-intensity lamps that allow numerous radiation passes through the test media. Thus, the sensitivity achievable with continuum sources is greater than that for the resonance lamp.

Measurements presented in this report indicate that UV absorption techniques have sufficient sensitivity to be pursued as a viable means of monitoring NO emission in automobile exhausts. However, these techniques yield a path-averaged NO number density so that quantification from such measurements depends upon a knowledge of the spatial and temporal dispersion of the exhaust gases. As observed in this study, measured transmittances varied for vehicle direction passing through the measurement station which may be attributed to the gusting wind velocity and/or tailpipe orientation. Absolute quantification could be avoided, however, by independently measuring an easily predictable species, such as CO_2 along the same line-of-sight measurement volume, a practice common in such measurement situations.

These gases would be well mixed so that the ratio of NO to CO_2 would be constant regardless of the exhaust dispersion, and the CO_2 would serve as a reference for the quantity of NO in the exhausts.

REFERENCES

1. Howard, R. P., Dietz, K. L., McGregor, W. K., and Limbaugh, C. C. "Nonintrusive Nitric Oxide Density Measurements in the Effluent of Core-Heated Airstreams." AIAA Paper 90-1478, Seattle, WA, June 1990.

2. Few, J. D. and Lowry, H. S., II. "Reevaluation of Nitric Oxide Concentration in Exhausts of Jet Engines and Combustors." AEDC-TR-80-65, August 1981.

3. McGregor, W. K., Seiber, B. L. and Few, J. D. "Concentration of OH and NO in YJ93-GE-3 Engine Exhausts Measured in Situ by Narrow-Line UV Absorption." AIAA Paper 73-[illegible] Conference on the Environmental Impact of Aerospace Operations in the High Atmosphere, Denver, CO, June 1973.

4. Davis, M. G., McGregor, W. K., and Few, J. D. "Utilizing the Resonance Line Absorption Technique to Determine the Collisional Broadening Parameters of a Diatomic Molecule: NO γ-Bands as an Example." *Journal of Quantitative Spectroscopy and Radiative Transfer*, Vol. 16, No. 12, December 1976, pp. 1109-1118.

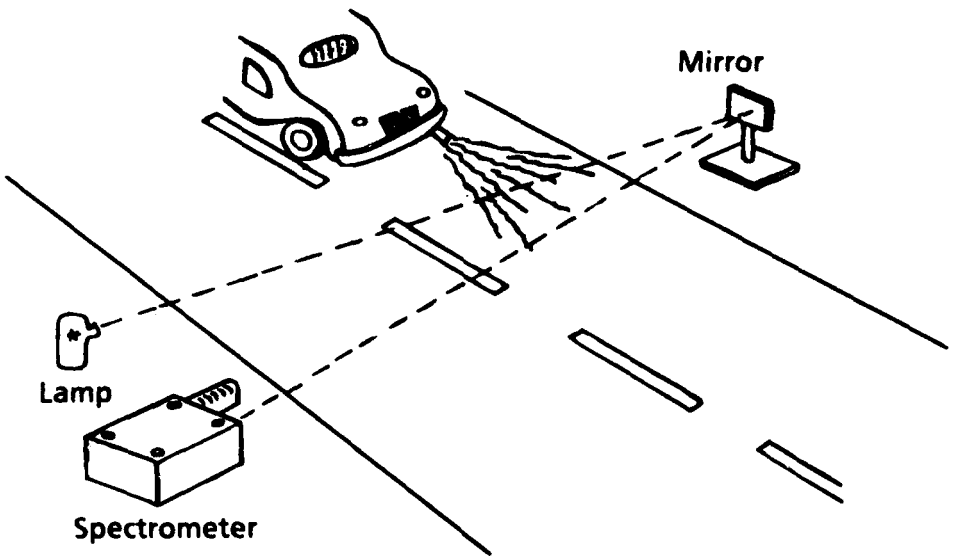


Figure 1. Illustration of the NO resonance absorption system setup for automobile exhaust measurements.

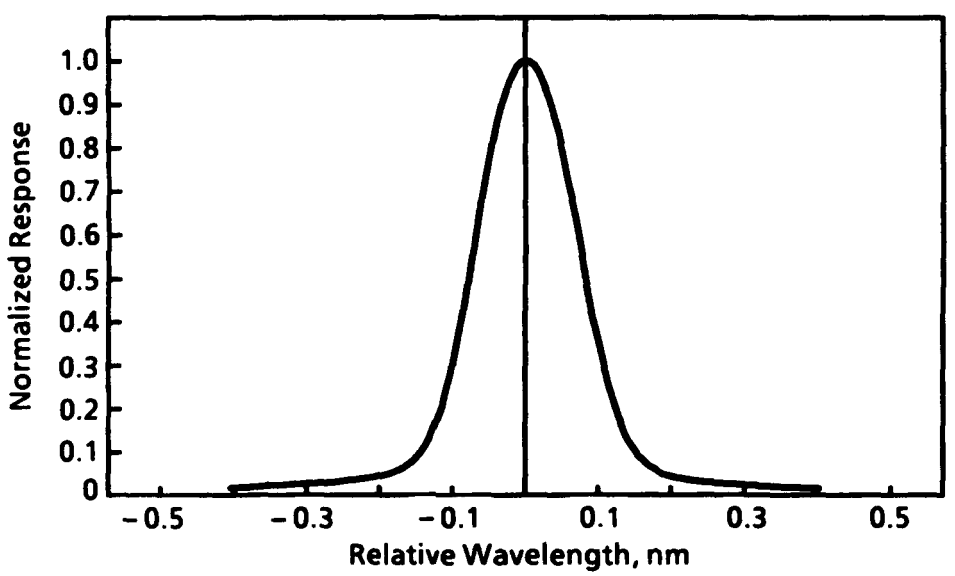
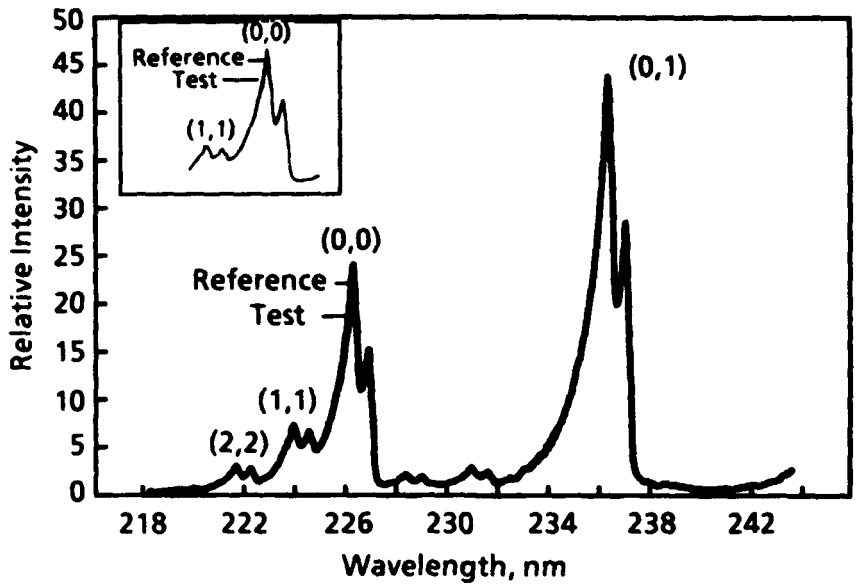
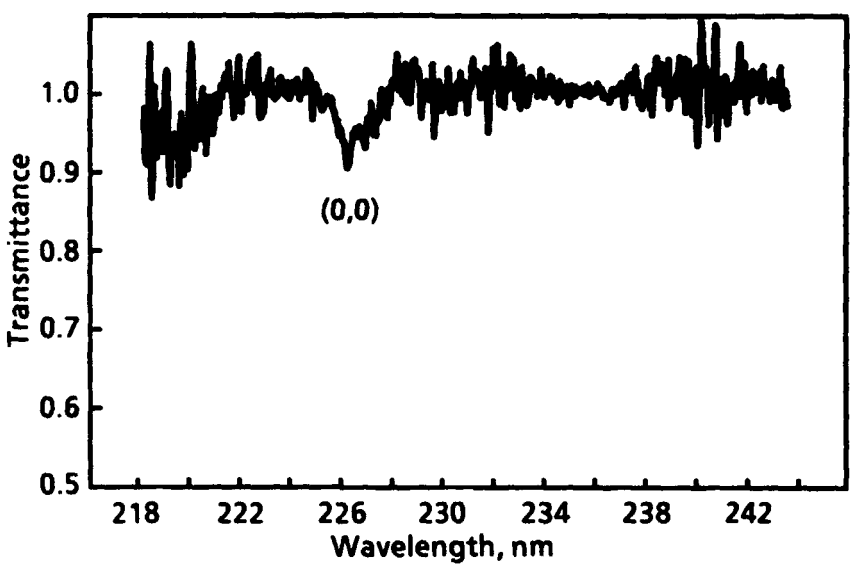


Figure 2. Instrument response function corresponding to a single detector array element.

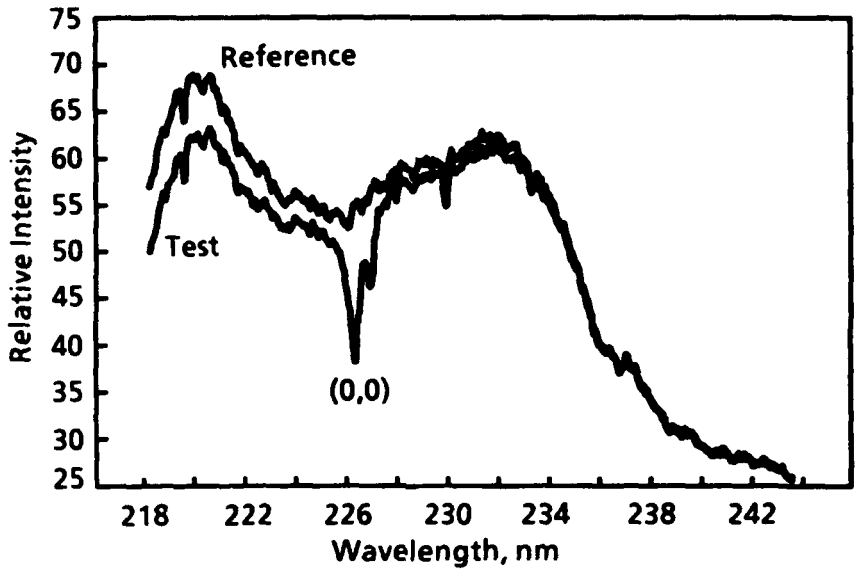


a. Lamp spectra

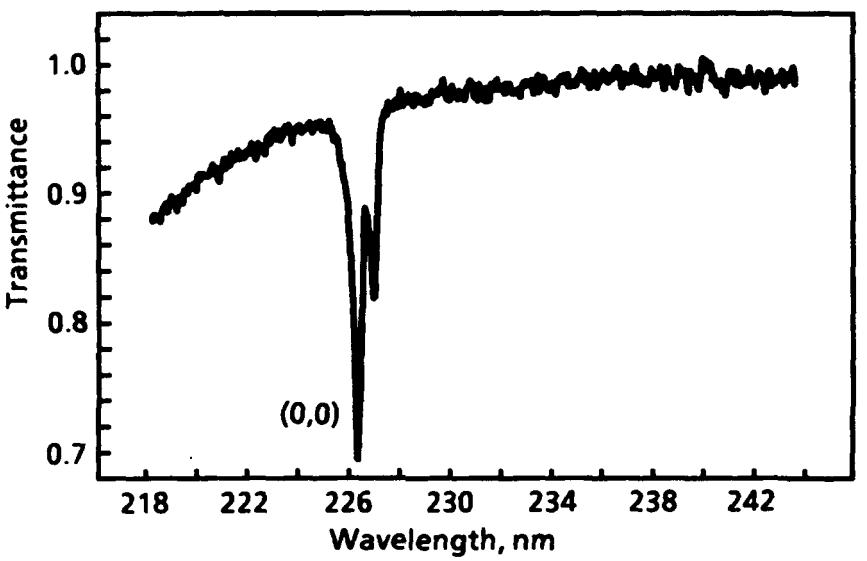


b. Transmittance

Figure 3. NO-resonance lamp spectra with NO gamma bands labeled.



a. Lamp spectra



b. Transmittance

Figure 4. Deuterium lamp reference with and without NO present in the optical path.

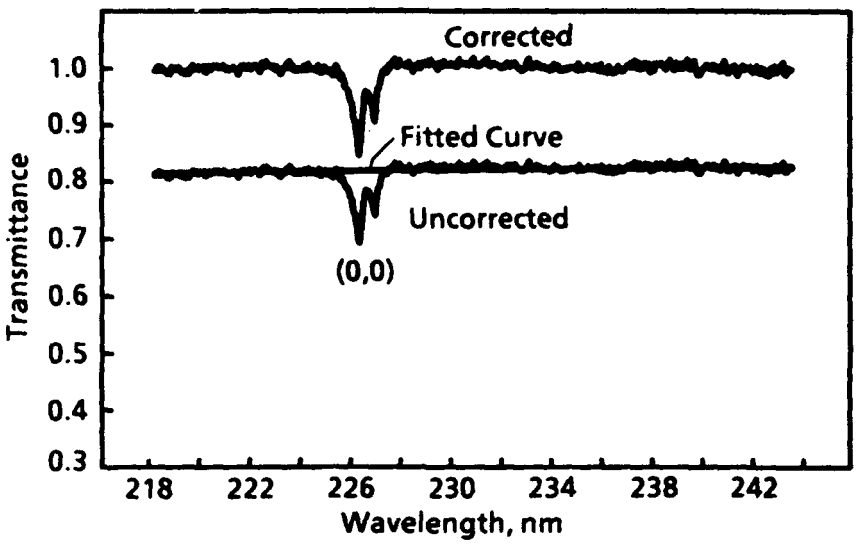


Figure 5. Illustration of transmittance correction for attenuation not attributable to NO absorption.

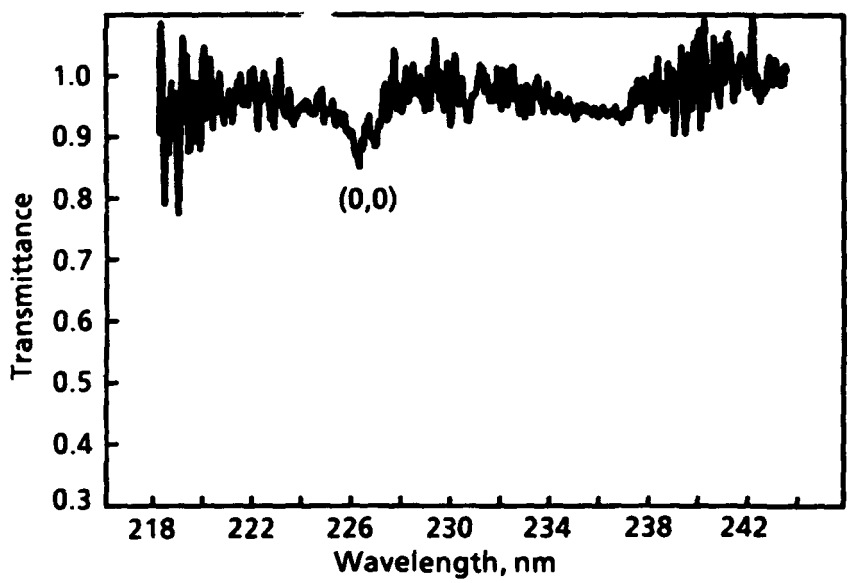


Figure 6. NO-resonance lamp transmittance with 12.84 slpm NO/N_2 flow rate.

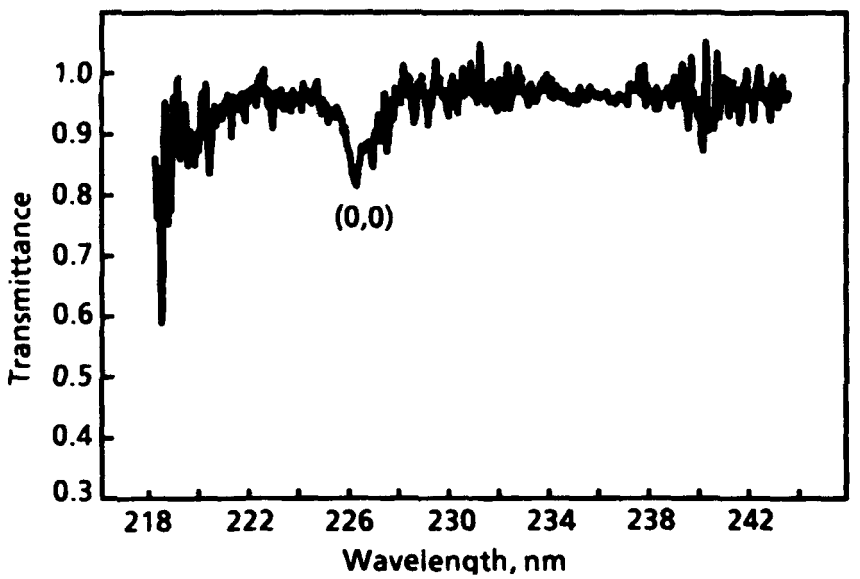


Figure 7. NO-resonance lamp transmittance with 17.2 slpm NO/N_2 flow rate.

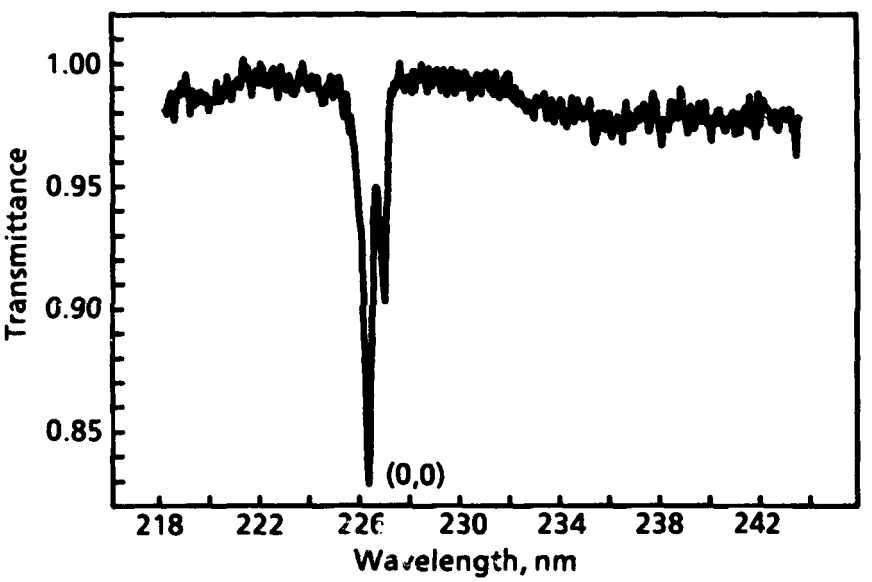


Figure 8. Deuterium lamp transmittance with 17.2 slpm NO/N_2 flow rate.

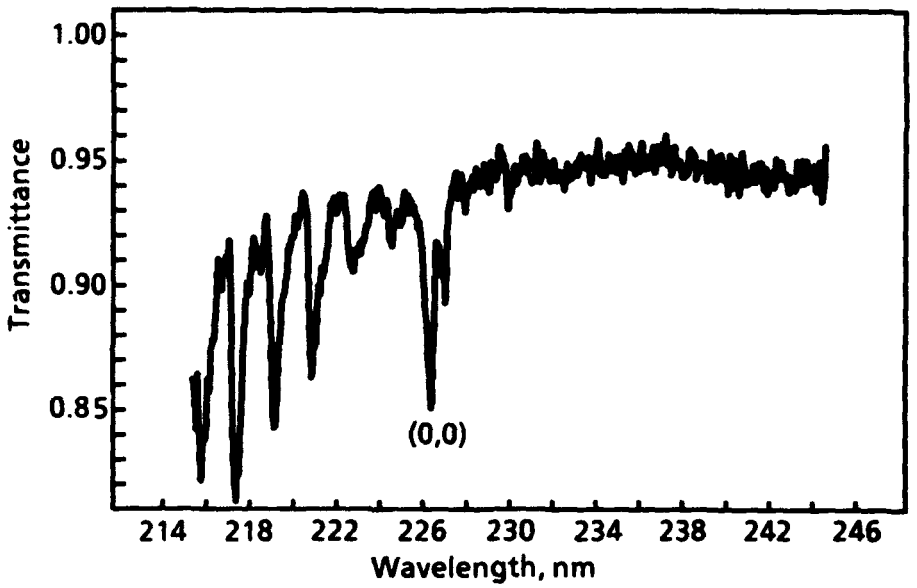


Figure 9. Transmittance spectra with unidentified absorption features.

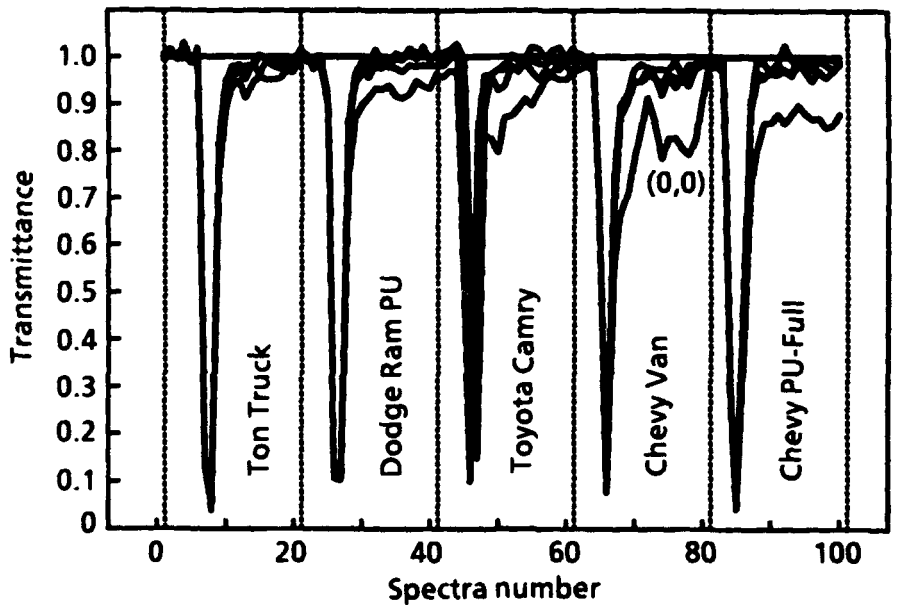


Figure 10. Transmittances at the NO gamma (2,2), (1,1), (0,0), and (0,1) bandheads for automobile exhaust measurements using the resonance lamp.

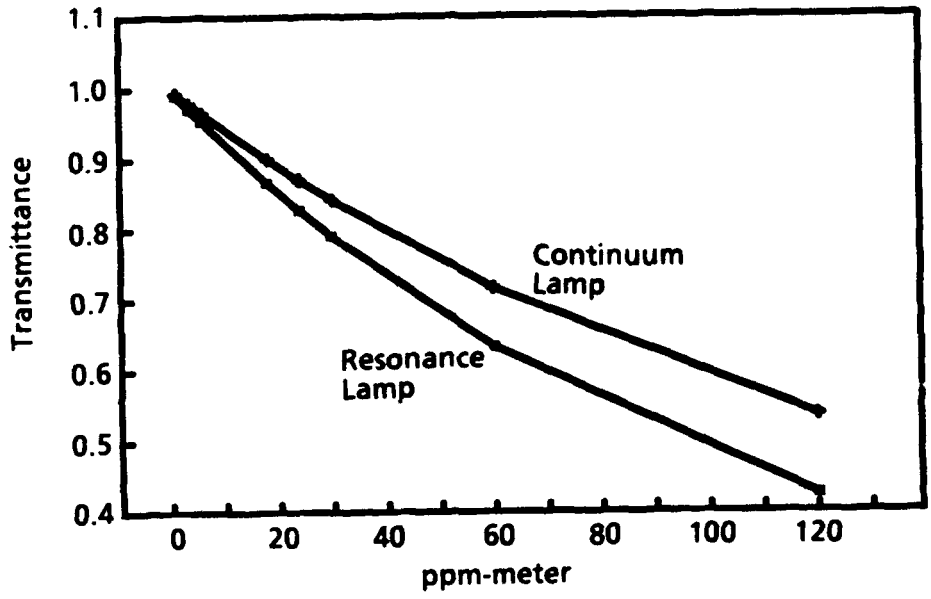


Figure 11. Transmittance calculations for resonance and continuum lamps at P = 1 atm and T = 300 K.