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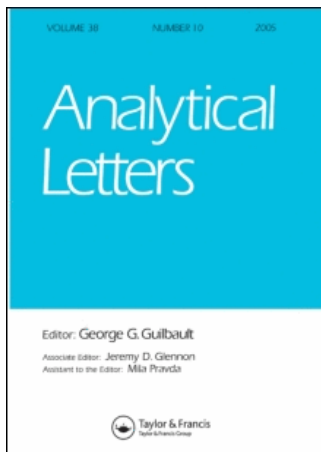
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ANALYSIS OF DIESEL ENGINE EXHAUST BY ULTRAVIOLET ABSORPTION SPECTROSCOPY

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ENVIRONMENTAL ANALYSIS

**ANALYSIS OF DIESEL ENGINE
EXHAUST BY ULTRAVIOLET
ABSORPTION SPECTROSCOPY**

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ABSTRACT

Ultraviolet absorption spectroscopy was used for the analysis of exhaust from internal combustion engines. This technique employs a single pass absorption cell with a high speed photodiode array detector. Differential absorption was used to quantify analytes and to correct for changes in cell transmission. Sulfur dioxide, ammonia, and nitric oxide were detected with little interference from other species. The results obtained using this method compared very favorably with the results obtained using infrared absorption and chemiluminescence techniques.

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Key Words: Diesel exhaust; UV; Photodiode array; Sulfur dioxide; Ammonia; Nitric oxide

INTRODUCTION

Stringent emissions regulations and fuel efficiency are two of the biggest issues facing automotive companies and engine manufacturers (1). Gasoline vehicles, in combination with exhaust gas recycling (EGR) and three-way catalysts, are approaching zero emissions for oxides of nitrogen (NO_x), carbon monoxide (CO), and non-methane hydrocarbons (2). Their fuel efficiency, however, is up to 40% lower than that of diesel engines (3). Diesel engines typically have high NO_x and particulate-matter (PM) emissions, and very low hydrocarbon (HC) and CO emissions. Thus, there has been a serious effort to develop exhaust emissions control systems that will enable the widespread use of diesel engines by reducing NO_x and PM emissions. This would allow manufacturers to meet upcoming regulations.

As manufacturers work to meet the regulatory requirements, they need better analytical techniques to evaluate new engine catalyst and system designs. As emissions levels drop, new analytical methods with faster response times and lower detection limits are required. Typical diagnostic requirements are a time resolution on the order of one second and part per billion detection limits (4). In some applications, such as monitoring cold starts, greater temporal resolution (< 1 s) is required to resolve cycle to cycle variations (5). A typical four-stroke engine requires a temporal resolution of less than 10 msec to resolve the intra-cycle variations under normal operating conditions.

Techniques capable of achieving high temporal resolution and low detection limits are often prohibitively expensive for wide spread application (6). Moreover, such techniques are often limited to analysis of a single analyte or class of analytes. Two of the most broadly used fast emission analyzers are based on fast response flame ionization detection and fast response chemiluminescence detection, and they quantify hydrocarbons and oxides of nitrogen, respectively (7). While these instruments provide the requisite temporal resolution, they provide limited insight into engine performance due to their species specificity. For most studies, the concentrations of multiple species must be quantified simultaneously.

A popular technique for detection of multiple species in engine exhaust is infrared absorption spectroscopy (8). With the development of new multivariate methods for interpretation of spectral data, FTIR spectrometers have been used to determine over a dozen analytes simultaneously in



engine exhaust (9–11). Due to overlapping absorption bands of the exhaust constituents, high spectral resolutions are often required to detect many species at low concentrations. This greatly limits the frequency at which spectra can be collected and correspondingly the temporal resolution of the diagnostic. An additional speed limitation of infrared techniques is associated with the pathlength required for analysis of trace gases. To detect some environmentally important exhaust species, pathlengths of 5 to 10 m are needed to quantify species at the part-per-million (ppm) level. This is due to the small infrared absorption cross section of these species (12). Multi-pass gas cells can provide the requisite pathlength, but often have volumes on the scale of 1 to 5 l (8). Such large gas-cell volumes limit the temporal resolution since the cell must be flushed with several volumes to completely change the sample gas.

For some applications ultraviolet (UV) absorption spectroscopy provides benefits not afforded by infrared absorption spectroscopy. UV absorption spectroscopy is one of the most well established of all analytical techniques, and numerous techniques have been developed, for atmospheric and flue-gas analysis, based on UV absorption spectroscopy (13, 14). While UV spectroscopy cannot detect as many species as infrared spectroscopy, it is well suited for measuring several environmentally important species such as nitric oxide, nitrogen dioxide, sulfur dioxide, ammonia, aromatic hydrocarbons, ozone, and formaldehyde (15, 16).

Recently, there has been an increased interest in using UV absorption for the analysis of engine exhaust (17, 18, 19). Compared to infrared instrumentation, UV instrumentation is relatively inexpensive and high speed detector arrays are available at relatively modest cost. In addition, the absorption cross sections of UV transitions are typically one to three orders of magnitude greater than those of infrared transitions (12). This allows the usage of single pass gas cells with very small volumes resulting in an increase in temporal resolution. In this work, a UV absorption spectrometer was constructed and evaluated for analysis of engine exhaust.

EXPERIMENTAL

A single pass UV absorption spectrometer was developed for this work, and it is described in Figure 1. A deuterium lamp (L6301, Hamamatsu) was used to provide a broad UV emission source. The gas cell was fabricated by boring a 12.5-mm diameter hole through a 0.3-m long piece of 50.8-mm diameter aluminum round stock. Quartz windows were sealed to the ends using o-rings. Although the cell was not heated directly, it was enclosed in a housing with the deuterium lamp, and exhaust



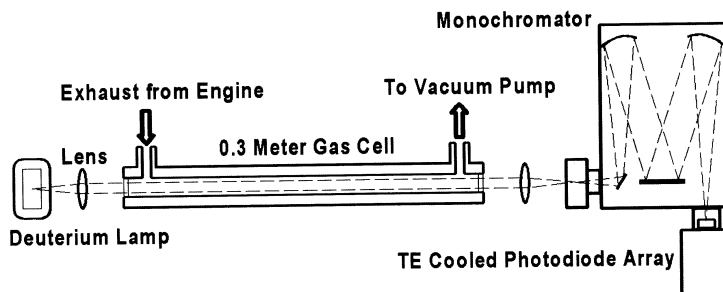


Figure 1. Drawing of the experimental set-up used in this work.

gases were transferred to the cell by heated transfer lines. The spectrograph used was a 0.32-meter monochromator with an entrance slit width of $14\ \mu\text{m}$, and it was configured with either a 250-nm blaze 2400-groove/mm grating or a 400-nm blaze 600-groove/mm grating (HR 320, ISA). The spectra were collected via a thermo-electrically cooled 2048 element linear high speed photodiode charge couple device (PCCD) detector with $14 \times 200\ \mu\text{m}$ pixels (LS 2000C, Alton Instrument). The PCCD was controlled using manufacturer software and user developed software written in Visual C++. Array exposure times of approximately 100 ms were used throughout this work. Qualitative absorbance spectra were collected using room air as a background. Quantitative measurements were made using the technique described in the results section.

The UV spectrometer was calibrated for nitric oxide and sulfur dioxide using certified gas mixtures prepared by gas vendors. To determine the sensitivity of the system over a range of concentrations a gas divider (SGD-710C, STEC Inc.) was used to reduce the concentration of the gas standards. The divider allows the concentration of the calibration gas to be diluted in 10% increments from 100 to 0% with a second diluent gas. In this work, nitrogen was used as the diluent gas.

Engine exhaust was generated using a 1.9 L turbocharged direct injection Volkswagen diesel engine and a 1.7 L turbocharge common rail Mercedes Benz diesel automobile. The Volkswagen engine was mounted to a Pohl 175 HP eddy current engine dynamometer which was controlled by a Dyne Systems digital dynamometer control. The Mercedes Benz was operated on a Sun 20 in roller chassis dynamometer. The exhaust from the Volkswagen engine was filtered using a <1 micrometer filter to remove any particulate matter from the exhaust. The Mercedes Benz exhaust was collected after passing through an experimental catalytic exhaust emissions control device.



A diaphragm vacuum pump downstream of the UV gas cell was used to draw the engine exhaust through the transfer lines and the gas cell. For both engines, a 9.5 mm transfer line heated to 190°C was used. The flow rate through the gas cell was approximately 60 l/min. This flow rate was determined by the pumping speed of the vacuum pump.

For some experiments, the engine exhaust was simultaneously monitored using the UV spectrometer, an infrared spectrometer, and a chemiluminescent analyzer. The Fourier transform infrared spectrometer (FTIR) was operated at 0.5-wavenumber resolution and was used to collect absorption spectra over the spectral range of 4000 to 400 wavenumbers (Rega 7000, Nicolet). It had a 10 m heated multi-pass gas cell with a volume of 1.5 l. The temperature and pressure of the FTIR cell were maintained at 150°C and 650 torr, respectively. A dedicated chemiluminescence analyzer (Model 400 HCLD, California Analytical) was used to quantify concentrations of oxides of nitrogen. The FTIR system and chemiluminescence instrument were operated and calibrated according to manufacturers specifications. The infrared system had a temporal resolution longer than 2 min, and the chemiluminescence system had a temporal resolution of approximately 30 s. These temporal resolutions are based on time for the systems to respond to changes in exhaust composition. Since variations in an engine exhaust occurs on a time scale of less than 1 s, these techniques are not able to resolve rapid variations in engine exhaust (5).

RESULTS

Figures 2 and 3 show UV absorption spectra of exhaust from the Mercedes Benz and Volkswagen engines, respectively. Unlike infrared absorption, water does not present a major source of spectral interference in the UV absorption spectral region from 200 to 400 nm. The water vapor concentration in typical diesel engine exhaust is 7%. This can be a significant problem in the infrared when weak analyte absorption bands are frequently measured in the presence of strong absorption bands of water. This often makes it necessary to record spectra at high resolutions of 0.5 wavenumbers to avoid or minimize spectral overlap (8). One way to mitigate water interferences is to remove it via condensation, as required by some analytical techniques used for exhaust analysis (14). However, this can remove some analytes that will condense with the water such as polar organic compounds and certain NO_x species.

Quantitative measurements were made using differential absorption spectroscopy. Differential absorption spectroscopy is frequently used for atmospheric measurements where it is not possible to obtain a true reference



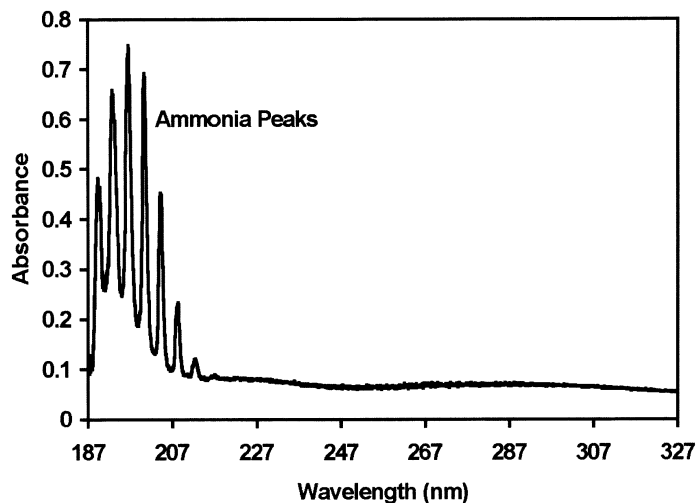


Figure 2. The absorption spectrum of engine exhaust from a 1.7 L turbocharged common rail Mercedes Benz diesel engine after passing through an experimental catalyst. This spectrum was collected with a 400-nm blaze 600-groove/mm grating.

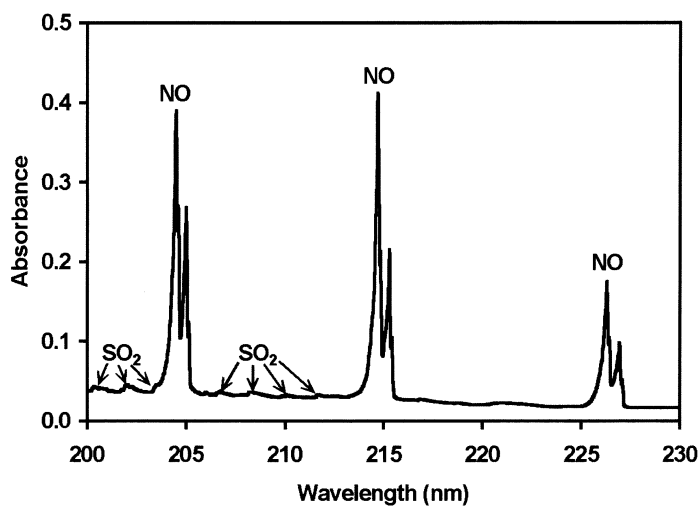


Figure 3. The absorption spectrum of engine exhaust from a 1.9 L turbocharged direct injection Volkswagen diesel engine at high load. This spectrum was collected using a 250-nm blaze 2400-groove/mm grating.



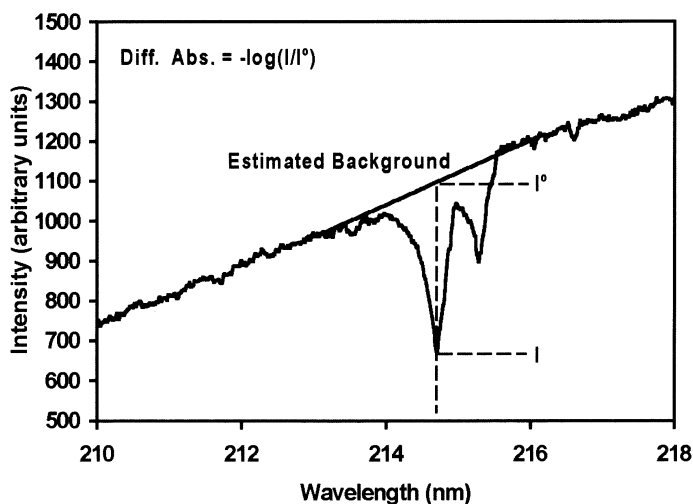


Figure 4. Differential absorption technique used to calculate nitric oxide absorption.

spectrum (20). In differential absorption, the absorbance of the analyte is quantified by comparing the signal at the wavelength of interest to that at a nearby wavelength where the analyte does not absorb. It was used in this study because of the instrument's single beam configuration and the changes in the gas-cell transmission due to water condensation or particulate matter collecting on the cells windows. For this work, the background transmission was determined by linear extrapolation between regions where the analyte does not absorb UV radiation. Figure 4 presents the method used for calculation of the differential absorption of nitric oxide.

The absorbance of nitric oxide was determined to be non-linear over the concentration range of 0 to 1000 ppm, Figure 5, and described by the equation,

$$\text{differential absorbance} = -2 \times 10^{-7} [\text{NO}]^2 + 0.0006 [\text{NO}] + 0.001$$

with a correlation of 0.9998 where [NO] is the concentration of nitric oxide in ppm. The nonlinearity is consistent with results reported in the literature and has been extensively described by Mellqvist and Rosén (21). The detection limit for nitric oxide based on three standard deviations of an air blank is approximately 1 ppm. Sulfur dioxide was quantified by the absorption



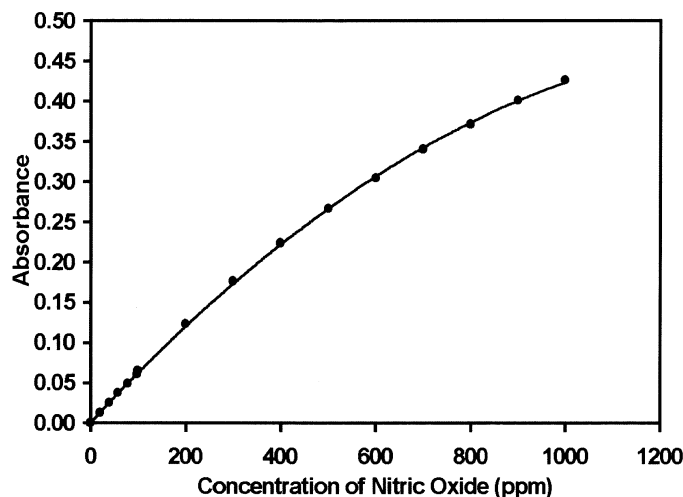


Figure 5. Calibration curve for nitric oxide. The standard deviation of the absorbance at a given concentration based on three to five consecutive measurements is smaller than the circle used to show the data point.

occurring at approximately 208 nm. It was found to have a linear absorbance up to 190 ppm with a detection limit of approximately 5 ppm. Since little background interference was observed, these detection limits potentially could be improved by increasing the pathlength of the gas cell.

To evaluate the ability of differential absorption to correct for changes in cell transmission, water condensation was allowed to form on the cell windows. Figure 6 shows the decrease in cell transmission due to water condensation on the windows of the cell while monitoring the exhaust from the Volkswagen diesel engine. Over the course of the evaluation, an approximate 85% decrease was observed in the transmission efficiency of the gas cell. After the evaluation was concluded, the cell was purged with air which restored the transmission of the cell to its initial level.

During this evaluation, the concentration of nitric oxide was simultaneously measured by the chemiluminescence, infrared absorption, and UV absorption instruments. By adjusting the operating conditions of the engine, the concentration of NO in the engine exhaust was varied. The engine was operated at 1200 rpm, and the torque varied from 5 to 100 Nm. In Figure 7, the differential UV absorption of nitric oxide is compared to the absorbance of nitric oxide measured by the FTIR and the concentration of nitric oxide determined by chemiluminescence analyzer. Based on the comparison



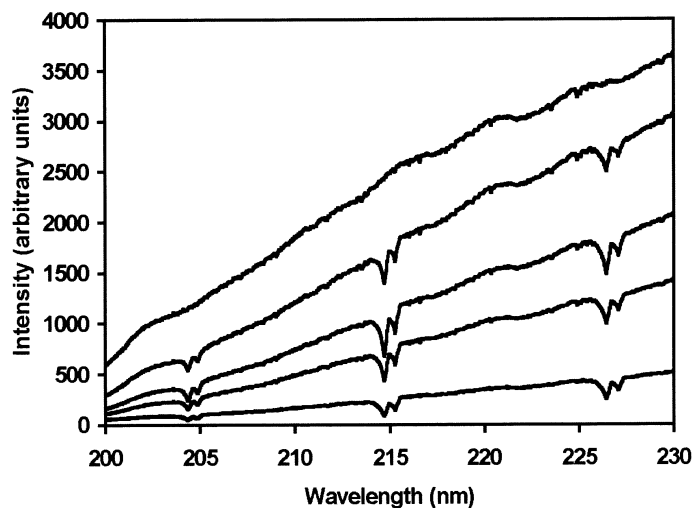


Figure 6. Changes in gas cell transmission due to water condensation on the cells windows.

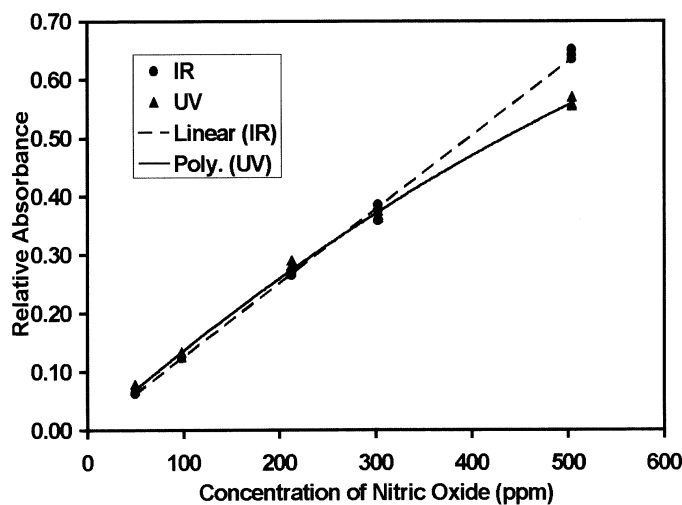


Figure 7. Comparison of infrared absorption, UV absorption, and chemiluminescence for the analysis of exhaust from the Volkswagen diesel engine. The x -axis is the concentration measured by the chemiluminescence analyzer. The UV absorbance was determined as shown in Figure 4, and the infrared absorbance was based on peak height of the absorption band at approximately 1900 wavenumbers. The absorbances have been scaled to show the comparison between UV and infrared.



between the absorbances and the measured nitric oxide concentration, good agreement was obtained between the three methods. The correlations between the infrared and ultraviolet techniques with the chemiluminescence results were 0.9986 and 0.9977, respectively. When it is considered that techniques for analysis of engine exhaust can disagree by as much as 30%, the methods compare very favorably (10).

The agreement also demonstrates the ability of differential UV absorption to quantify exhaust species concentrations in the presence of water and condensation on the cell windows. Even with the large decrease in cell transmission, the ultraviolet and chemiluminescence results agree. In an actual engine test, the cell would be heated to avoid water condensation. Nevertheless, correction is required to account for the reduction of cell transmission due to PM deposits on the cell windows.

One of the goals of this work was to monitor in real time environmentally important species in engine exhaust. The temporal variation of ammonia produced by an experimental catalytic exhaust emissions control device was monitored over several 100-second intervals. This catalyst stores various nitrogen oxide species when an engine is operating under lean conditions. These species are then converted to N_2 and/or ammonia when the catalyst is operated under reducing conditions. In this study, additional fuel was introduced into the exhaust stream after the engine and upstream of the catalyst. When the excess fuel reached the catalyst, it allowed the release of the stored nitrogen species which were rapidly reduced to N_2 and NH_3 . Catalyst temperature and exhaust NO_x concentration variations contribute to the differences in NH_3 production. For instance, the large emission of NH_3 shown in Figure 8 occurred during a very high speed portion of the driving cycle. The high engine load at this speed resulted in high NO_x production and subsequent storage on the catalyst. Thus, when the catalyst was regenerated under the reducing condition, it resulted in a substantial release of NH_3 .

Nitric oxide was also monitored during the cycling of a diesel engine through different operating conditions. As can be seen in Figure 9, a rapid increase in nitric oxide concentration was observed in the engine exhaust as engine loads increases. This was the result of increasing combustion temperatures (3). Based on the flow rate of gas through the gas cell, it was estimated that the time resolution of the system was approximately 100 ms. Since the detector array used in this work has a minimum scan time of 5 ms, it should be possible to improve the temporal response of the system by decreasing the cell diameter. This would reduce the cell volume and the time required to completely replace the gas in the cell.



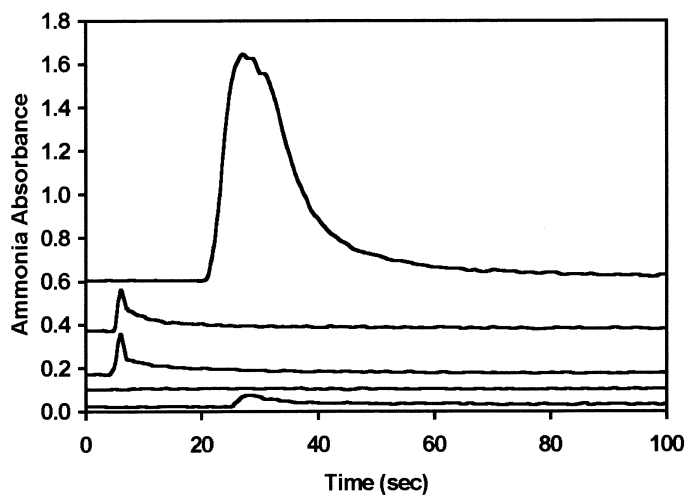


Figure 8. Change in ammonia absorbance in the exhaust from the Mercedes Benz diesel engine after passing through an experimental catalyst. The zero time is referenced to the change of operating condition of the catalyst from an oxidizing to a reducing environment. The spectra have been offset to show differences.

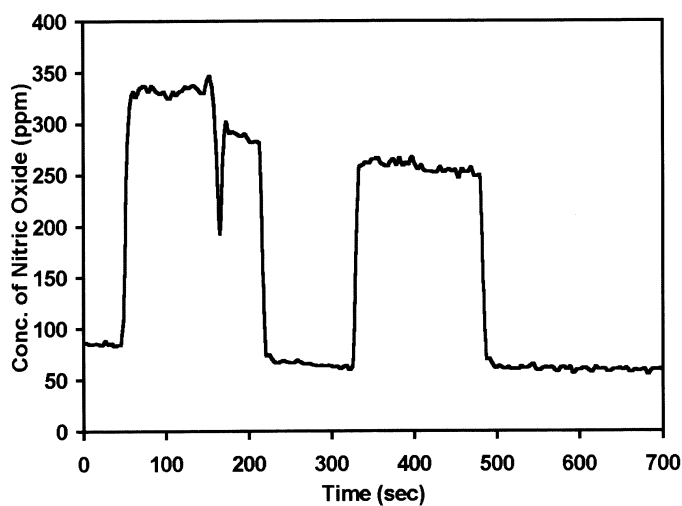


Figure 9. Variation in nitric oxide concentration in engine exhaust of the Volkswagen diesel engine operated at 1200 rpm. The rapid increases in nitric oxide concentration occurred when the torque of the engine was increased from 5 to 90 Nm and from 5 to 60 Nm.



CONCLUSIONS

UV absorption spectroscopy is well suited for detections of some environmentally important species in engine exhaust. While it cannot be used for the detection of as many species as infrared absorption spectroscopy, UV absorption can be faster, less expensive, and has no significant spectral interference from water in the spectral range of interest. The results obtained demonstrate high speed monitoring with accuracies equivalent to those of established steady-state analytical techniques.

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