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# Vehicle Remote Sensing for Nitrogen Dioxide

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# VEHICLE REMOTE SENSING FOR NITROGEN DIOXIDE

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## Introduction

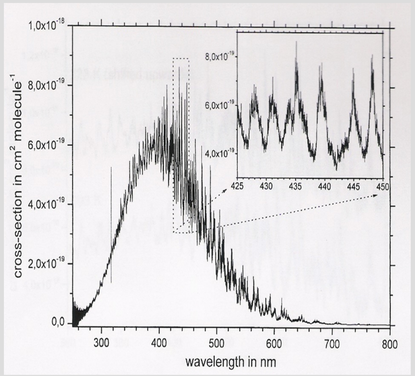
Diesel vehicles produce significant quantities of oxides of nitrogen ($NO_x$) and particulate matter (PM). By the end of the decade both the United States and the European Union will have implemented strict standards governing the emission of both of these species. Of concern is the use of continuously regenerating particulate filters to reduce PM emissions in diesel vehicles. The downside to this technology is that it involves the production of primary $NO_2$.[2-4] This is of concern, as $NO_2$ has been implicated in both the formation of aerosol species and certainly accelerates ozone formation.[1] To this end the California Air Resources Board has proposed a regulatory limit for vehicular $NO_2$ emissions that will go into effect Jan. 1, 2007. It limits post-control $NO_2$ emissions to less than 20% of pre-control $NO_x$. Current emission standards state that a 1998-2003 model year heavy-duty diesel engine must emit less than 4g/bhp•hr $NO_x$. Currently FEAT (Fuel Efficiency Automobile Test) 3000 technology has already been used to measure NO. Current work is focused on adapting this technology to the detection of $NO_2$ with the eventual goal of producing and instrument capable of detecting real time on-road emissions of NO and $NO_2$. The $NO_2$ system has been tested both in the lab and in parking lot studies. Preliminary results and complications of this process are presented.

1 Butcher, S. S.; Charlson, R.J. *An Introduction to Air Chemistry;* Academic Press: New York, 1972; pp 117-149.
2 Shorter, J.H.; Herndon, S.H.; Zahniser, M.S.; Nelson, D.D.; Wormhoudt, J.; Demerjian, K.L.; Kolb, C.E. Real-time Measurements of Nitrogen Oxide Emissions from In-use New York City Transit Buses using a Chase Vehicle. *Environ. Sci. Technol.*, in press.
3 Carslaw, D.C.; Beevers, S.D. New Directions: Should road vehicle emissions legislation consider primary NO2. *Atmospheric Environment.* **2004,** *38,* pp 1233-1234.
4 Tang, S.; Graham, L.; Shen, L.; Zhou, X.; Lanni, T. Simultaneous Determination of Carbonyls and NO2 in Exhausts of Heavy-Duty Diesel Trucks and Transit Buses by HPLC following 2,4-Dinitrophenylhydrazine Cartridge Collection. *Environ. Sci. Technol.* **2004,** *38,* pp 5968-5976.

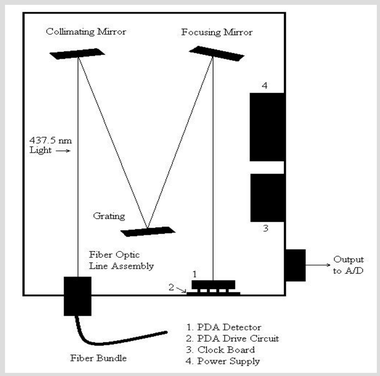
## Goals

- Adapt current FEAT technology towards developing a remote unit that can detect $NO_2$ at a mixing ratio of 500 ppm • cm at 100 Hz with a signal to noise ratio of 3 or better.
- Test commercially available NO/$NO_2$ detection system and use to verify FEAT $NO_2$ detection technology.

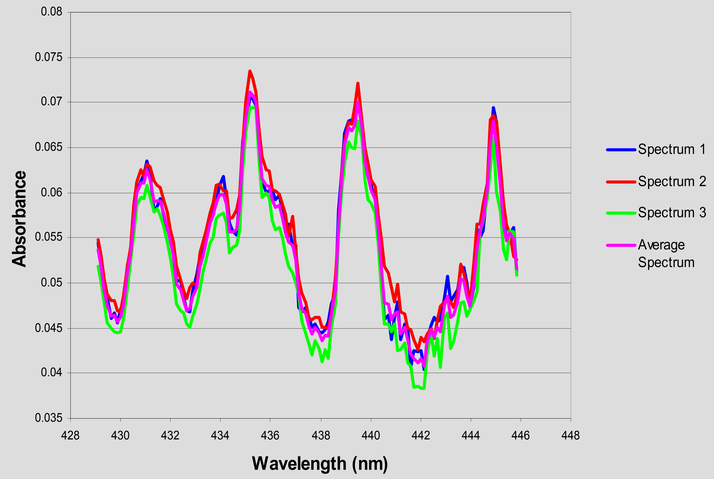
## Monochromator Modification



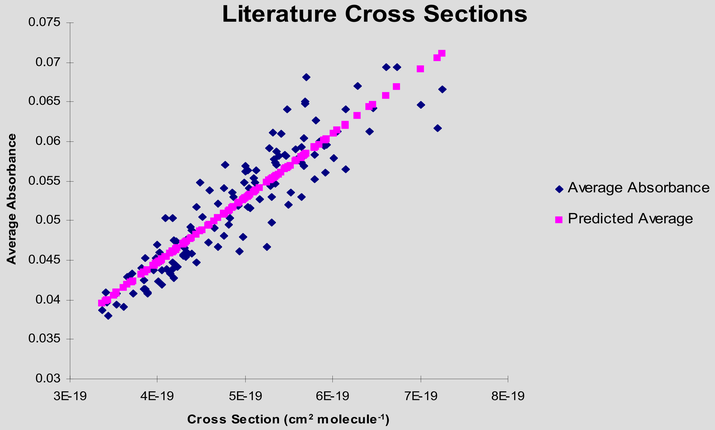

- For $NO_2$ the region of 425-450 nm has the largest peak-to-valley absorbance.
- The monochromator was originally designed for NO detection in Littrow for 226 nm.
- A 5° wedge was inserted under the grating mount to bring 435.8 nm in Littrow.
- $D^{-1}$ = 2.64 nm/mm at Littrow for 437.5 nm.
- 6.4 mm detector → 17 nm bandpass, 429-446 nm.
- Spectral resolution = 0.132 nm/diode.
- Actual resolution = 2 (0.132 nm/diode) = 0.264 nm/diode (fiber width =100 µm, diode width = 50 µm).
- Calibrated with a 435.8 nm mercury line.




**Absorbance vs. Wavelength for 498 ppm $NO_2$ in an 8 cm Cell**




**Pixel by Pixel Correlation of Absorbance to Literature Cross Sections**




| Manufacturer Cylinder Mixing Ratio[5] | Mixing Ratio Determined by Literature Cross Sections[6,7] |
|---|---|
| 498 ± 10 ppm $NO_2$ | 503 ± 20 ppm $NO_2$ |

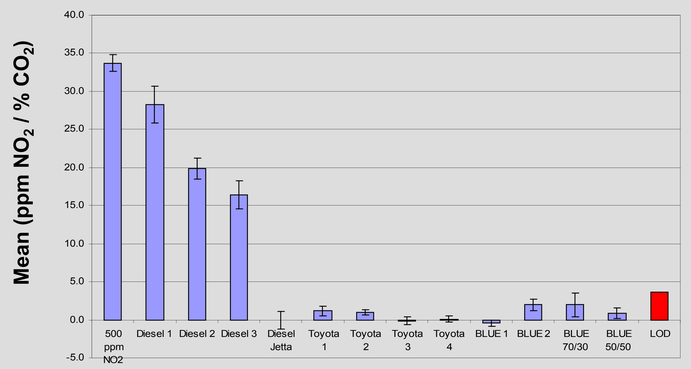
- Scott Specialty Gases, Longmont, CO
- Voigt, S.; Orphal, J.; Burrows, J.P. The temperature and pressure dependence of the absorption cross- sections of $NO_2$ in the 250-800 nm region measured by Fourier-transform spectroscopy. *Journal of Photochemistry and Photobiology A-Chemistry.* **2002,** *149,* pp 1-7.
- Cross sections scaled by 0.95. (Rainer Volkamer, personal communication, June 7, 2004)

Comparison of manufacturer and experimentally determined specifications for an onboard NO/$NO_2$ detector. (Sensors, Inc., NDUV NO/$NO_2$ module, 9110-141 Rev. B)

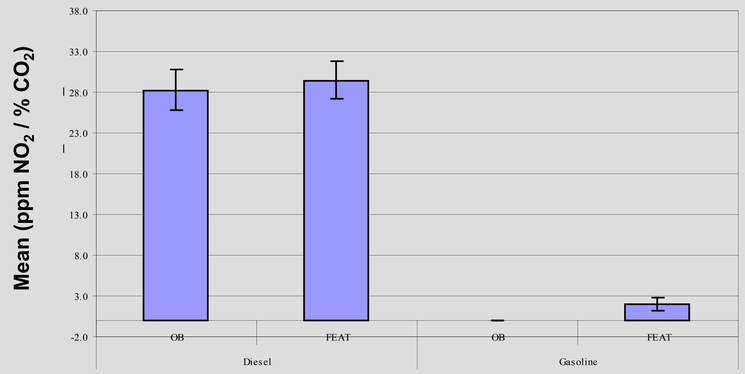
| | $NO_2$: Manufacture Specifications | $NO_2$: Experimentally Determined Specifications |
|---|---|---|
| Accuracy | ±3 % of reading or 10 ppm, whichever is greater | ±1.3 % of reading or 6.5 ppm, whichever is greater |
| Precision | ±1 % of reading or 5 ppm, whichever is greater | ±0.99 % of reading or 4.9 ppm, whichever is greater |
| Baseline Drift | NA | 0.068 ppm/min |
| Span Drift | ±0.021 ppm/min | 0.16 ppm/min |
| Response Time | =2 seconds | 6.5 seconds |

## Successful Real-Time Measurements of $NO_2$

**$NO_2$ Emissions Measured with FEAT**




**Onboard and FEAT Measurements of Exhaust $NO_2$**




## Summary

- Current FEAT Technology was successfully adapted for the detection of $NO_2$.
- The target detection limit was 500 ppm • cm, this goal was met with a detection limit of 414 ppm • cm.
- $NO_2$ emissions meeting the proposed 2007 CARB 20% $NO_2$ limit will be measured with S/N > 10.
- A commercially available NO/$NO_2$ detector was used to verify the new technology. Measurements show good agreement.

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