

Development of a High-Speed Ultraviolet
Spectrophotometer Capable of Real-Time NO and
Aromatic Hydrocarbon Detection in Vehicle Exhaust

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Introduction

While it has been shown that current remote sensing technology is entirely capable in measuring the carbon monoxide and total hydrocarbon components of motor vehicle exhaust, nitric oxide has proven to be difficult to measure in an on-road situation. A previous addition to the remote sensing system developed at the University of Denver has been demonstrated to measure NO, but this instrument is more effective at fleet evaluation, rather than the measurement of individual vehicles (1,2). We have developed a new instrument which has shown promise not only in quantifying NO emissions from individual vehicles, but also in the measurement of aromatic hydrocarbons. The new instrument still measures the traditional CO, CO₂, and HC, making it more versatile than the laser diode system reported in 1996 (3). In addition, this concept is also easily modified for use as an on-board NO monitor, capable of measurements at a frequency of 100 Hz.

Instrumentation

The new University of Denver remote sensing system is shown schematically in Figure 1. Colinear beams of infrared and ultraviolet light are passed across the roadway in a bistatic arrangement. The beams enter the main CO/CO₂/HC unit, are collected by a 2" *f*/6 mirror, and focused towards a dichroic mirror, which serves as a beam splitter. The infrared light passes through the dichroic mirror, onto the spinning polygon mirror which spreads the light across the four infrared detectors (CO, CO₂, HC and reference).

The ultraviolet light is reflected off the first surface of the dichroic mirror, and focused into the end of a quartz fiber optic bundle, which is mounted on an SMA-type connector on the side of the main detector unit. This fiber optic cable, 1 m in length, is a bundle of 37 100 μm diameter ultraviolet grade quartz fibers. The fibers are arranged in a round bundle at the front end of the cable, where the UV light is focused into the cable, but are mounted in a line configuration at the back end. In this arrangement, the fibers are stacked one upon another effectively forming an image surface 100 μm wide by 4.2 mm high. This end of the cable then serves as the entrance slit for a Czerny-Turner ultraviolet monochromator. In this unit, detection is presently accomplished by means of a 128 diode photodiode array detector. With the 1200 line/mm holographic grating used in this monochromator, the spectral range of this instrument is 16 nm, spanning 218-234 nm when measuring the gamma band of NO at 226.5 nm, or 253-269 nm when measuring absorption by aromatic hydrocarbons.

At present, the entire system is controlled by two computers. The main computer controls the IR detection unit, and is responsible for most of the preliminary car detection, data processing and video capture controls. The photodiode array detector in the UV monochromator is controlled by a separate computer. In operation, the UV system is alerted by the main computer that a car is present, and then captures 50 intensity spectra, each with an exposure time of 10 ms. This 100 Hz sampling rate over a period of 0.5 s behind the car is identical to that of the IR unit. Each of these 50 spectra are analyzed in real time, by first being converted to absorbance space using a reference spectrum gathered with no vehicle exhaust present. For each absorbance spectrum, the amount of NO in the light path is determined by a classical least-squares analysis, compared to a calibration spectrum gathered in the laboratory. Figure 2 shows an absorbance calibration spectrum for NO, with the doublet absorption band at 226.5 nm centered at diode 64.

The least squares fit is accomplished by plotting the absorbance values for diodes 50 to 80 of the sample spectrum vs. the absorbance values for diodes 50 to 80 of the calibration spectrum. One such plot is shown in Figure 3, for a sample spectrum of 100 ppm•m NO. The slope of this plot gives the concentration of the sample spectrum, relative to the calibration standard. Determining the concentration of the sample spectrum by this method offers a number of advantages over a simple peak height or peak area analysis; not only does plotting a 30 diode region of the spectrum allow one to obtain an average of 30 absorbance values from a single spectrum, but also there is an inherent peak shape investigation being carried out as well. While an interfering peak may have the same height or area as that of an NO peak in the same region, if it does not have the same doublet shape, the absorbance of the sample spectrum will not rise and fall in the same manner as the calibration spectrum, and thus will return a high error value for the least squares fit.

The concentration of NO in the light path, as compared to a calibration cell in the laboratory, is then reported back to the main computer for each of the 50 spectra. Each of these values are then ratioed to the CO₂ values gathered at the same time. With the NO/CO₂ ratio of the vehicle exhaust, as well as the CO/CO₂ and HC/CO₂ values, the main computer then uses the combustion equations to calculate and report CO, CO₂, HC and NO percentages in the exhaust (4).

Results

Figure 4 represents fifty NO and CO₂ concentration readings for the 0.5 s of data collected behind a 1985 Chevrolet Celebrity driven in the parking lot of the chemistry building at the University of Denver. This plot shows the correlation between the NO and CO₂ concentrations behind the car,

allowing calculation of the NO/CO₂ ratio and therefore the %NO in the exhaust. This car was reported to have 0.201 %, or 2010 ppm NO in it's exhaust, which is consistent with the age of the vehicle and the fact that it was being driven under load.

An estimate of the noise in the NO channel of this instrument was made by taking 50 one half second measurements of the exhaled breath of two of the authors. Since hydrocarbons are burned for fuel in human cells in a fundamentally different way as in an internal combustion engine, human breath contains CO₂ but does not contain NO. Thus, human breath is an excellent wet sample of NO-free "exhaust". The mean value for these 50 measurements was 3 ppm, with a standard deviation of 20 ppm. The best values achieved for NO-free gas samples by the previous University of Denver NO remote sensor had a standard deviation of 130 ppm (5). Fifty measurements were also taken of a 1995 Ford Windstar, where the average NO measurement was 6 ppm with a standard deviation of 23 ppm. This is in good agreement with the values obtained for the human breath, since any noise estimates made with a real vehicle will be somewhat conservative due to part of the observed variation being assignable to the vehicle (1). Not only does the new spectrophotometer system simultaneously measure CO, CO₂, and HC, but it also has a signal-to-noise ratio comparable to the laser diode system reported in 1996 (3).

A simple adjustment to the holographic grating in our system has allowed us to gather some very preliminary data about the potential for using this system to speciate the aromatic hydrocarbons in vehicle exhaust. The current 16 nm spectral range of the instrument described here makes it possible to investigate the region from 253 to 269, where benzene and toluene are known to absorb. Figure 5 shows two absorption spectra in this region, one of gasoline vapor collected in the laboratory by evaporating gasoline in the path of our instrument, and one of the exhaust of a passing car in an on-road situation. The vehicle was a 1985 Chevrolet Celebrity with one spark plug disconnected. The peaks assignable to benzene and toluene (from spectra previously taken of these compounds) are indicated in the spectrum of gasoline vapor, and it can clearly be seen that the analytical peak of benzene at diode 8 and the analytical peak of toluene at diode 115 are visible in the car exhaust. The dichroic mirrors presently being used in the system are optimized to reflect 227 nm light for measuring the absorption band of NO. With dichroic mirrors optimized to reflect in the 260 nm region, the light throughput of the instrument should increase in this region, thereby improving the signal-to-noise ratio as well. Additionally, it should also be possible to replace the 128 pixel photodiode array detector with a 512 pixel photodiode array. This would give the instrument a spectral range of approximately 64 nm, making it possible to simultaneously measure NO in the 220 nm region as well as the aromatics hydrocarbons, in the 250-280 region, including benzene, toluene, and the

various isomers of xylene that absorb at wavelengths slightly longer than aromatic spectra shown here.

Finally, the ultraviolet monochromator described here has been modified for use as an on-board NO detector. This system is capable of noise levels of less than 4 ppm in a 10 cm cell, at a sustained sampling rate of 100 Hz. As with the on-road system, extending this version of the instrument for the measurement of aromatic hydrocarbons should also be possible.

References

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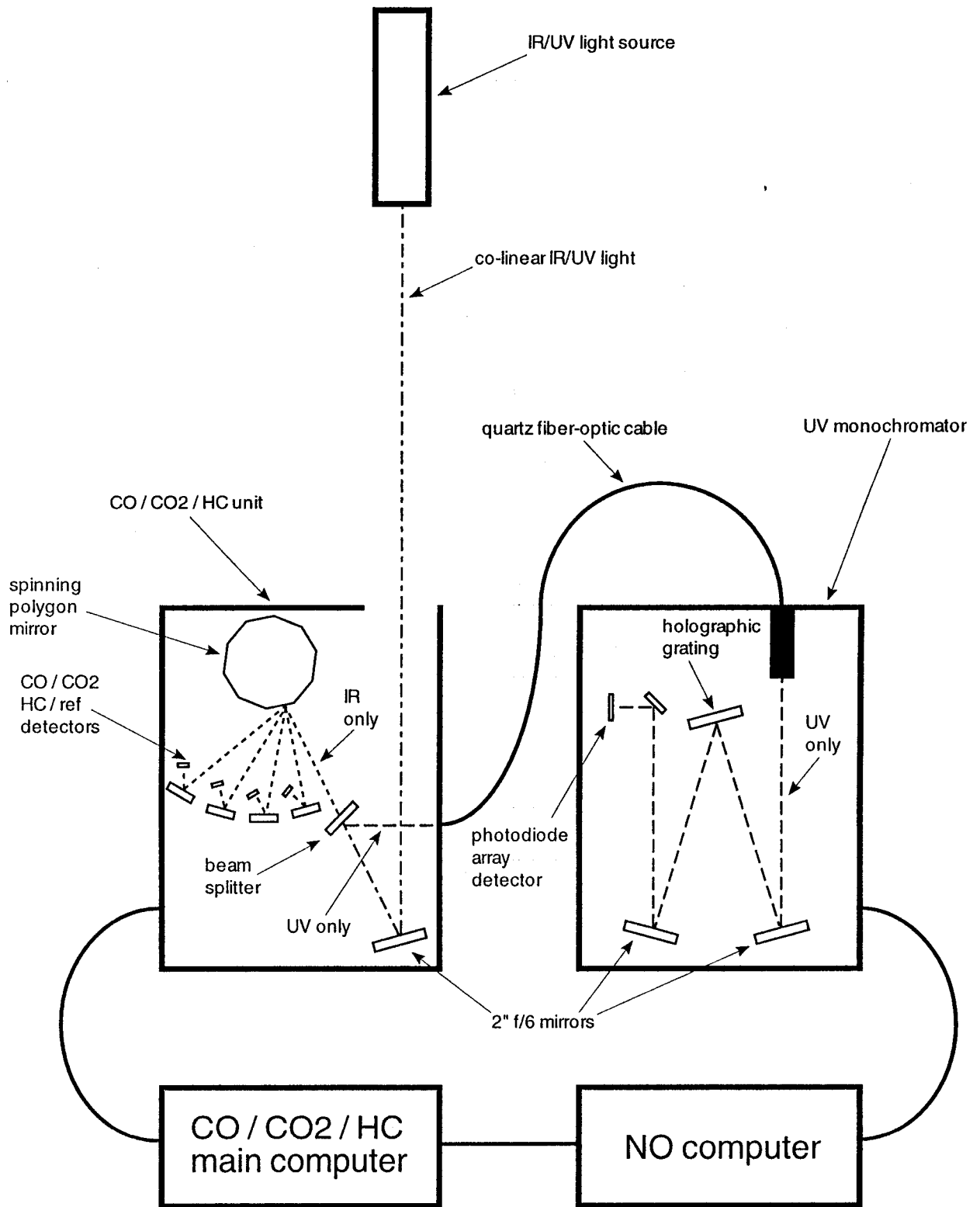


Figure 1. Schematic diagram of the new University of Denver UV/IR remote sensor.

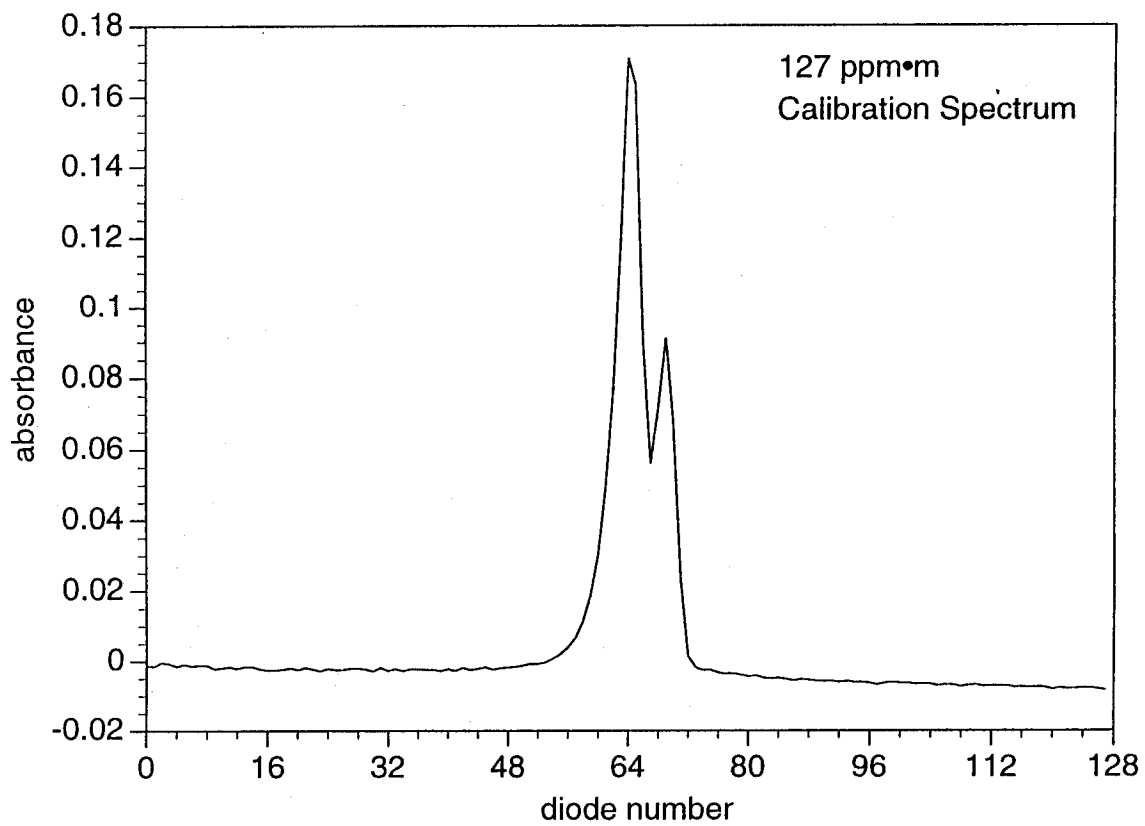


Figure 2. Calibration spectrum of NO, showing the gamma absorption band centered at 226.5 nm (diode 64).

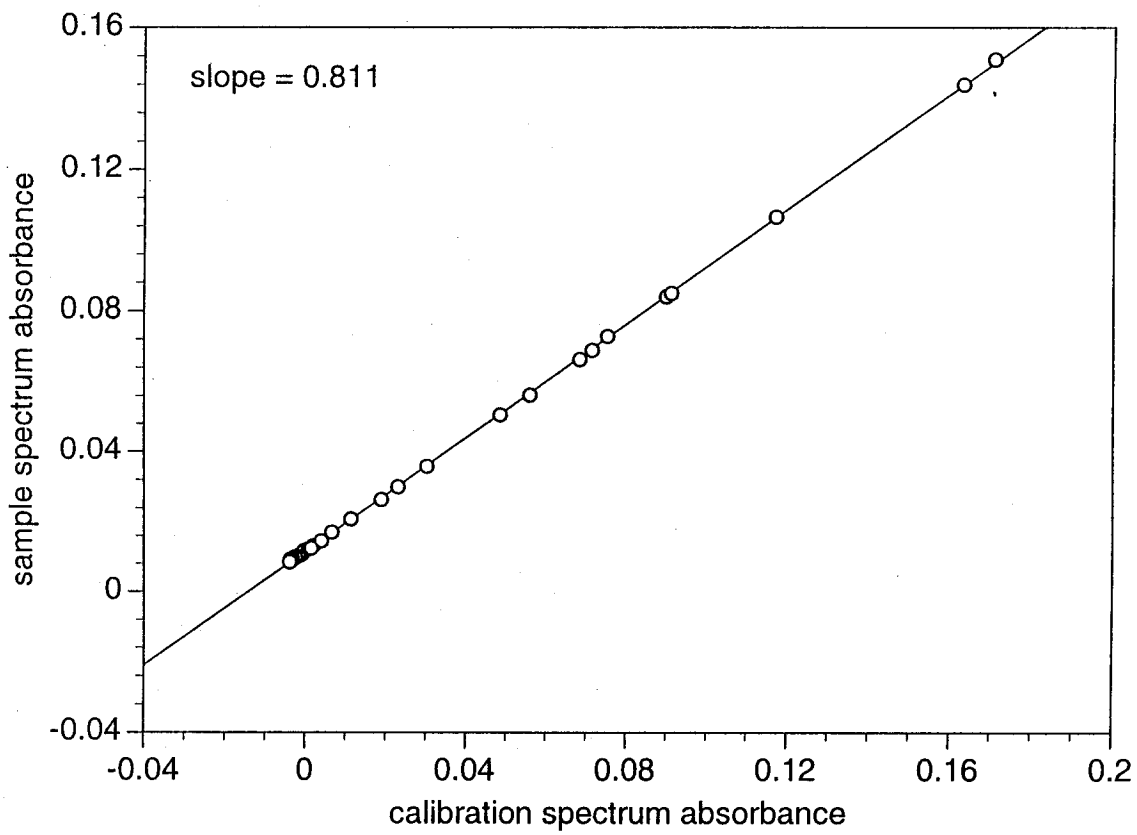


Figure 3. Least squares plot of the absorption values for diodes 50 to 80 of a 100 ppm•m NO sample vs. a 127 ppm•m NO calibration spectrum.

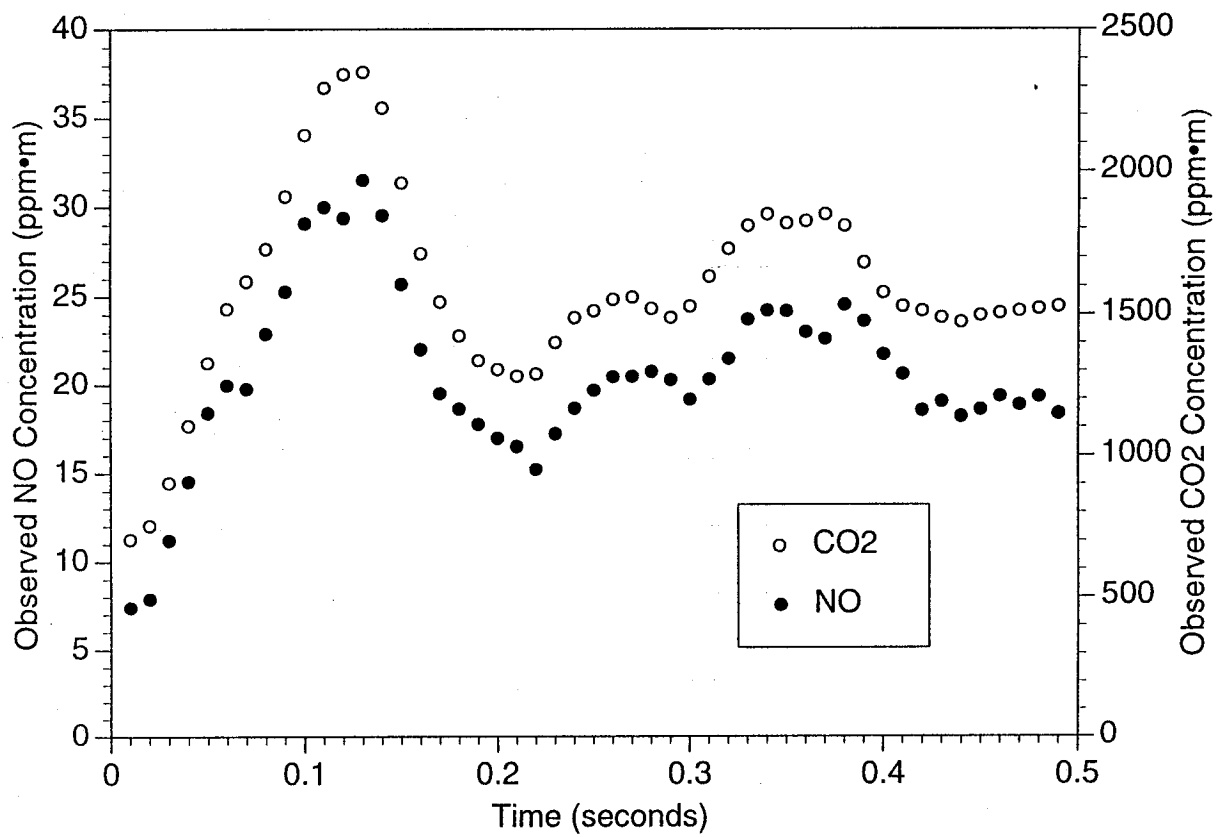


Figure 4. Observed NO and CO₂ concentrations collected in 0.5 s behind a 1985 Chevrolet Celebrity.

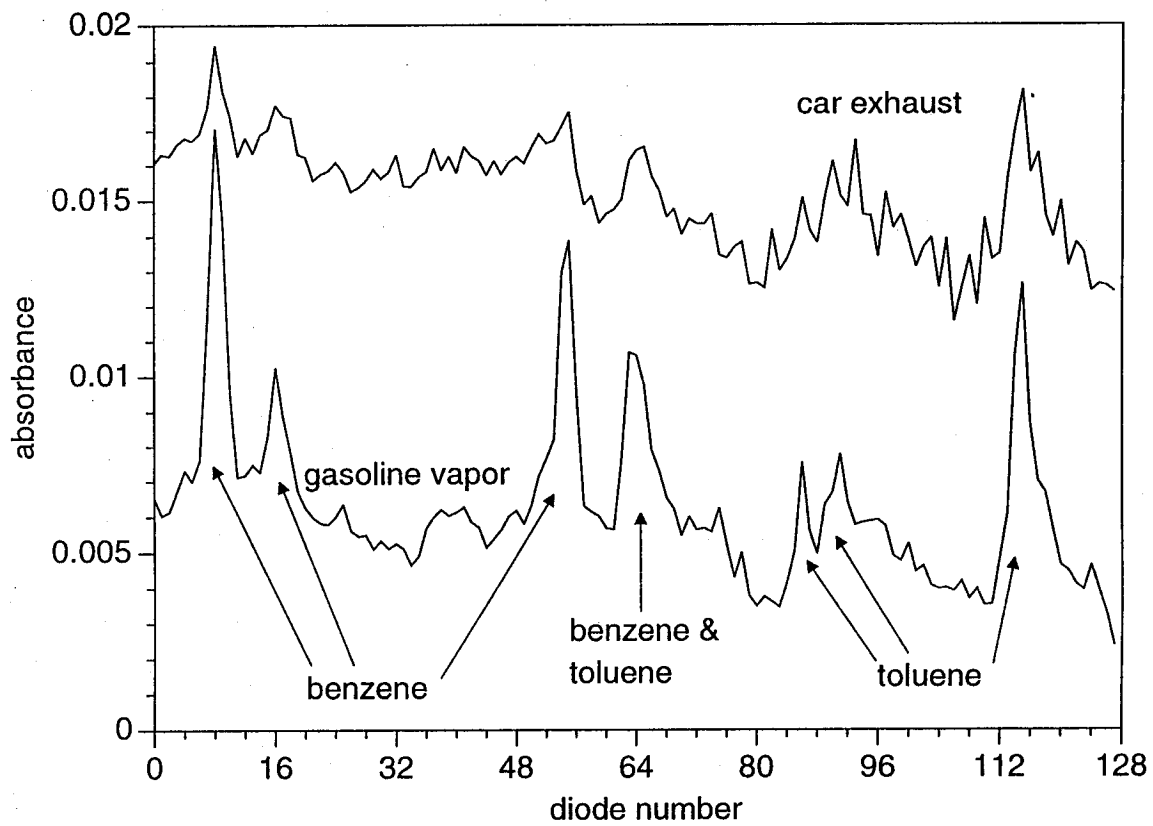


Figure 5. Ultraviolet absorption spectra of gasoline vapor and car exhaust in the region from 253 to 269 nm, showing absorption bands attributed to benzene and toluene.