

Development of a High-Speed Ultraviolet Spectrometer for Remote Sensing of Mobile Source Nitric Oxide Emissions

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ABSTRACT

The University of Denver (DU) has developed a new remote sensor for the measurement of mobile source nitric oxide (NO). This system is integrated with an existing infrared remote sensor and is capable of measuring carbon monoxide and hydrocarbons in addition to NO, at a rate of more than 1000 vehicles/hr. The detection limit on a low-emitting vehicle under typical measurement conditions is 24 parts per million NO (3σ). Measurements from this instrument correlated well in a side-by-side comparison with the previous NO remote sensor developed at DU, and we have used this study to confirm a suspected interference by aromatic hydrocarbons in the older instrument. The results of an extended field experiment using the new instrument, conducted in fall 1997, are also presented. The NO emissions of the fleet measured in this study (averaging 15.0 g NO/gal) exhibit a skewed distribution typical of mobile sources. This paper also describes the relationship between NO emissions and model year and NO emissions and vehicle acceleration, as measured by the new remote sensor.

INTRODUCTION

The role of nitric oxide (NO) as a tropospheric air pollutant is well documented.^{1,2} Along with organic species, NO is a principal precursor in the photochemical production of tropospheric ozone, a major component of urban smog. NO has also been shown to be involved in the production

of atmospheric particulate matter and acidic precipitation, and may contribute to aquatic algal blooms.

According to the U.S. Environmental Protection Agency, in 1996, on-road motor vehicles were responsible for 30% of all combined nitrogen oxide (NO_x) emissions in the United States.³ Although NO_x represents the sum of NO and nitrogen dioxide (NO_2), it has been shown that NO is the dominant species produced in an internal combustion engine.⁴ Previous remote sensing studies have shown that automobile NO emissions, like carbon monoxide (CO) and hydrocarbon (HC) emissions, are statistically gamma-distributed.⁵ Most of the NO emissions for which on-road vehicles are responsible are contributed by a relatively small percentage of very "dirty" cars, while the majority of vehicles in operation are clean-burning and contribute little to the NO_x inventory.

According to Heywood,⁴ NO emissions are maximized at high temperatures when the air/fuel ratio is only slightly lean of stoichiometric, while CO and HC emissions are at a maximum during a rich combustion process due to incomplete combustion. NO production is limited during rich combustion by a lack of excess oxygen, and during extremely lean burning by low combustion temperatures. Although NO production is possible in the flame front, most production occurs in the post-flame gases. Production in the post-flame gases dominates because the flame reaction zone itself is so small, and because burned gases behind the flame front are compressed to even higher temperatures as cylinder pressure rises throughout the combustion process. In contrast to CO emissions that are load-independent, or HC emissions that are elevated at low load, NO_x emissions are increased under high load.⁴

This paper describes the development of a new remote sensor for NO emissions, based on an existing instrument developed at the University of Denver (DU) for the remote measurement of CO and HC emissions. The results of a comparison between the instrument presented here and our previous NO remote sensor,⁵ based on non-dispersive ultraviolet (NDUV) technology, will be

IMPLICATIONS

Motor vehicles represent a major source of NO emissions in the United States. Control measures to reduce mobile source emissions include inspection and maintenance programs, oxygenated fuel mandates, and transportation control measures. The development of an accurate, economical, and easily operated remote sensor for NO emissions is important both for inventory evaluation and possible enhancement of control strategies.

presented. The data analysis from a field measurement conducted in Chicago, IL, in September 1997 will also be presented as an illustration of instrument performance.

INSTRUMENTATION

The new DU remote sensing system is shown schematically in Figure 1. The infrared (IR) light source is a 110V AC silicon carbide igniter element (Carborundum, Inc.), and the ultraviolet (UV) light is generated by a 75-w high pressure xenon arc lamp (Osram). Inside the light source, the IR and UV components are combined using a dichroic mirror (Acton Research, Inc.), and the collimated beam is passed across a single lane of roadway. Utilizing a single lane, such as an expressway on-ramp or interchange, eliminates the problem of multiple exhaust plumes entering the optical path at the same time. Inside the main detector unit, the beam is focused toward another dichroic mirror that serves as a beam splitter. The IR light is passed through the beam splitter onto a spinning 12-faceted mirror that directs the light across the four IR detectors (CO, carbon dioxide [CO₂], HC, and reference). Operation of the IR component of this instrument, for the detection of CO, CO₂, and HC, is described in the literature.⁶

The UV light arriving in the detector is reflected off the first surface of the beam splitter, and focused into the end of a quartz fiber-optic bundle, which is mounted on a miniature coaxial connector on the side of the main detector unit. This fiber optic cable, 1 m in length, is a

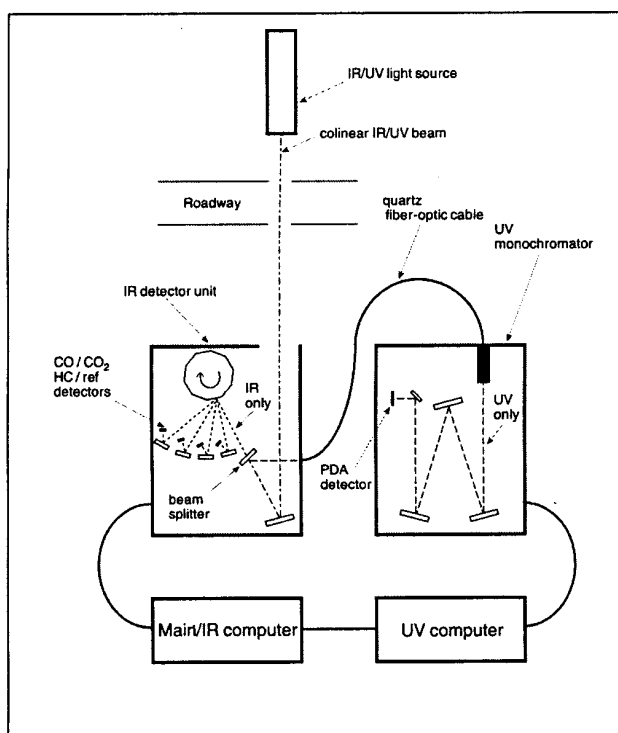


Figure 1. Schematic diagram of DU's NO remote sensor.

bundle of 37 UV-grade quartz fibers, 100 μm in diameter (C. Technologies, Inc., CeramOptec Industries). The fibers are arranged in a round bundle where the UV light is focused into the cable, but are mounted in a linear configuration at the exit end. In this arrangement, the fibers are stacked one upon another, effectively forming a corrugated slit 100 μm wide by 4.2 μm high. This end of the cable then serves as the entrance slit for a Czerny-Turner UV monochromator. In this unit, detection is accomplished by means of a 128-diode silicon photodiode array detector (Hamamatsu, Inc.), which gives the instrument a spectral range of 16 nm and a resolution of 0.3 nm. During normal operation, the instrument investigates the UV region from 218 to 234 nm, and measures the gamma absorption band of NO at 226.5 nm.

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 in the UV monochromator is controlled by a separate computer. When in operation, the UV system is alerted by the main computer that a car is present; it then captures 50 intensity space spectra, each with an exposure time of 10 msec. This 100-Hz sampling rate, over a period of 0.5 sec behind the car, is identical to that of the IR unit. Each of these 50 UV spectra are analyzed in real time by conversion to absorbance space, using a reference spectrum gathered with no vehicle exhaust present. The amount of NO in the light path is calculated for each absorbance spectrum, as compared to a calibration spectrum collected during instrument set-up at the beginning of the data collection period.

The NO calibration spectrum is collected using a 3-mm sealed quartz cell containing a known amount of NO. The observed concentration of NO in each of the 50 data spectra is determined using a least-squares regression routine. The grating in the UV monochromator is fixed in a position such that the gamma absorption band of NO is centered at diode 64. The least-squares fit is accomplished by plotting the baseline-corrected absorbance values for diodes 50 to 80 of the sample spectrum versus the absorbance values for diodes 50 to 80 of the calibration spectrum. The slope of this plot gives the concentration of the sample spectrum, relative to the calibration spectrum. Determining the concentration of the sample spectrum by this method allows one to obtain an average of 14 absorbance values, since the observed band covers approximately 14 diodes.

The concentration of NO in the light path is then reported back to the main computer for each of the 50 spectra. From these concentrations and the CO₂ concentrations gathered at the same time, the NO/CO₂ ratio in the vehicle exhaust is determined, along with the CO/CO₂

and HC/CO₂ values determined by the IR system. Since the NO/CO₂ ratio in the exhaust is constant regardless of plume density or dilution, measuring ratios in an observed plume eliminates the need for a precise calculation of optical path length. All ratios are corrected based on gas puffs from a roadside calibration cylinder. The main computer then uses the combustion equations⁶ to calculate and report the CO, CO₂, HC, and NO percentages in the exhaust, as they would be observed by a tailpipe probe. The reported percentages are corrected for exhaust moisture and any excess oxygen not involved in combustion. The mass emissions per gallon of fuel can also be calculated similarly.⁶

Detection Limit and Operating Range

To determine the detection limit of the new NO instrument, the remote sensor was used to measure emissions from a late-model, low-mileage vehicle 50 times in a circular parking lot at DU. The vehicle, a 1998 Isuzu Rodeo with approximately 2500 miles on the odometer, was driven at 18 mph in second gear after allowing a period for the vehicle to warm up. This vehicle was expected to exhibit very low NO emissions, with a normal distribution and mean close to zero.

The mean NO value of the 50 measurements was determined to be 7 parts per million (ppm), with a standard deviation of 18 ppm. Assuming that 7 ppm is the real non-zero emission from this vehicle, this would indicate an NO detection limit (3σ) of 54 ppm for the new instrument. In actuality, this detection limit is high since the mean value reported is driven by one outlying reading of 122 ppm that we suspect is due to a variation in the automobile's emissions. If this data point is excluded from our statistical analysis, the mean value of the measurements is 5 ± 8 ppm NO, indicating a detection limit of 24 ppm. This is still a conservative estimate of the NO detection limit in the instrument, since some of the variation in these measurements is due to the vehicle itself and not the instrument.

The instrument working range depends on the amount of plume observed (as a result of dilution) and the amount of NO in the original exhaust. Automatic software limits plume dilution to a minimum of 160 ppm·m of CO₂; lower observed plumes result in an invalid measurement. Exhaust is rarely measured above 8000 ppm·m of CO₂. When we see large plumes with high NO concentrations in the same vehicle, deviations from Beer's law result in artificially low measurements. Out of 5329 vehicles observed at a site in Denver, only 15 vehicles incurred an error of greater than 5% from this cause. Of the remaining 5314, the highest 1% reported NO emitters averaged 3750 ppm, which is an estimate of the upper limit for the current

instrument as operated without accounting for Beer's law deviations.

RESULTS AND DISCUSSION

Comparison to the NDUV Instrument

In March 1998, a one-day on-road intercomparison was conducted between the dispersive instrument presented in this paper and NDUV instrument previously developed at DU. The study was carried out in central Denver, at the exit ramp between I-25 and 6th Avenue. 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.⁷ The instruments were arranged so that the two sample paths were parallel and as close together as possible, approximately 6 in. apart. Using the time indices incorporated into each measurement, the data files from both instruments were integrated into one database. After deleting records that contained valid measurements by only one of the instruments, the final database contained 4205 records of individual vehicles from which NO emissions were measured by both instruments.

The higher level of noise observed in the NDUV NO measurements made a direct correlation between the two instruments difficult. It was possible to make a comparison by rank-ordering the measurements according to the readings from the new instrument, and averaging the data in 21 groups of 200 measurements each. This analysis resulted in a linear relationship between the two instruments with a statistical r^2 value of 0.997. It is interesting, however, that the mean NO measurement was 641 ppm from the NDUV instrument and 571 ppm from the new instrument. We have long suspected a slight HC interference in the NO channel of the NDUV instrument⁸ as a result of absorption by aromatics from high HC-emitting vehicles. Due to the spectroscopic technique by which the new instrument investigates the shape of the NO absorption band at 226.5 nm, it should be immune to the broader absorption band of aromatic hydrocarbons in this region.

To investigate the possibility that an HC interference may be responsible for the difference in the average NO reading between the two instruments, the data were rank-ordered according to the HC reading from the NDUV instrument and divided into groups of 200 measurements. The difference between the group average NO readings from the NDUV instrument and the new instrument were plotted against the average HC reading for each group, as illustrated in Figure 2. One can see how the difference in the mean NO measurement increased with the mean HC measurement, indicating a positive interference in our previous instrument.

Field Measurements

In September 1997, DU conducted a five-day remote sensing study in the Chicago area using the new remote sensor described in this paper. In addition to measuring CO, CO₂, HC, and NO, the system used in this study was configured to determine the speed and acceleration of the vehicle, and was accompanied by a video system to record the license plate of the vehicle. Five days of fieldwork were conducted at the on-ramp from Algonquin Road to southbound I-290 in west Chicago. This ramp serves both east and westbound traffic on Algonquin Road, and has an uphill grade of approximately 2%. A database was compiled containing 18,320 records for which the State of Illinois provided make and model year information from the license numbers. All of these records contained valid measurements for CO and CO₂, and more than 17,500 contained valid measurements for HC and NO.

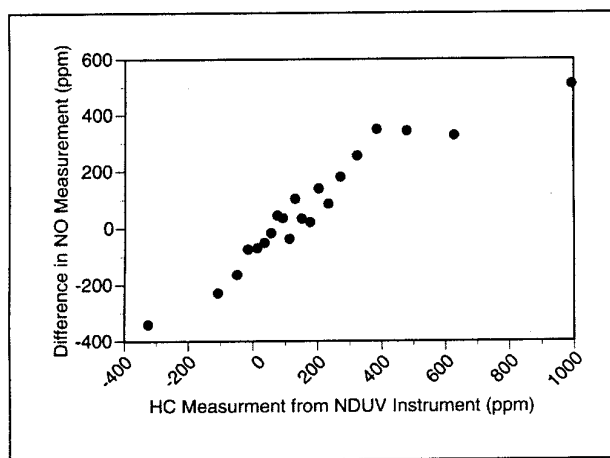


Figure 2. Difference in group-averaged NO measurements (NDUV-new instrument) as a function of group-averaged HC emissions measured by the NDUV instrument.

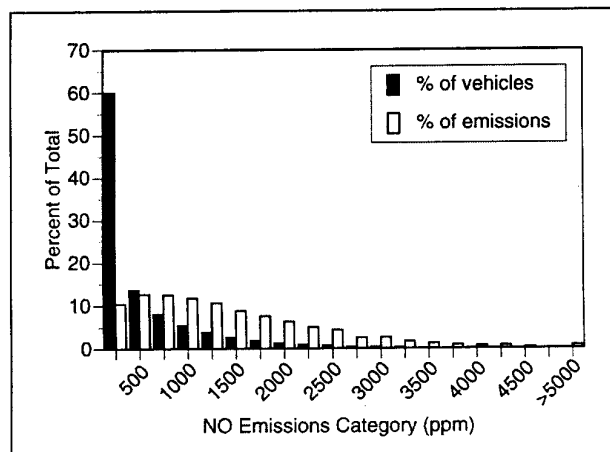


Figure 3. Nitric oxide emissions distribution.

The mean NO emission of the vehicle fleet measured in this study was 400 ppm (15.0 g NO/gal), with a median measurement of 150 ppm. The highest-emitting 10% of this fleet is responsible for 46% of the total NO emissions. It is well known that mobile source NO emissions, like CO and HC emissions, are highly skewed,^{5,9} and the fleet reported in this study is not an exception. Figure 3 shows the distribution of the fleet by NO emission category, with the solid bars representing the percent of the measured fleet in a given category and the clear bars representing the percentage of the total emissions contributed by the given category. The fact that the lowest-emitting 60% of the vehicles are responsible for only 10% of the emissions further demonstrates how the emissions picture can be dominated by a small number of high-emitting vehicles.

Figure 4 shows the mean and median NO emissions as a function of model year, illustrating the expected inverse relationship that has previously been reported.^{5,9} Note that the NO emissions for model years prior to 1988 appear to level out, and vary around 700 ppm. This is in contrast to the CO and HC emissions for the same vehicles, which increase steadily with increasing age and continue to rise through the 1983 and older model-year category.¹⁰ Zhang et al. reported this phenomenon in 1996, and proposed that the tendency for older vehicles to lose compression and operate under fuel-rich conditions (the result of which is lower combustion temperatures and decreased NO production) negates the tendency for poor maintenance and catalyst deterioration to result in increasing average emissions with age.⁵

The apparent increase in the mean and median emissions for the 1998 model year is an artifact. The data were collected in September 1997, but the State of Illinois did not match the license plate information until May 1998.

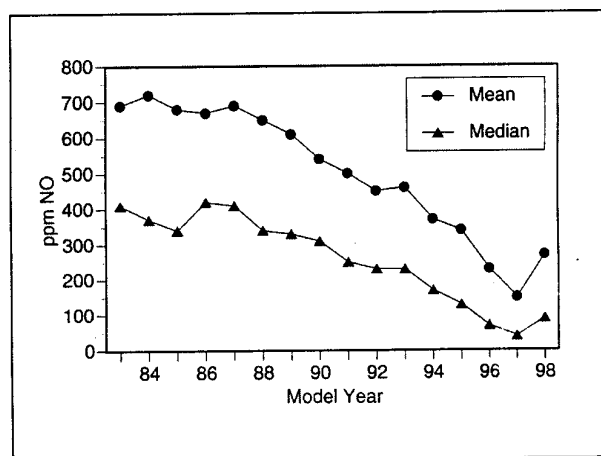


Figure 4. Mean and median NO emissions illustrated as a function of model year. The 1983 model year category contains all vehicles of model year 1983 and older. The increase in the 1998 model year is a plate matching artifact.

Owners may keep their plates in Illinois when a new vehicle is purchased. Some older vehicles were sold during the period between data collection and plate matching, and replaced with 1998 model-year vehicles. As a result, a small number of older vehicles with comparatively higher emissions appeared in the database as 1998 vehicles. This became apparent when four 1999 model-year vehicles appeared in the database, which would have been impossible for a study conducted in September 1997. We do not believe that this is a significant source of bias, since the reported fleet numbers of 1996, 1997, 1998, and 1999 model-year vehicles were 2275, 2509, 568, and 4, respectively.

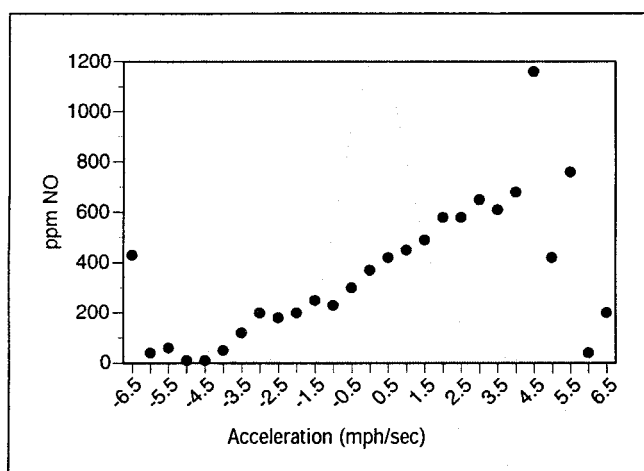


Figure 5. Nitric oxide emissions as a function of vehicle acceleration. The line represents the distribution of vehicles according to acceleration bin, with the maximum of 3330 vehicles in the -0.5 to 0 mph/sec bin.

The relationship between NO emissions and vehicle acceleration is illustrated in Figure 5. To generate this plot, the data were grouped according to acceleration category and the average emissions measurement for each group was calculated. The line represents the distribution of the vehicles according to acceleration group, with the maximum of 3330 vehicles occurring at -0.5 to 0 mph/sec. There appears to be a strong positive correlation between NO emissions and acceleration when there are significant numbers of vehicles present. This result illustrates the expected relationship between engine load (in this case caused by acceleration and uphill driving) and NO production.^{4,9,11}

Plotting NO emissions by model year, but dividing each model year into emission quintiles, results in the plot shown in Figure 6. Each bar represents the mean NO measurement for the given quintile, determined by rank ordering the readings for each model year and dividing the measurements into five equally sized groups. This plot is very revealing because the lowest emitting 40% of the measurements, regardless of vehicle model year, make an insignificant contribution to the total emissions. At the same time, the highest-emitting 20% of the measurements from the newest vehicles contribute more NO than the lowest-emitting 60% of the measurements from the oldest vehicles measured (on a per gallon of fuel basis). This observation, first reported by Stedman et al.¹² for CO and HC, continues to show that broken emissions control equipment has a greater impact on fleet emissions than vehicle age. The hypothesis that this observation was affected by acceleration/deceleration was tested, and it failed to explain the observed phenomenon.

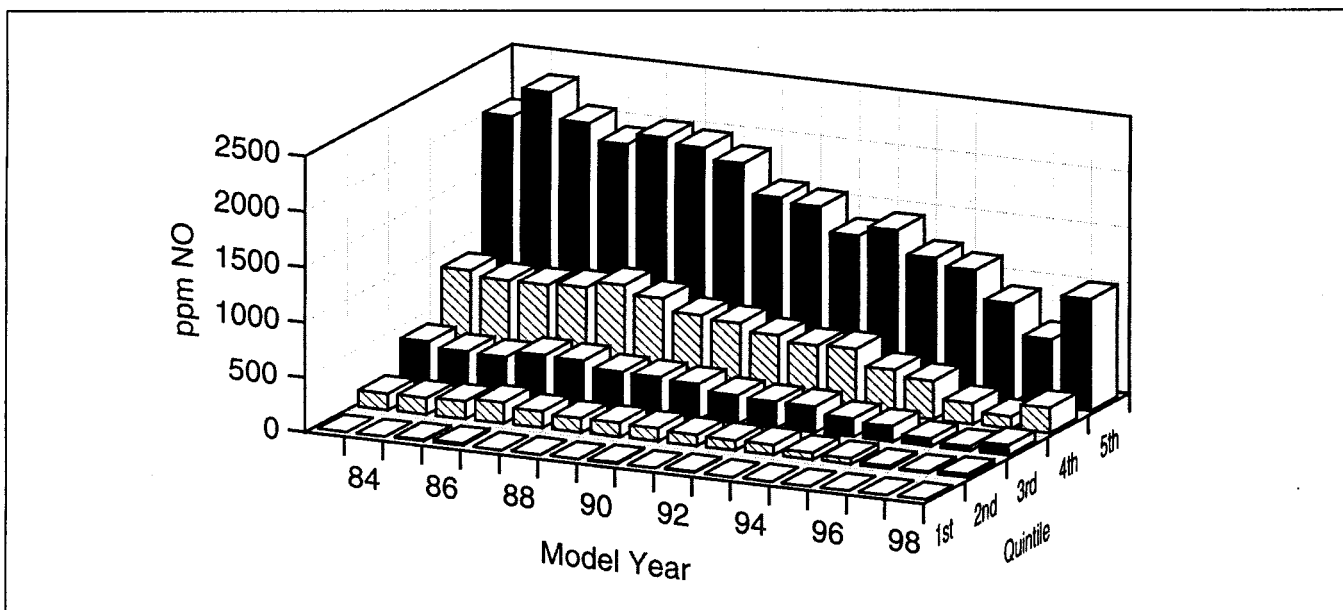


Figure 6. Nitric oxide emissions by model year, divided into emission quintiles. The 1983 model year category contains all vehicles of model year 1983 and older. The increase in the 1998 model year is a plate matching artifact.

CONCLUSION

A new remote sensor for the measurement of mobile source nitric oxide has been developed at DU. This system is based on an existing infrared remote sensor and is capable of measuring CO and HC, in addition to NO. At sites where an adequate plume size can be observed, the new instrument has a detection limit of 24 ppm NO. The results of a direct comparison between the previous remote sensor and the new system reported here show a positive correlation in the readings by the two instruments, and a positive interference in the previous detector caused by aromatic hydrocarbons. The results of a field study conducted in Chicago in September 1997 show that the NO emissions of the measured fleet exhibit a skewed distribution. A study of NO emissions versus model year showed that the lowest-emitting 40% of the vehicles in the measured fleet, regardless of model year, make a negligible contribution to the total emissions. Similarly, the highest-emitting 20% of the late-model vehicles emit more NO than the cleanest 60% of the oldest vehicles measured. A system to measure vehicle speed and acceleration was also used in the field study, and we have demonstrated a positive correlation between average NO emissions and acceleration.

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