

"PREPRINT EXTENDED ABSTRACT"
Presented before the Division of Environmental Chemistry
American Chemical Society
New Orleans, LA March 24-28, 1996

CARBON MONOXIDE AMONGST OTHER CHEMICALS

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In 1973 we discovered that there was a need for a better detector for nickel carbonyl. It turned out that chemiluminescence with ozone, catalyzed by means of added carbon monoxide was perfect. The device was patented and is sold today to all of the few people who need a fast sensitive Ni(CO)₄ detector. In the process of developing this tool we discovered that all carbon monoxide, even when passed through a liquid nitrogen trap, is contaminated with metal carbonyls. We also discovered that a solid-state trap consisting of a few crystals of iodine upstream of activated charcoal achieves their complete removal. Much of the literature on reactions of carbon monoxide is compromised by not using this trap (1,2).

Ten years later we were developing the chemical amplifier technique to measure atmospheric free radicals. To make that work we again needed pure carbon monoxide. The iodine/charcoal trap again turned out to be essential. That free radical detector is now in use in atmospheric chemistry research laboratories around the world (3,4)

In the late 1980's we developed the sulfur detector based upon SO chemiluminescence with ozone. It has almost taken over the sulfur GC detector market from the flame photometer (5). Our last, and potentially most important invention is the remote sensor for automobile exhaust (6,7).

Automobiles emit pollutants which have been studied and understood by mechanical engineers for decades thankfully, books such as John Heywood's Internal Combustion Engine Fundamentals (8) are a great source of information. We have had to learn this material because we invented a device which measure the exhaust emissions from each car as it passes by using remote sensing. Figure 1 shows a diagram of the system. The video camera takes a picture of the rear of each passing vehicle, from which the license plate can be identified.

Technologically the remote sensor is not different from a conventional tailpipe emission test. In a conventional test, the exhaust is pumped from the tailpipe into an instrument. A source of Infra-red (IR) light shines through an optical cell in the instrument. At the other end of the cell, detectors measure the absorption of the IR and thus determine the pollutant concentrations. Effectively we have taken a hack saw to the box, placed the IR light on one side of the road, the detector on the other and allow the car to drive through. The system has been tested since 1987 and at speeds between 2 and 152 mph. In 1991 in California, the CO readings were found independently to be within 95% of correct, while the HC were within 85% (Lawson and Gunderson, 1991 Report to California I/M Review Committee)

We measured passing cars on Southbound Rosemead Blvd. in El Monte, CA. in a roadside pullover program. When we identified an apparent gross polluter, we radioed ahead for a California Highway

Patrol officer to pull it over for a roadside Smog-Check test. Two teams of testers were used. The USEPA also had a portable dynamometer (treadmill) set up for a test called IM240 (now familiar to Coloradans) in the roadside park. In ten days, the remote sensor was able to take 60,487 emission readings from 58,063 vehicles. Two Smog-check teams were able to measure 307 while one IM240 system measured only 80. Although we are not professional economists, it seems to us that there must be some cost/benefit implications when a single remote sensor can measure tailpipe emission from 58,063 vehicles without inconveniencing the drivers during same time period that two teams can do 307 traditional inspections and EPA can only carry out 80 of their new test.

With so many cars easily measured, we started to look into the statistics. To our surprise, our data, Federal Test Data, indeed all the data we could find showed half the pollution from less than 10% of the vehicles. These vehicles we call gross polluters. Figure 2 shows ten blocks whose height matches the average CO emissions of 10% of the cars in Denver. Notice how much higher emitting are the gross polluters than the majority of the cars. Very few new cars are gross polluters (about 2% of two-year-old cars), but for even the oldest cars (1974 and older, all without catalysts) the majority (60%) are NOT gross polluters. When a distribution this skewed is observed, it is easy to justify an air pollution program which identifies the gross polluters and targets them for treatment. It is correspondingly hard to justify programs which treat all cars as equal (oxygenated fuels, periodic mandatory emission testing, ride-sharing, etc.)

Results from three countries are shown in Figure 3. The black triangles are data from 1991 in Los Angeles. New vehicles have low average emissions. As the vehicles get older, the average emissions increase. Notice that there is no discernable break in 1974 or 1980 when new technology (catalysts, 1974 closed-loop computer systems, 1980) was introduced. The line close to the L.A. data was obtained in 1991 in Sweden. Sweden introduced catalysts 50% in 1987, and 100% in 1988. The break is clearly discernable and Swedish catalyst equipped cars have lower average emissions (by half) than similarly equipped vehicles in Los Angeles. There are a number of social/personal reasons to expect better car maintenance in Sweden. Not the least, my Swedish friends assure me that there is no word in Swedish for "tampering" with your emission control equipment.

If, as we believe, good maintenance is even more important than catalysts, then as L.A. cars age one might expect to see the (apparently badly maintained) catalyst equipped cars in L.A. having higher emissions than non-catalyst cars in Sweden. This effect is observed in the 1975-1981 model years. Contrasting with the lower two lines is the upper line of data from the United Kingdom. The UK introduced catalysts in 1990, but it is apparent that my home country suffers from a fatal combination of both poor technology and poor maintenance.

Despite these research results, there remain critics who believe that our results are random (Pittsburgh Tribune Review, May 15, 1995). This is hard to believe since we routinely show new cars averaging lower emissions than old cars. The video camera and license plate data are independent of the emissions data, thus these results could not be obtained with a random detector.

So far, I have shown carbon monoxide data with older cars (on average) higher emitters than new cars. This result is observed everywhere, and is independent of speed/load. The same age effects are observed for HC and NO (7,9,10) BUT in both cases, the averages depend on vehicle speed and load.

In all cases, the average readings tend to obscure as much as they illuminate. When we use our large on-road data bases to divide up each model year into five groups (quintiles) from lowest to highest

emitting, a more startling result appears. The observed effect of increasing average age on increasing average emissions is overshadowed by the dramatic differences between well and badly maintained cars in a given model year. Thus, 20% of the early 1970's cars have LOWER emissions than the broken 1990's cars.

These results are illustrated for HC in Figure 4. We believe that these graphs can be used to show that a number of programs currently proposed or underway are not cost effective. These programs include alternative and reformulated fuels (which treat all cars as equal); scrappage programs which treat all old cars as gross polluters (which they are in the EPA computer model, but are not in reality); tighter new car standards which attempt to lower the already negligible emissions of well maintained new vehicles; and scheduled emission testing programs which also inconvenience all cars in an attempt to influence the behavior of a few. Most of these points are amplified more quantitatively in the Policy Review section of the journal Science (11).

Acknowledgements: Air Products and Chemicals are appreciated for their generosity in providing for this award. The work described herein was performed by numerous graduate students and staff who really deserve the credit. Various government and private agencies have provided research support which is much appreciated, however the opinions expressed are solely the responsibility of the author.

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CO, HC and NO Remote Sensing

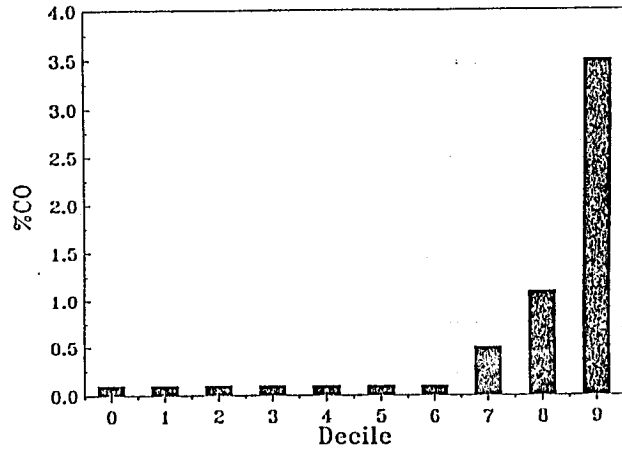
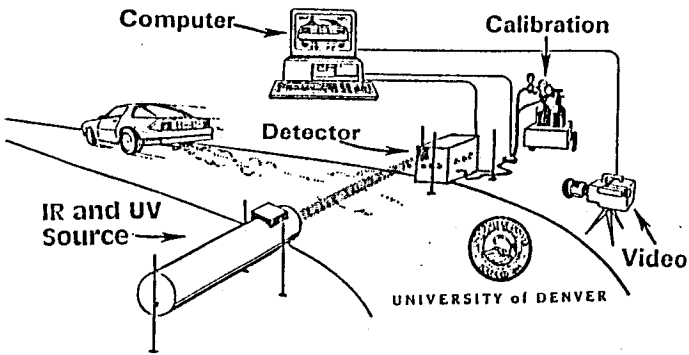


Figure 1 System Schematic Diagram

Figure 2. CO emissions from ten representative cars.

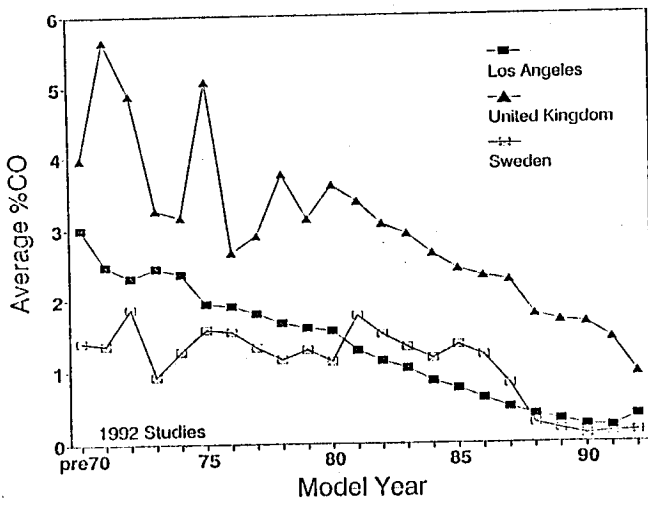


Figure 3. CO emissions versus model year for three countries.

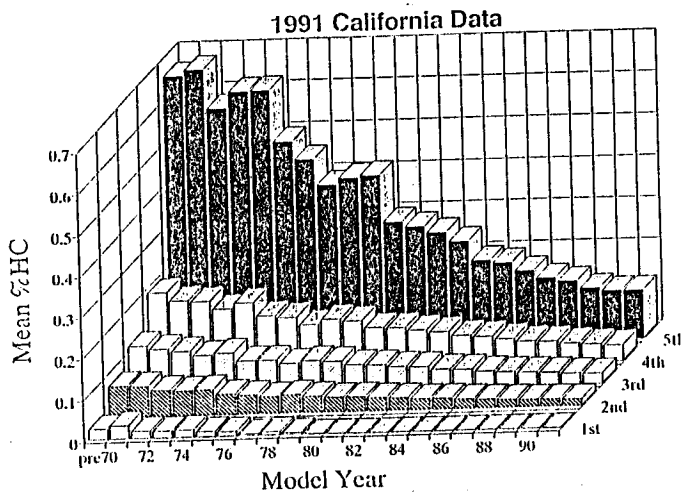


Figure 4. HC emissions versus model year with each year sorted into five groups.