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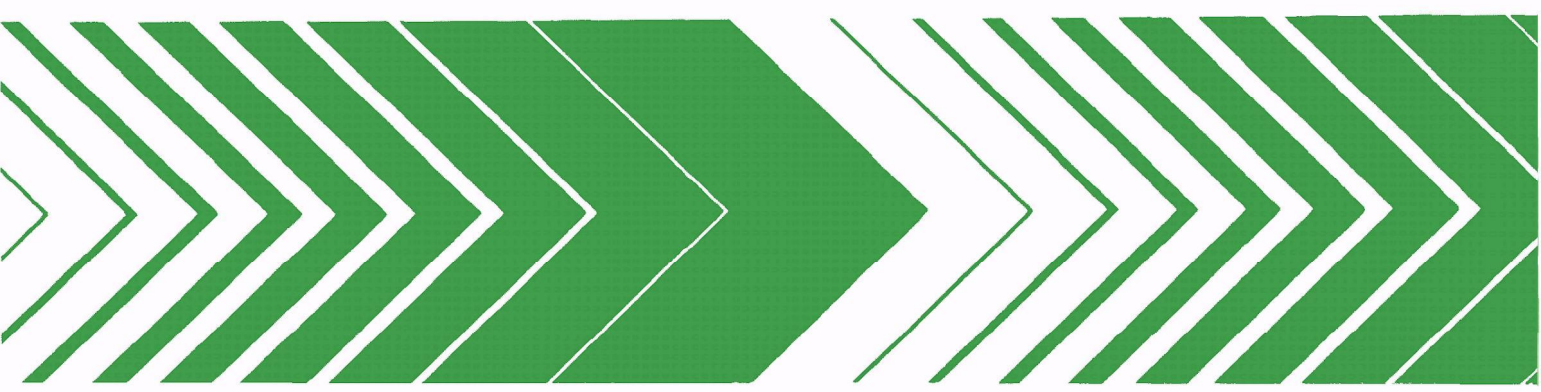
# Ambient Air Carbon Monoxide Measurements



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# AMBIENT AIR CARBON MONOXIDE MEASUREMENTS

by

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## ABSTRACT

This report discusses the application of a new type CO monitor to special ambient field measurement problems. The monitor, a gas filter correlation (GFC) instrument was designed specifically for use in the St. Louis Regional Air Pollution Study (RAPS), but has been applied to several other measurement requirements. The monitor has an inherently fast response of less than one second and has proved useful in documenting extremely variable monitoring situations.

The monitor was used in a total of ten separate studies and typical data is presented from all tests with the exception of the last which is still being reduced.

The most significant contribution from these studies has been the ability to document the extreme variability of carbon monoxide in our urban environment.



This report was submitted in fulfillment of Grant R-803399 by the University of Michigan under the sponsorship of the U. S. Environmental Protection Agency. This report covers a period from November 1, 1974 to October 31, 1977 and the work was completed as of October 31, 1977.

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# ABBREVIATIONS AND SYMBOLS

## ABBREVIATIONS

| | | |
|---|---|---|
| CO | --- | carbon monoxide |
| DOT | --- | Department of Transportation |
| EPA | --- | Environmental Protection Agency |
| GFC | --- | gas filter correlation |
| MIT | --- | Massachusetts Institute of Technology |
| ppm-v | --- | parts per million by volume |
| RAMS | --- | Regional Air Monitoring Station |
| RAPS | --- | Regional Air Polution Study |
| SAI | --- | Science Applications Incorporated |
| $SF_6$ | --- | sulfur hexafluoride |

## ACKNOWLEDGEMENTS

The studies reported here required the cooperation of numerous groups in many locations. The author is grateful to the permanent Regional Air Pollution Study staff which responded to the many requests for data and, particularly, to Stan Kopczynski who arranged the instrument calibration tests. The author appreciated the cooperation of Dr. D. Burch of Ford Aeroneutronic who was responsible for the monitor design and Dr. F. F. Marmo of the Department of Transportation who arranged several of the roadway tests.

Thanks also go to the student staff for their whole hearted cooperation in collecting most of the data: Michael Travis, Jeff Kochelek, Carol Chaney, and David McKinley.

The author's special thanks are extended to Dr. W. A. McClenny for his many suggestions and review of this report prior to final preparation.

# SECTION 1

# INTRODUCTION

The monitor used in the studies to be discussed was designed and built for the U. S. Environmental Protection Agency (EPA) by Ford Aeronutronic and described by Burch.[1] The expressed reason for obtaining the monitor was for use in the St. Louis Regional Air Pollution Study (RAPS)[2] to evaluate a Long Path Laser CO monitor developed by MIT Lincoln Laboratory.[3] It was also intended for use in a sub-grid characterization study.[4] However, as a result of its proved usefulness in conducting the intended studies, it was also used in several ancillary studies. The purpose of this report is to discuss and document carbon monoxide measurements made with the GFC monitor as a part of the EPA grant studies conducted by the University of Michigan.

## SECTION 2

## CONCLUSIONS

The GFC monitor proved to be extremely useful for microscale studies which involve rapid fluctuations in the ambient concentration of carbon monoxide. The monitor's rapid response of less than one second permitted the documentation of the very rapid change in concentration as well as the magnitude, which can exceed three orders of magnitude in a few seconds.

The original hope was that the monitor would be sufficiently portable (gross weight about 35 pounds) so that it could be back-packed to permit path averaged measurement. Although this goal was not realized, the fact that it could be easily transported from one location to another, set up to operate in an automobile, or an airplane, made very interesting experiments possible. The data obtained has added to our knowledge of the nature of the microscale variations in the concentration of carbon monoxide.

## SECTION 3

## RECOMMENDATIONS

The GFC monitor should be considered for any field program requiring the measurement of the microscale variations in the concentration of carbon monoxide.

The technical problems involving the monitor which should be examined are as follows:

1) The precise reason for the zero drift with temperature should be determined and corrections made in order to extend the temperature range for uncorrected operation.

2) The battery supply should be re-designed so that the drain on all the batteries is equal or approximately so during the operation. It would be very desirable to extend the battery operation to one complete working day.

## SECTION 4

## MEASUREMENT SUMMARY

Many of the measurements made with the Ford Aeronutronic Gas Filter Correlation (GFC) carbon monoxide monitor for the Environmental Protection Agency (EPA) have been previously reported.[4-9] A chronological list of the individual studies and measurements is given in Table 1.

The monitor itself has been adequately described by Burch[1] and is also briefly described in Appendix A. The individual studies are briefly described in this section following the order listed in Table 1.

RAPS POLLUTANT VARIABILITY STUDY -- July and August 1975 and July and August 1976 St. Louis, Mo.

This study was performed over a period of three years 1974-1976 in St. Louis and has been described in a previous report.[4] The GFC monitor was the primary CO measurement tool during the final two years of the study. Although the original plans were to use the monitor as a portable instrument and the final weight made this impossible, it was small enough to be easily transportable which proved to be advantageous.

The monitor was operated during the St. Louis study inside an air conditioned mobile van which was usually parked adjacent to a Regional Air Monitoring Station (RAMS).

Air samples were collected in the area at distances up to one kilometer away from the station and brought to the monitor for analysis. The data collected was used in the pollutant variability study. In addition, ambient measurements were made for comparison with the Lincoln Laboratory CO laser system housed in the same mobile van.[3,5] Spatially integrated bag samples were collected by walking along the laser path for comparison with the laser measurements.[6] An example of an ambient measurement comparison between the CO laser and the GFC is shown in Figure 1. Further details of the laser comparison were reported by Lincoln Laboratory -- MIT.

TABLE 1

Gas Filter Correlation (GFC) Carbon Monoxide
Monitor Field Studies

1. Regional Air Pollution Study (RAPS) Pollutant Variability Study, July-August 1975 and July-August 1976 St. Louis, Mo.

2. RAPS Quality Assurance Study, July-August 1975 St. Louis, Mo.

3. RAPS Department of Transportation (DOT) Roadway Study, July 1975 St. Louis, Mo.

4. General Motors DOT Roadway Study, October 1975 Milford, Mich.

5. RAPS Roadway Study, August 1976 St. Louis, Mo.

6. RAPS Helicopter Installation, July 1976 St. Louis, Mo.

7. Moving Vehicle Emission Study, March 1977.

8. DOT, Silver Strand Roadway Study, April 1977 San Diego, Calif.

9. Los Angeles Freeway "On" Ramp Measurements, May 1977 Los Angeles, Calif.

10. Chicago Plume Study, July 1977 Muskegon, Mich.

RAPS QUALITY ASSURANCE STUDY -- July and August 1975 St. Louis, Mo.

The quality assurance study was conducted for a period of one week prior to the RAPS 1975 summer intensive period and for one week following the summer period. The main purpose was to independently measure the pollutant concentrations at the RAMS measurement locations and compare the results. The CO measurements were intended to be taken by collecting bag samples at the RAMS stations and then measure the CO concentrations in the bags with the GFC. This led to the surprising result that many of the stations were reading low, but in an inconsistent manner. As a result, the GFC monitor was compared directly with a gas chromatograph monitor in the RAPS Laboratory. The two instruments reported identical results over a period of 24 hours. The monitor was subsequently placed inside a RAMS station and attached to the air sampling manifold. Several stations were sampled for periods of at least 24 hours. Two samples of the data collected are shown in Appendix A Figures 4-A and 5-A. The final conclusion was that the difference in measurement was the result of the method of sampling the data rather than the method of measurement. The RAMS sampling procedure was to collect a sample for a few seconds for analysis every five minutes. Hence, variations in concentration with periods faster than 10 minutes could not be accurately reproduced. This fact has been pointed out in previous reports.[4] The chief advantage of the GFC monitor in this study was its portability and ease of installation.

RAPS-DOT ROADWAY STUDY -- July 1975 St. Louis, Mo.
GENERAL MOTORS-DOT ROADWAY STUDY -- October 1975, Milford, Mich.

These two studies are being reported together since they were a part of the same cooperative effort with the Department of Transportation. The study in St. Louis was essentially a trial run for the measurements carried out later in the year at General Motors Proving Grounds under controlled conditions. The basic carbon monoxide measurements were made with a long path GFC[10] monitor developed especially for this purpose. During the St. Louis study, sets of simultaneous measurements both upwind and downwind of the roadway were made by collecting bag samples. During several of the tests, five simultaneous samples were collected and immediately taken to St. Louis University about one and one-half miles away for analysis on the GFC monitor. Several such sets were collected and analyzed during one rush hour time period.

Based on the experience gathered during the St. Louis study, it was decided that a real time measurement of the background concentration would be the preferred measurement for the General Motors Study. The monitor, recorder, and calibrating gases were mounted in the rear seat of a passenger

car which was parked about 50 feet upwind of the roadway. The sample was collected through a tube extending about 5 feet above the roof of the automobile. The roadway monitoring instrument used in the experiment was developed by Science Applications Inc. (SAI) and described by Bartle.[10] The instrument is an open path GFC capable of measurements up to 40 meters. A description of the experiment is the subject of a SAI report[11] and additional analysis of the data was done by Dr. Fred Marmo,[12] the Department of Transportation Project officer.

RAPS ROADWAY STUDY -- August 1976 St. Louis, Mo.

The study was conducted at two sites in the St. Louis area for a period of two weeks. The main purpose in conducting the study was to measure the magnitude of the real time variation in the CO concentrations near a roadway and at specified distances away from the roadway. An example of the extreme magnitude of the variation is contained in the data shown in Appendix A Figure A-2a. Data taken at a distance of 100 meters from the roadway showed virtually no rapid variation in concentration. The data collected during the study was also the subject of a student project.[13]

RAPS HELICOPTER INSTALLATION -- July 1976 St. Louis, Mo.

The RAPS helicopters were normally equipped with Andros CO monitors. These monitors were adversely affected by the aircraft environment. Hence, as a result of the success achieved in using the GFC, arrangements were made to fly it on one of the RAPS helicopters. Two flights were carried out and some of the data collected on one trip is shown in Appendix A, Figure A-6. The instrument performed very well in this application. The data shown is for two passes through a power plant plume which is very clearly defined as a result of the rapid response. Levels as low as 0.1ppm were measured on both flights.

MOVING VEHICLE EMISSIONS STUDY -- March 1977

This study was designed to measure the CO concentration along interstate highways.[8] In the process of making the measurements, it was determined that the effect of emissions from individual vehicles could be measured. A paper describing the study is attached as Appendix B.

DOT-SILVER STRAND ROADWAY STUDY -- April 1977 San Diego, Calif.

The study, organized by DOT, had as its goal the measurement of the roadway CO emission rates as a function of traffic density. The basic plan was to release measured amounts of $SF_6$ on the upwind edge of the roadway as a tracer gas and measure both $SF_6$ and CO on the downwind edge of the roadway. The background concentration of CO on the upwind side was subtracted from downwind CO concentration and ratioed with the $SF_6$ measured downwind to determine the effective CO emission from the roadway. The wind speed, wind direction, temperature, relative humidity, and traffic count were measured throughout the test period.

The background measurements of the CO concentrations were made with the GFC monitor operating on a battery pack. The monitor could be placed on either side of the road in any selected location. Data was taken with the optical cell completely open so that real time measurements were made with a one second time constant. During one of the tests when the wind was blowing from an unfavorable direction, the Ford Aeronutronic GFC and the long path GFC system[10] used as the primary monitor were compared on the same side of the roadway (Figure 2). The data illustrates the rapid variation in the roadside concentration of CO as well as the excellent agreement between the instruments.

LOS ANGELES FREEWAY "ON" RAMP MEASUREMENTS -- May 1977
Los Angeles, Calif.

The purpose for collecting this data was to determine the feasibility of monitoring the CO emission from individual vehicles using the Los Angeles Freeway system. The data (Figure 3) was collected with the monitor placed on top of a parked automobile beside an "on" ramp. It can be seen that the peaks from individual vehicles are not quite resolved. However, it is believed that with minimal instrument modification individual resolution could be achieved.

LAKE MICHIGAN PLUME STUDY -- July 1977 Muskegon, Mich.

The Lake Michigan Plume Study is a multi-year program funded by the Department of Energy and conducted by Battelle Northwest. The purpose of the study is to analyze the urban plumes from Chicago and Milwaukee as they move across Lake Michigan and observe the change in composition. In order to carry out the study, Battelle has outfitted a DC-3 with a complete complement of air pollution instruments. The monitors available for measuring the CO concentration were not completely satisfactory. Hence, it was arranged to have the Aeronutronic GFC flown on several missions. The flights were carried out during the late summer of 1977, but the data has not yet been reduced.

## SECTION 5

## DISCUSSION

The measurement of the carbon monoxide concentration as an indicator of air pollution has been an established practice for many years and as a consequence adequate monitoring techniques are available. This is particularly true if the major interest is to determine the health hazard due to ambient concentration. Many of the present monitoring instruments set one ppm as the minimum detectable signal which is reasonable from the standpoint of possible health hazards. However, the accepted background concentration for the northern hemisphere is 0.15 ppm-v. Hence, in order to study the normal ambient background concentration, a more sensitive instrument is required.

The unique GFC monitor used in these studies has permitted the measurement of ambient CO background concentrations in difficult to measure locations. These measurements have contributed to our knowledge of both the spatial and temporal variations of CO in the ambient environment. This information should be useful to air pollution modelers who must use and interpret existing data to verify their models. Hopefully, the data collected on individual vehicles will help those responsible for implementing air pollution control strategies. Furthermore, in any future microscale studies which involve the measurement of carbon monoxide, serious consideration should be given to using such a monitor because of its ability to follow the real time variations in ambient concentrations of carbon monoxide.

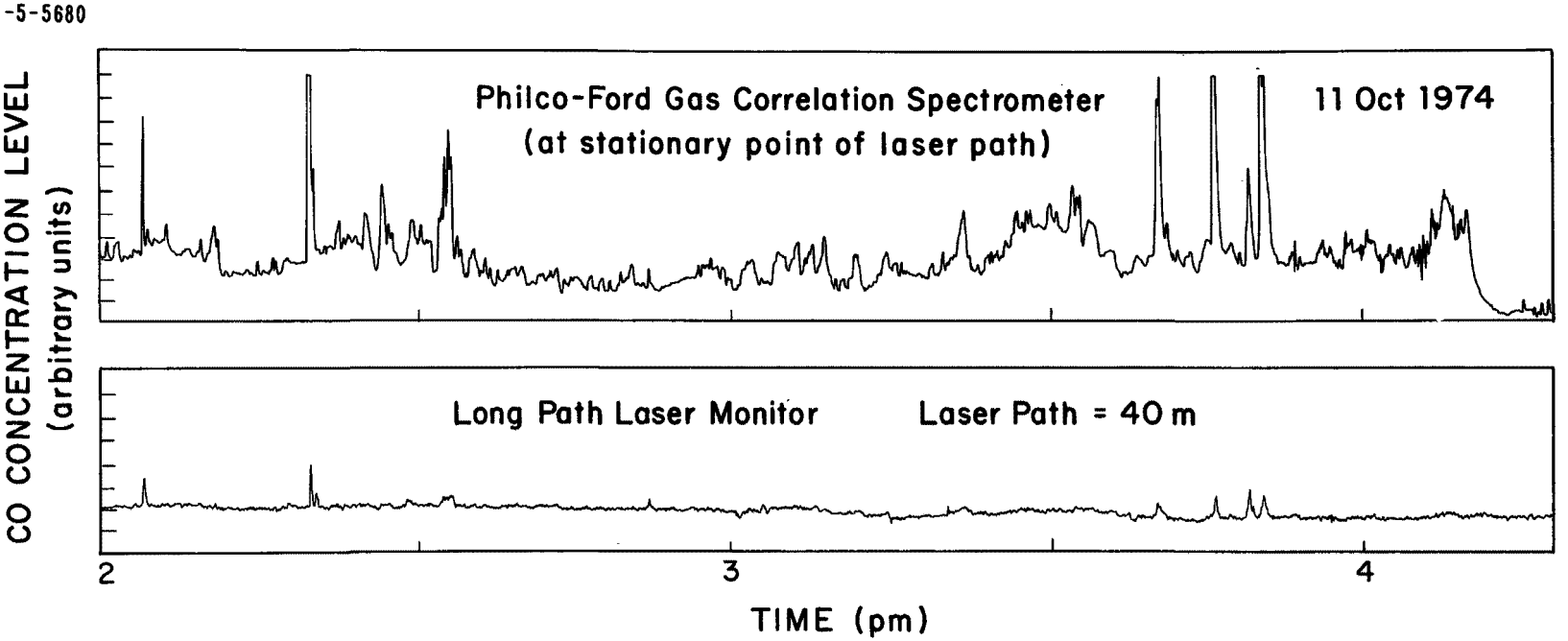


Figure 1. Comparison between GFC monitor and Lincoln Laboratory Long Path Monitor.

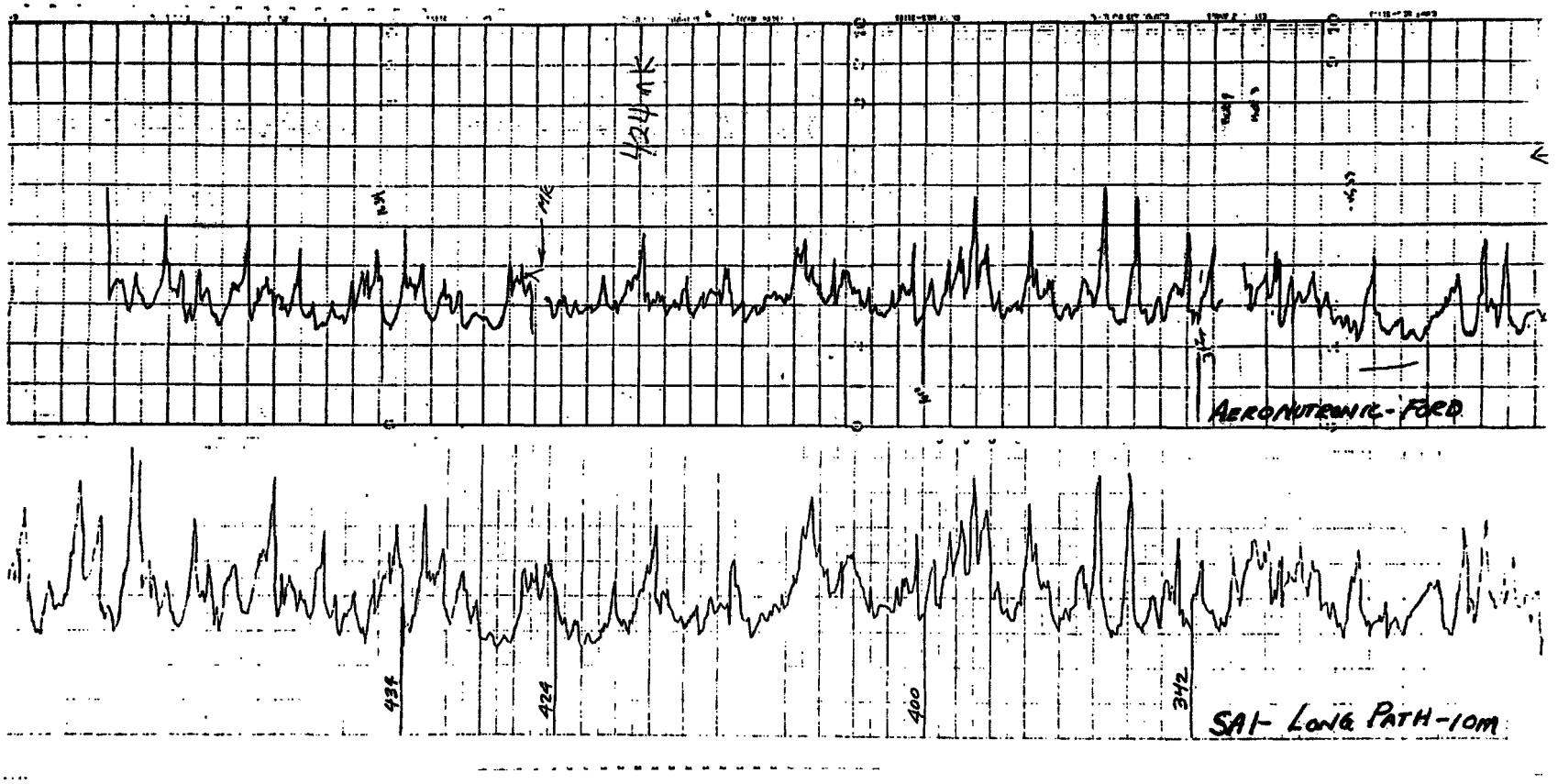


Figure 2. Comparison with SAI Long Path Monitor -- Silver Strand Emission Study -- San Diego 5-4-77.

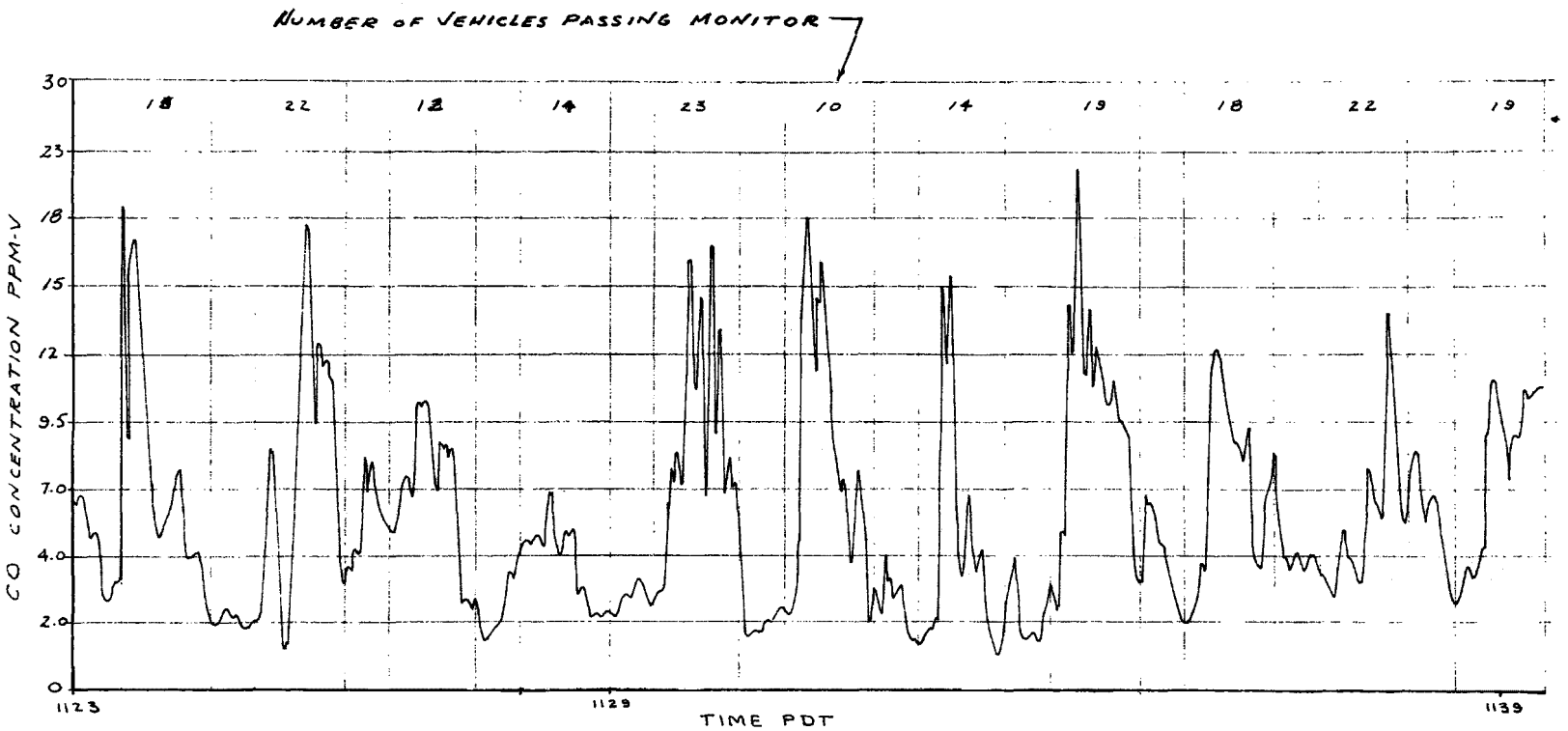


Figure 3. San Diego Freeway "On" Ramp Data.

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# APPENDIX A

## Unique Ambient Carbon Monoxide Monitor Based on Gas Filter Correlation: Performance and Application

# Unique Ambient Carbon Monoxide Monitor Based on Gas Filter Correlation: Performance and Application

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■ A new type of ambient air monitor for carbon monoxide was developed. The monitor was based on an infrared absorption technique termed "gas filter correlation". Water vapor was measured independently in the monitor, and a correction for interference in the CO measurement was made automatically. Initial applications of the monitor demonstrated its low noise equivalent concentration of 20 ppb-v and a linear range of response up to 100 ppm-v. In studies near roadways, the temporal and spatial characteristics of automotive emissions were established by placing the absorption cell directly in the ambient air. Comparisons with a second type of CO monitor in a regional air monitoring network resulted in specific recommendations for CO sampling techniques.

During recent studies as part of the Regional Air Pollution Study (RAPS) in St. Louis (*1*), the need for specialized instrumentation for air quality monitoring and atmospheric modeling studies led to several developmental efforts by the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency. The result of one of these efforts was a specific, sensitive, fast-response carbon monoxide monitor for use over the full range of likely CO concentrations, from background levels of 50 ppb-v to the part-per-million levels encountered in urban areas. This monitor is the first ambient CO monitor based on the technique of gas filter correlation (*2*). Burch et al. (*3*) have described the design and fabrication of the monitor. This paper is an account of the results of field and performance tests with emphasis on special applications.

The gas filter correlation (GFC) monitor is one of a class of instruments that measure the changes in transmission of radiation due to absorption by gaseous species. Some perspective on the evolution of instruments similar to the GFC monitor can be obtained by reference to Hanst (*4*). The uniqueness of the GFC technique is the manner in which the target gas absorption is separated from the absorption due to other species. This specificity is accomplished in a signal processing procedure that involves the use of an optical filter cell containing a high concentration of the target gas. The gas filter cell provides an optimal filter for radiation at wavelengths readily absorbed by the target gas, i.e., the filter transmission characteristics anticorrelate with the absorption spectrum of the target gas. The specific manner in which the gas filter correlation is applied to CO detection is discussed in the next section.

Although the present results represent the first application of the GFC technique to ambient air monitoring of a criteria pollutant, the technique already plays a basic role in pollutant monitoring of various sources. Previous uses of the technique have included source monitoring for a number of gases: in industrial effluents (*5*) for NO, CO, and $SO_2$; in automotive exhaust (*6*) for CO, $CH_4$, $CO_2$, and $CH_2O$; and in exhaust clouds from rocket launch sites (*7*) for HCl and HF. The technique is generally applicable to simple molecules whose spectra exhibit vibrational, rotational fine structure at atmospheric pressure. Short-path, open-air instruments based on GFC are finding applications in situations where the measurement region of interest is inaccessible, such as across highways (*8*) or airport runways (*9*). Long-path, open-air measurements of the HDO molecular species are also being applied over path lengths of up to 10 km (*10*).

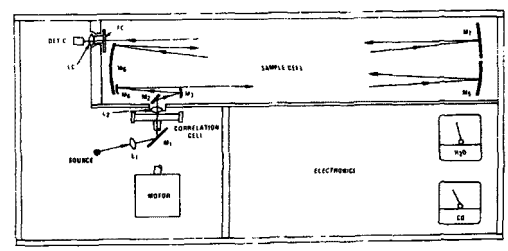


**Figure 1a.** Optical layout of gas filter correlation (GFC) monitor for CO

Arrow emanating from source indicates light path for CO detection

*Description*

The GFC carbon monoxide monitor was designed and fabricated by Burch et al. (*3*). Details of the design features for optical, electronic, and mechanical components are given in ref. *3*. The description presented here is meant to provide a basis for understanding the main operational features of the monitor.

A top view of the GFC monitor is presented schematically in Figure 1a, showing the components of the optical path for CO detection. During operation, sample air is continuously pushed through the sample cell. Radiation from the source is directed by optical transfer elements through the two main optical subsystems: the rotating gas filter (designated as correlation cell in Figure 1a) and the optical multipass (sample) cell. The beam exits the sample cell through interference filter FC, which limits the spectral passband to a few of the strongest CO absorption lines in the 4.6-$\mu$m region. Detection of the transmitted radiation occurs at the PbSe thermoelectrically cooled detector, C. The multipass system, originally described by White (*11*), is ordinarily adjusted to 28 passes, giving a total optical pathlength in the cell of 11.2 m.

Although the passband of filter FC is chosen to minimize interference from other gases, some residual $H_2O$ interference occurs. Therefore, $H_2O$ is also monitored, and the resulting signal is used in real-time to automatically correct for $H_2O$ interference in the CO reading. The optical path for $H_2O$ detection consists of a double pass through the sample cell. This is arranged by having a portion of the radiation that leaves mirror $M_4$ overfill $M_6$ and fall on $M_7$. The radiation reflected from $M_7$ is focused on a window above FC and passes to a pair of filter-detector combinations, one of which monitors radiation in a spectral interval of weak $H_2O$ absorption and the other of which monitors radiation in a spectral interval of strong $H_2O$ absorption. By comparing the amounts of radiation in the two spectral intervals, $H_2O$ concentration can be determined. The filter-detector combinations for $H_2O$ de-

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tection lie in a plane above the elements FC, LC, and Det C of Figure 1a but are not shown.

The gas correlation cell is constructed with two compartments (Figure 1b): one compartment (gas cell 1) is filled with one-half atmosphere of CO, and the other compartment (gas cell 2) is filled with pure $N_2$. Radiation transmitted through cell 1 is completely attenuated at spectral positions where CO absorbs strongly. The radiation transmitted by cell 2 is reduced by coating the exit window of the cell with a neutral attenuator. In this way, the amounts of radiation transmitted by the two cells are made approximately equal in the spectral passband that reaches detector C through filter FC.

In operation, radiation passes alternately through the two cells as they are rotated by a synchronous motor drive. This establishes a signal modulation frequency of 33.3 Hz. Transmission to the detector is constant if no absorption by the ambient sample occurs. If CO is present in the sample, the radiation transmitted through cell 1 is not appreciably changed, while that through cell 2 is changed. This imbalance is linearly related to CO concentration for small concentrations. Other gas species absorb the radiation transmitted by cells 1 and 2 in approximately equal amounts since their absorption structure does not correlate with that of CO (see ref. 2 for a more detailed treatment).

Superimposed on the entrance window of the cell is a typical light chopper pattern (Figure 1b) that creates a carrier frequency 12 times the signal modulation frequency, i.e., a carrier frequency of 400 Hz. The detector output from the CO channel is fed to two phase-sensitive amplifiers that separate the detector response at the signal frequency from the detector response at the reference (carrier) frequency. The signal due to CO is divided by the reference signal to substantially reduce many of the causes of sensitivity change, such as accumulation of material on optical components and variation in detector sensitivity.

*Zero and Multipoint Calibration*

During the performance tests and applications to be discussed, the instrument zero was determined by flushing the sample chamber with a gas containing negligible amounts of carbon monoxide. Four sources of "zero" air were used and found to agree within the noise limit of the instrument. These sources were: "ultrapure zero" air sold by Scott-Marrin, Inc.; prepurified argon; high-purified-grade helium sold by Air Products and Chemicals, Inc.; and zero grade air sold by Linde, Inc. The zero grade air (Linde) was further purified by passage through a "Hopcalite" CO scrubber sold by Mine Safety Appliance, Inc. A Standard Reference Material (SRM) purchased from the National Bureau of Standards, CO in $N_2$ at 100 ppm-v, was diluted by dynamic mixing with one of the "zero" air sources and used to provide a multipoint calibration. The instrument was shown to be linear over the range from 20 ppb-v to 20 ppm-v for the 11.2-m pathlength. Adjustment of the number of passes in the multipass cell can be used to extend the upper limit of linearity to 100 ppm-v.

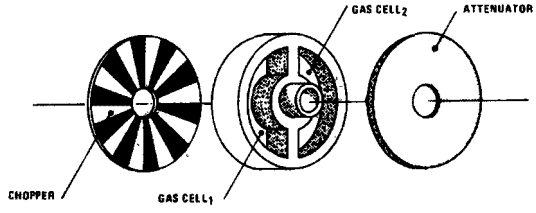


**Figure 1b.** View of components for gas filter cell; chopper and attenuator attached with epoxy onto cell during assembly

The $H_2O$ channel was calibrated by establishing reference signal levels at 0% relative humidity and 100% relative humidity at 25 °C by bubbling zero air through water. The water vapor interference for 100% relative humidity at 25 °C was 0.1 ppm-v of equivalent CO without any correction; with a correction the interference was reduced to less than the monitor noise level of 20 ppb-v. Carbon dioxide interference was tested by comparing $CO_2$ free air with air known to contain 330 ppm-v. The signal difference was undetectable.

*Performance*

Convenience of operation is one of the main performance features of the GFC monitor. No comsummables, pressurized gases, mixer gases, or chemicals are required for operation. The instrument response is independent of flow rate through the sample cell and reasonably independent of temperature. Chamber tests of the monitor, in which the ambient temperature was varied to different controlled levels, showed small variations in response to temperature changes over the range 16–32 °C. On a 2 ppm-v scale the sensitivity decreased 0.3% of full scale per degree Celsius increase, indicating the change in signal expected as the sample gas density decreases with temperature. The zero reference level increased 0.3% of full scale per degree increase; the exact cause of this effect is unknown. Ambient pressure changes (usually ±3% of the mean pressure) are also expected to alter instrument response due to corresponding gas density changes. Particular care must be taken when using the monitor on an airborne platform since the pressure decrease with altitude is roughly 0.1% per 10 m. The light weight (20 kg or 40 lb) of the monitor and the small size (62 by 27 by 12 cm) make it easily transportable. A dc-to-ac converter along with a set of six 6-V, 20-A-h batteries permit operation in almost any location for at least 4 h.

A unique feature of the monitor is that the top and one side of the sample section (Figure 1a) can be opened to the ambient air. As a result of the open path, the response time can be optimized to permit accurate temporal characterization of the CO from rapidly varying sources such as automobiles. For reactive gases like HCl, which can be detected by the GFC technique, integrity of the target gas can be maintained in an open path configuration since no actual sampling occurs.

*Applications*

Three types of field tests have been selected to demonstrate the application of the GFC monitor to monitoring problems: roadside measurements, long-term comparisons with a gas chromatograph–flame ionization detector for CO at selected stationary sites in the RAPS, and helicopter measurements. All measurements occurred during field experiments in the RAPS during 1975 and 1976. Additional studies of comparisons with CO monitors that incorporate different types of monitoring techniques, e.g., standard nondispersive infrared and electrochemical monitors, have been made with excellent results. Two of the initial applications of the GFC monitor have been reported elsewhere, i.e., laser long-path evaluations (*12*) and comparisons of RAPS station readings with area averages (*13*).

**Roadside Measurements.** For routine monitoring, ambient air is pushed through the enclosed sample cell at a rate determined by the pumping speed. The time required to exchange a factor $e^{-1}$ of the gas volume (2 L) of the sample cell, assuming a well-mixed sample, was 40 s for the usual flow rate of 3 L/min.

With the top and side panels of the monitor's sampling cell removed, the measurement time constant depends on the electronics (1 s minimum) rather than the gas exchange rate. Hence, an in-situ measurement can be made in which the measurement path is essentially immersed in the ambient air.

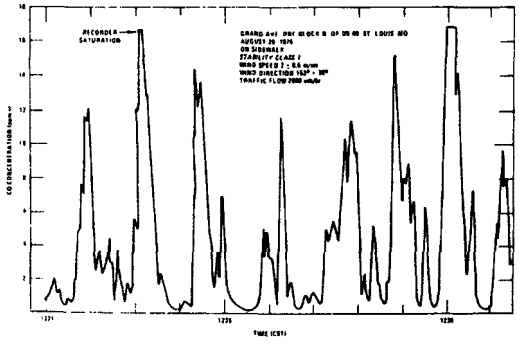

**Figure 2a.** CO concentration vs. time on sidewalk near inner-city roadway

Actual temporal variations of CO concentrations can be obtained in this way.

A set of roadside measurements was planned in which the in-situ monitoring feature was required. Two questions were to be addressed: What are the temporal characteristics of the CO concentrations near a roadway? How far from the roadway can the characteristic temporal fluctuations be distinguished? These are basic questions that have implications to roadway modeling and to placement of stationary monitoring sites with respect to street and highway traffic.

Although the combination of the monitor, battery pack, and chart recorder could not be hand-carried, they were easily mounted on a small laboratory cart that could be rolled along the sidewalk or across the surrounding area. The monitor sampling space was approximately 1 m off the ground. Measurements were made on the downwind side of the roadways, at the roadway edge, and then at intervals of 25 m to a distance of 100 m. Data were recorded at two locations. One was an inner-city location near Grand Avenue on the campus of St. Louis University, and the other was near Page Road, a four-lane suburban highway at a location 1 mile east of interstate highway 270.

Figure 2 gives two in a set of measurements taken at Grand Avenue. Figure 2a, showing data taken at roadside, indicates a minimum measurement of approximately 0.2 ppm-v and a maximum of more than 17 ppm-v, at which point the recorder saturates. The peaks, which occur every 1.5 min, are synchronized with a nearby traffic light. The concentration minima appear to represent the urban background, while the peaks are due to the local automotive traffic. This separation is exactly what is required for microscale measurements.

In Figure 2a, note that the concentration changes from 0.2 ppm-v to more than 17 ppm-v in only 30 s. The maximum frequency component in the data is about 10 cycles/min or 600 cycles/h. This characterization of the temporal variation of the CO concentration will be used in the next subsection to explain the results of comparison studies between the GFC monitor and a monitor that takes discrete samples. The electronic time constant during this measurement was 3 s. Thus, with a 1 m/s wind speed, a spatial variation of 3 m could be resolved. This is more detailed spatial resolution than is normally required, but illustrates a capability that has been lacking in previous microscale studies.

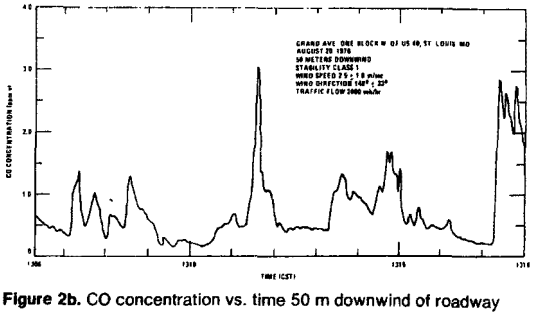

**Figure 2b.** CO concentration vs. time 50 m downwind of roadway

Figure 2b illustrates the decrease in CO variability as the distance between roadway and monitoring location is increased. Additional measurements at Page Road (*14*) and at Grand Avenue provided the basis for a more generalized observation. At no time in this study was the effect of roadway traffic measurable 100 m from the roadway. Although this set of observations is very limited and is not considered a sufficient study of CO variability near roadways, the main conclusion is essentially in agreement with the results of urban survey measurements by Ott (*15*). Whenever Ott measured CO sufficiently far away (200 m in his results) from a road or local source, he measured the urban background. Since integrated samples were used in his studies, the nature of variations in CO concentrations as a function of distance was not apparent as with a real-time monitor.

A few examples of previous studies that could have benefited from the use of the GFC monitor are the San Jose street canyon study (*16*), the St. Louis street canyon study (*17*), a San Jose urban survey (15), the Oakbrook shopping center study (*18*), and the New York City Roadway Configuration Study (*19*). In addition, the following proposed studies are now possible: the measurement of peak to average concentrations (*20*) and the measurement of the distribution of pollutants on the near-freeway microscale within the freeway corridor (*17*).

**Long-Term Comparison in Selected Regional Air Monitoring Stations.** Prior to and following the 1975 summer "intensive" period of research studies in the RAPS, a quality assurance study was made of the entire Regional Air Monitoring System (RAMS) network. During the study, bag samples of ambient air were collected at the manifold inlet to individual stations for periods of 20 min. Subsequently, the bag samples were analyzed for CO with the GFC monitor, and the resulting readings were compared with the reported station average for the same time period. Each of the RAMS stations was equipped with a Beckman 6800 gas chromatograph with a flame ionization detector. For this instrument, ambient CO measurements were continually obtained, with updates at the end of 5-min intervals. Readings were digitized to the nearest 0.1 ppm-v (this digitization is especially evident in Figure 4, which is presented later). During the 20-min period of bag sampling, four gas chromatographic cycles were completed. A total of 19 preintensive and 16 postintensive data sets were collected. The corresponding 35 data comparisons are shown in Figure 3. Also shown in Figure 3 are 20 data sets of the same type taken at site 105 (an urban site near the center of St. Louis) in the RAMS network. Assuming that the GFC readings were correct, these measurements indicate that the RAMS network was reporting low values for the majority of the comparisons, with a few exceptionally high station readings. Both the set of network monitors taken as a whole and the monitor at station 105 showed roughly equivalent scatter diagrams.

As a result of the comparison measurements, the following question was addressed: Do the RAMS stations report low values and if so, why? In an attempt to answer this question, the GFC monitor was installed in several of the RAMS sites, and a direct comparison was made over extended periods of time.

There are a total of 25 RAMS sites located on approximately concentric rings centered on downtown St. Louis.

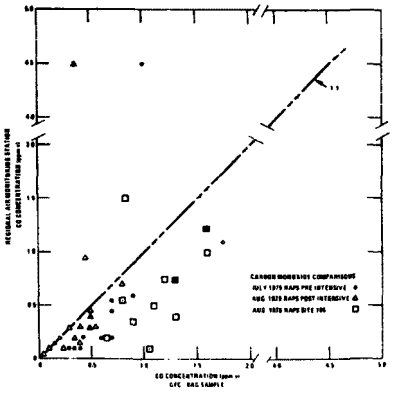

**Figure 3.** Scatter diagram showing comparison between measurements of 20-min bag samples and simultaneous RAMS monitor measurements

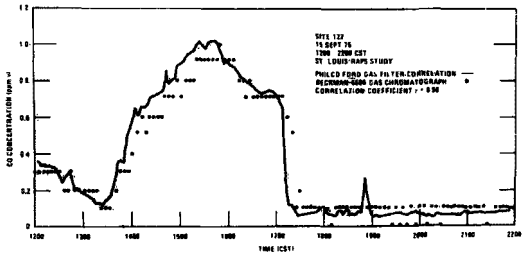

**Figure 4.** Comparison of CO concentration as measured by GFC and RAMS monitors at site 122

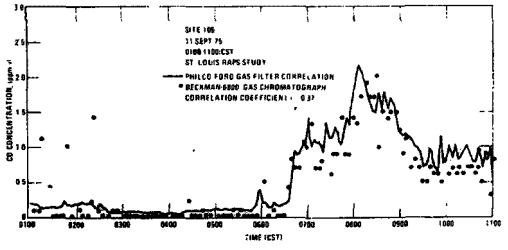

**Figure 5.** Comparison of CO concentration as measured by GFC and RAMS monitors at site 106

There is one station near the center, six inner-city sites located on a 4-km radius, six near-suburban locations on a 9-km radius, eight far-suburban locations on a 15-km radius, and four rural sites on a 40-km radius. All the stations used a Beckman 6800 gas chromatograph to measure CO concentrations, and there was an identical unit in a central laboratory maintained by the RAPS staff. It was decided to compare the monitors in the laboratory and in at least one station on each concentric ring.

The comparison between the GFC monitor and the Beckman 6800 in the central RAPS laboratory was performed over a period of approximately one day. Both instruments were calibrated with the same gas, a Standard Reference Material (SRM) obtained from the National Bureau of Standards. The data proved to be virtually identical, having a correlation coefficient of 0.99.

Examples of data collected at one of the RAMS stations are shown in Figure 4. This station, site 122, was in a rural area; lack of local sources evidently accounts for the correlation coefficient value of 0.96 and the close agreement with respect to absolute concentration. Monitoring sequences at sites 119 (far-surburban site), 106 (near-surburban site), and 105 (inner-city site) were also taken. The data were similar to Figure 4, although the range of concentration variation was larger, e.g., from a maximum of 3.5 to 0.1 ppm-v at site 119. The correlation coefficients for sites 119 and 106 during 10-h monitoring sequences were 0.96 and 0.37, respectively, while the correlation coefficient for a 4-h monitoring sequence at site 105 was 0.72. The data from site 106 are shown in Figure 5. The most significant difference in response between the two monitors at site 106 was during the initial 2-h period. Exclusive of this period the correlation coefficient was 0.95. However, the RAMS data are consistently lower than the GFC data during the remainder of the 10-h sequence.

Agreement between the two monitors at sites 122 and 119 was excellent with a high correlation. Data from sites 105 and 106 indicated significant differences between the 5-min readings provided by the Beckman 6800 and the corresponding GFC monitor readings. In summary, the laboratory data and data from the more remote sites demonstrated basic agreement between the two types of instruments, but the data from urban sites and the quality assurance data indicated a lack of agreement for short-term comparisons. This set of observations could be explained by considering the gas chromatograph sampling procedure and the data on temporal fluctuations in CO concentrations obtained in the near-roadway study.

The RAMS manifold pump moves at least 400 L of air/min through the station manifold. The gas chromatograph extracts 10 mL of air during injection and repeats this sampling procedure every 5 min. The number of samples measured per hour is then 12. Since the data in Figure 2 indicate the likely existence of frequency components in the ambient CO concentration of up to 600 cycles/h, it is obvious that the average of a limited number of gas chromatographic readings can be in error. The use of an integrating flask between the RAMS manifold and the gas chromatograph would serve to reduce the temporal variations in the sampled air and hence reduce the error. The best solution would be to use a continuously sampling monitor.

A straightforward "yes" or "no" answer cannot be given to the original question, "Does the RAMS network report low CO concentration?" However, it has been established that the reported concentration average for 20-min readings can misrepresent the true time-averaged concentration and that an explanation can be formulated in terms of the sampling technique. In other words, due to the nature of temporal variations in ambient CO concentrations, the probability that discrete sampling intervals occur during a period of low CO concentration can be significantly greater than during a period of high CO concentration. Since most of the RAMS sites are located near lightly traveled streets where high concentrations occur infrequently and in an erratic manner, the probability that any sample measurement will be lower than the true average concentration is increased, that is, a predominance of low readings is recorded by the Beckman 6800 with a few exceptionally high readings. The data represented in Figure 3 are consistent with this explanation. It also seems obvious from the Figure 3 data that, as averaging time is increased, the RAMS average for CO approaches the average for the GFC monitor.

**Helicopter Measurements.** In addition to the 25 stationary monitoring stations that form the backbone of the RAPS data collection program, data were also collected during the summer intensive periods by two instrumented helicopters which provided vertical profiles of pollutant concentrations by monitoring during downward spirals over selected RAMS sites. As a result of the need for a better CO monitor for in-flight measurements, two test flights for the GFC monitor

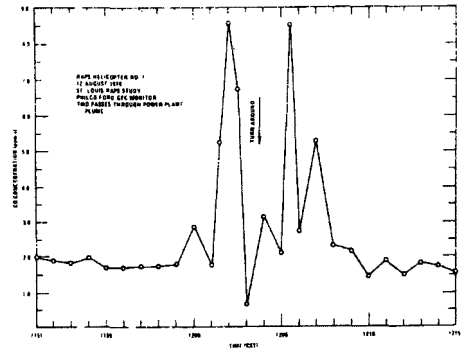

**Figure 6.** Measurements of CO concentration in industrial plume with GFC monitor mounted in RAPS helicopter

were arranged, one on July 21 and the second on August 12, 1976.

For the first test flight, during which routine monitoring spirals were flown, the ambient concentration never exceeded 0.2 ppm-v. During the second flight, the helicopter made two passes through a power plant plume. Variations in the monitor response as a function of time are shown in Figure 6. Data were only available as 1-min averages. The flight path carried the monitor through the plume, and after turning, back through the plume again. While in the plume the monitor saturated at 8.5 ppm-v. During the same flight the concentration dropped to less than 0.1 ppm-v. However, during most of the flight the concentration exceeded 1 ppm-v.

Calibrations of the monitor just prior to and immediately after the second flight agreed within ±0.05 ppm-v. However, because no in-flight calibrations were made, the data in Figure 6 must be considered qualitative. There are no known problems associated with flying the GFC monitor, and the data appear reasonable.

## *Conclusions*

An ambient real-time CO monitor based on gas filter correlation has been developed. The monitor is sensitive enough, with a noise equivalent concentration of 20 ppb-v, to monitor background CO levels, or it can be used to monitor compliance with Federal air quality criteria levels for CO (9 ppm-v for an 8-h average and 35 ppm-v for a 1-h average). Operation is simple and flow independent; no consummables are required. The monitor incorporates a unique feature that reduces response time to a minimum.

The monitor is particularly useful for roadway or microscale studies where short time variations in concentrations are important. Measurements to demonstrate the monitor's capability to characterize the temporal and spatial variations in CO concentrations near roadways suggest its use in future microscale studies. Successful use in a helicopter has also been demonstrated.

The monitor has been used to determine the reason for apparently low CO concentrations reported by the RAMS stations. Comparisons between the GFC monitor and the discretely sampling monitor being used in the RAMS stations were made at selected stations. The nature of CO variability, especially in urban areas, can bias a discretely sampling monitor unless an appropriate means for sample integration is provided. Information and insight gained in this study should prove valuable in planning for future studies.


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# APPENDIX B

## Carbon Monoxide Automobile Emissions Measured from the Interior of a Traveling Automobile

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SCIENCE

# Carbon Monoxide Automobile Emissions Measured from the Interior of a Traveling Automobile

Lucian W. Chaney

# Carbon Monoxide Automobile Emissions Measured from the Interior of a Traveling Automobile

Abstract. *During a procedure to monitor carbon monoxide (CO) concentrations inside a traveling car, it was discovered that CO emissions from individual passing vehicles produced accurately measurable increases in the CO concentration. The CO produced by individual vehicles varied by three orders of magnitude; this finding demonstrates that a relatively small number of cars can be responsible for a high percentage of total vehicle CO emissions.*

The purpose of this study was to determine the CO concentrations to which the driver of a typical passenger car was exposed while traveling under a variety of traffic conditions. The maximum concentrations of CO permitted by the Federal Ambient Air Quality Standards, (FAAQS) (*1*) set in accordance with the Clean Air Act, are 9 parts per million (ppm) for 8 hours and 35 ppm for 1 hour. While recording CO concentrations inside automobiles on lightly traveled sections of an interstate highway, I observed that CO emissions from individual passing cars produced clearly defined peaks on the strip chart recorder. Subsequent measurements on 760 vehicles showed a surprisingly wide variation in CO concentrations from 0.05 ppm to 45 ppm. Analysis of the data showed that a large proportion of the vehicles monitored produced only a small amount of the total CO, whereas a relatively small number of the total vehicles contributed almost half of the total monitored CO.

The gas filter correlation monitor used for this study was especially designed for the Environmental Protection Agency for use in modeling studies (*2*) carried out during the St. Louis Regional Air Pollution Study (*3*). The monitor is portable and can be battery-operated; hence, the monitor can readily be operated on the front passenger seat of an automobile. I determined the CO concentrations by measuring the attenuation of a focused infrared beam which makes 28 traverses of a cell 0.6 m long. This is accomplished with mirrors placed at each end of the cell. The top of the cell compartment was removed to permit an in situ measurement of the CO concentration. The time constant was set at 3 seconds. The windows of the automobile were closed, and the ventilation was forced by operating the automobile blower fan at the maximum speed. The data were recorded on a portable strip chart recorder mounted directly under the monitor so that the record could be observed and marked by the driver. Two small (15 cm in outside diameter and 51 cm long) high-pressure cylinders, one containing argon and the other containing 3.0 ppm of CO in nitrogen were placed on the floor behind the front seat. The gases in these two cylinders were used in a daily, zero and span, two-point calibration, usually carried out at a rest stop. Before and after the trip, I carried out a five-point calibration, using a gas mixture calibrated by the National Bureau of Standards. The average difference between the calibrations was 3 percent, and I estimate that the maximum measurement error is 10 percent.

The data were collected during a two-part, cross-country trip. Part 1 was from Chicago to New Orleans, 18 to 20 March 1977, and part 2 was from New Orleans to San Diego, 27 March to 2 April 1977. The expectation was that the average CO concentration would gradually increase as cities were approached, reach a maximum near the center of a city, and fall to a minimum in the rural areas. In general, this was found to be true; however, very large fluctuations occurred depending mostly on traffic density and traffic speed.

Examples of data collected on heavily traveled interstate highways are those from the Dan Ryan Expressway (I-94) in Chicago (Fig. 1a) and the San Diego Freeway (I-405) in Los Angeles (Fig. 1b). The peaks in the concentration are primarily the result of traffic slowing down as a result of congestion. When the traffic slowed to 10 miles per hour (mph) or less (1 mile = 1.6 km), the CO concentration usually exceeded 15 ppm; when it halted completely, the CO concentration was about 45 ppm.

In order to compare the CO concentration on interstate highways with that in maximum downtown traffic, I made a trip through downtown New Orleans between 1200 and 1230 C.S.T. on 23 March 1977. The traffic moved at only a few miles per hour and stopped at every traffic light. The CO concentration varied from 2 to 50 ppm, depending primarily on the number of stationary or accelerating vehicles in close vicinity to the

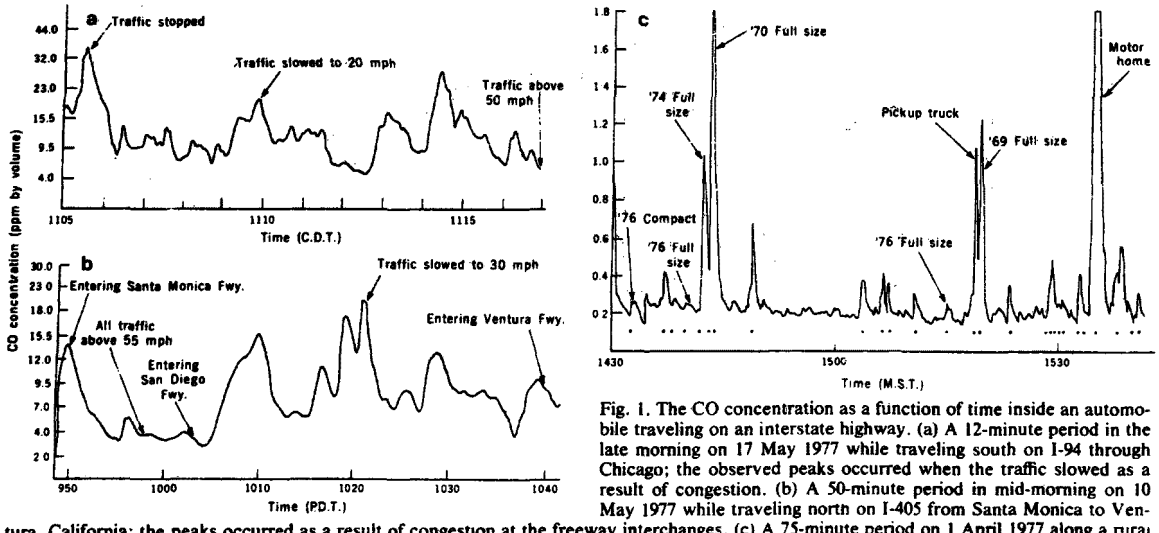


Fig. 1. The CO concentration as a function of time inside an automobile traveling on an interstate highway. (a) A 12-minute period in the late morning on 17 May 1977 while traveling south on I-94 through Chicago; the observed peaks occurred when the traffic slowed as a result of congestion. (b) A 50-minute period in mid-morning on 10 May 1977 while traveling north on I-405 from Santa Monica to Ventura, California; the peaks occurred as a result of congestion at the freeway interchanges. (c) A 75-minute period on 1 April 1977 along a rural section of I-8 (starting point, 150 miles west of Tucson, Arizona); the peaks are due to the passage of individual vehicles.


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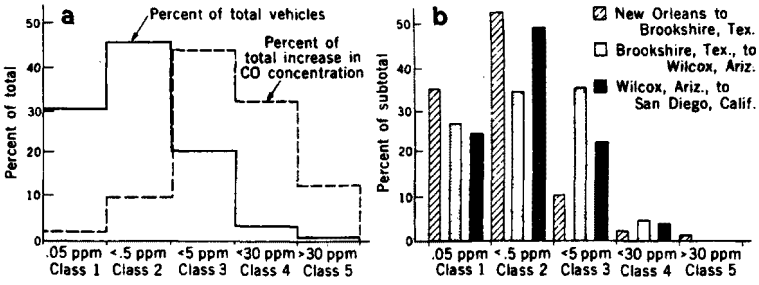


Fig. 2. Data summary of 760 vehicles monitored on I-8 from New Orleans to San Diego (28 March to 2 April 1977): (a) distribution of vehicles and CO emission by class; (b) distribution of vehicles by class for three subgroups of the total sample.

monitoring vehicle. The results of these experiments correlated with the expectations.

The surprising results occurred along the rural, rather than the urban, portions of the route. The strip chart used for recording the rural data required that the sensitivity and chart speed be adjusted to accommodate the maximum CO concentration and the traffic density. As a result of the attention required to make these adjustments, the speed of the monitoring vehicle was somewhat slower than normal. Thus, many of the other vehicles on the highway were passing at their normal cruising speed of about 60 mph. I noticed that the CO concentration in the instrumented vehicle would increase abruptly a few seconds after the passage of some but not all vehicles. I decided to monitor the increase in CO concentration due to the passage of single vehicles in a uniformly controlled manner. The procedure that I adopted was to drive the monitoring vehicle at about 52 mph so that most of the other traffic passed with a differential speed of from 3 to 10 mph. The usual pattern of the passing vehicles after passing was to return to the traveling lane about 50 feet ahead of the monitoring vehicle. If for some reason the passing vehicle remained in the passing lane and there was no other vehicle approaching, then I also moved the monitoring vehicle into the passing lane. A sample recording of some of the data collected by this technique is shown in Fig. 1c. A few of the peaks that were positively identified with a given vehicle are noted.

The monitoring procedure described above was developed during the trip from Chicago to New Orleans and was used during the trip from New Orleans to San Diego to collect the data summarized in Fig. 2. The only vehicles included in the tabulation were those that passed singly with sufficient distance between the other vehicles to permit a clear identification of the peak in the monitored CO concentration with the passing vehicle. In order for this condition to hold, the traffic density had to be sufficiently low. Hence virtually all the data were collected in rural areas, usually 20 miles or more from a metropolitan area.

While recording the data, I observed that heavily loaded vehicles produced high CO concentrations. Also, whenever a grade was being ascended, the CO concentrations increased. In order to determine the effect of a steep grade, I followed a truck over the Sierra Nevada mountains. The CO concentrations increased and decreased by more than one order of magnitude, depending on the grade. The CO concentration inside the monitoring vehicle reached 50 ppm on the most severe part of the grade and remained over 25 ppm for ½ hour. Clearly, under some circumstances the potential to exceed the FAAQS exists.

I monitored a total of 760 vehicles by this technique on part 2 of the trip. These were divided into five classes based on the maximum increase in CO concentration measured inside the monitoring vehicle. The classes were as follows: class 1, maximum increase less than 0.05 ppm; these vehicles were all 1975, 1976, or 1977 models lightly loaded (less than half of the designed load); class 2, maximum increase between 0.05 and 0.5 ppm; these were mostly 1970 through 1974 models and some newer cars carrying heavy loads (100 percent or more of the designed load); class 3, maximum increase between 0.5 and 5 ppm; this class includes largely older cars but also some heavily loaded newer vehicles such as motor homes and pickup trucks; class 4, maximum increase between 5 and 30 ppm; these were all heavily loaded vehicles, most of them older than 1970; and class 5, maximum increase greater than 30 ppm; there were two vehicles in this class: one was a pickup truck pulling a four-horse trailer; the other (CO concentration, 45 ppm) was a no-brand fuel oil delivery truck.

The peak measured increase in CO concentrations for all the vehicles in each class were added, and the percentage contribution of each class to the total concentration was computed. The results are shown in Fig. 2a. If the vehicles falling in class 1 and class 2 are grouped together, they represent 76 percent of all the vehicles observed and contribute 12 percent of the total CO; class 4 and class 5 combined represent 3.3 percent of the total vehicles and contribute 45 percent of the total CO. The finding that 30 percent of the vehicles monitored appeared to be equipped with catalytic converters is in agreement with a recent study done in California (*4*).

In order to develop some feeling for the variability of the data, I divided the total data set into three nearly equal parts. The first third contained the data collected from New Orleans to Brookshire, Texas; the second third from Brookshire, Texas, to Wilcox, Arizona; and the last third from Wilcox, Arizona, to San Diego, California. The percentage of vehicles in each class was determined for each third of the total sample (Fig. 2b). In the second third of the sample, there was a smaller percentage of the vehicles in class 2 and a greater percentage in class 3 than for the sample as a whole. The reason is probably due to more uphill grades in this section of the route as well as differences in wind speed and wind direction. However, the overall pattern is much the same for all three sections of the route, which reaffirms the character of the total distribution

As a result of the experiments conducted in the urban areas, I conclude that most drivers are not exposed to toxic doses of CO but that under certain circumstances the potential exists to exceed the FAAQS. The major observations resulting from the data are that the CO automobile emissions can vary by three orders of magnitude depending on a number of factors and that more attention should be directed toward that small minority of vehicles which are the major polluters.

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6 October 1977; revised 5 December 1977

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16. ABSTRACT

A new type CO monitor was applied to special ambient air measurement problems. The monitor, a gas filter correlation (GFC) instrument, was designed specifically for use in the St. Louis Regional Air Pollution Study (RAPS), but has been applied to several other measurement requirements. The monitor has an inherently fast response of less than one second and has proved useful in documenting extremely variable monitoring situations. The monitor was used in nine separate studies and typical data are presented. The most significant contribution from these studies has been the ability to document the extreme variability of carbon monoxide in urban environments.

17. KEY WORDS AND DOCUMENT ANALYSIS

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