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16. ABSTRACT

When an air pollution monitoring system is put into operation, it should be analyzed to determine whether system variables will affect the output of analytical instruments within the system. An analysis of the monitoring system of a Caltrans air pollution research van is presented. This analysis investigates the effects of several system variables on instrument response, including the length of the sample intake lines, variation in instrument supply voltage, van interior temperature, soiling of intake line filters and the retention time of air samples in teflon bags. Where system variables are found to affect instrument response, regression equations were developed which correct for the effects of these variables.

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DEPARTMENT OF TRANSPORTATION
DIVISION OF STRUCTURES & ENGINEERING SERVICES
OFFICE OF TRANSPORTATION LABORATORY

June 1977

FHWA-CAL-TL-7080
DOT-FH-11-7730

Mr. C. E. Forbes
Chief Engineer

Dear Sir:

I have approved and now submit for your information this interim research project report titled:

VARIABLES AFFECTING AIR QUALITY
INSTRUMENT OPERATION

Study made by ..... Enviro-Chemical Branch

Under the Supervision of ..... E. C. Shirley, P. E.

Principal Investigators ..... C. R. Sundquist, P. E.
and
A. J. Ranzieri, P. E.

Report Prepared by ..... K. O. Pinkerman, P. E.
and
R. R. Peter, P. E.

Very truly yours,

George A Hill

GEORGE A. HILL
Chief, Office of Transportation Laboratory

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Attachment

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FOREWORD

This report describes the analysis of an air quality monitoring system to determine the effects of several system variables on the response of the analytical instruments. This air quality monitoring system was used by the California Department of Transportation to study the relationship of air pollution to roadway location, design and operation. The study was performed in cooperation with the Federal Highway Administration (FHWA) and was largely funded by FHWA. Due to the nature of the overall project, there will be several other research reports covering individual aspects of the project.

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ACKNOWLEDGEMENTS

Funding for this research project was provided by the Office of Research, Federal Highway Administration. Dr. Howard Jongedyke, and Mr. Kenneth Jones have been the project managers for the Federal Highway Administration.

Acknowledgement is gratefully given to Dr. Kenneth Kerri of California State University, Sacramento, who assisted in the design of the experiments and with the review of this report. Special acknowledgement is given to the California Department of Health and Transportation Laboratory personnel who calibrated the analytical instrumentation and otherwise assisted with this study. These persons include Ed Jeung, Barbara Wright, Vince Povard and Jane Jang of the Department of Health and Bob Breazile and Lloyd Batham of the Transportation Laboratory.

Special acknowledgement is also given to the Department of Transportation personnel in Los Angeles who assisted with the collection of data in the field. These included Jean Smart, field supervisor, Clark Gipson, Rudy Abangan, Jim Ito and Arnold Mahalona.

Without the team effort of these people, this project would not have been possible.

The contents of this report reflect the views of the Transportation Laboratory, which is responsible for the facts and the accuracy of the information presented herein. The contents do not necessarily reflect the official views of the State of California or the Federal Highway Administration. This report does not constitute a standard, specification, or regulation.

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INTRODUCTION

An air quality monitoring research van was constructed by the California Department of Transportation's Transportation Laboratory as part of a research project entitled: "Air Pollution and Roadway Design, Location, and Operation". This research van was designed to monitor meteorological parameters and air pollutant concentrations on and adjacent to freeways. Data obtained in these monitoring operations are to be utilized in developing and calibrating mathematical pollutant dispersion models, which are necessary as a highway design and planning tool.

The research van was initially designed to draw air samples from a maximum of 15 points at a sampling site and to analyze the following pollutants:

Continuous Analysis	Intermittent Analysis
1. carbon monoxide	1. ozone
	2. sulfur dioxide
	3. hydrocarbons (total and methane)
	4. oxides of nitrogen (NO, NO_2, NO_x)

The research van sampling train includes up to 15 sampling lines which may be of varying lengths - in practice they range from about 150 to 600 feet. These lines are connected to a vacuum manifold as shown in Figure 1. Samples drawn into the lines by this vacuum are partially diverted either directly into the carbon monoxide analyzers or into the bag sampling chamber. All air flows in the sampling train are regulated by air pressure-actuated valves, depicted as black circles in

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PROCESS CONTROL FOR AIR SAMPLING AND ANALYSIS SYSTEM

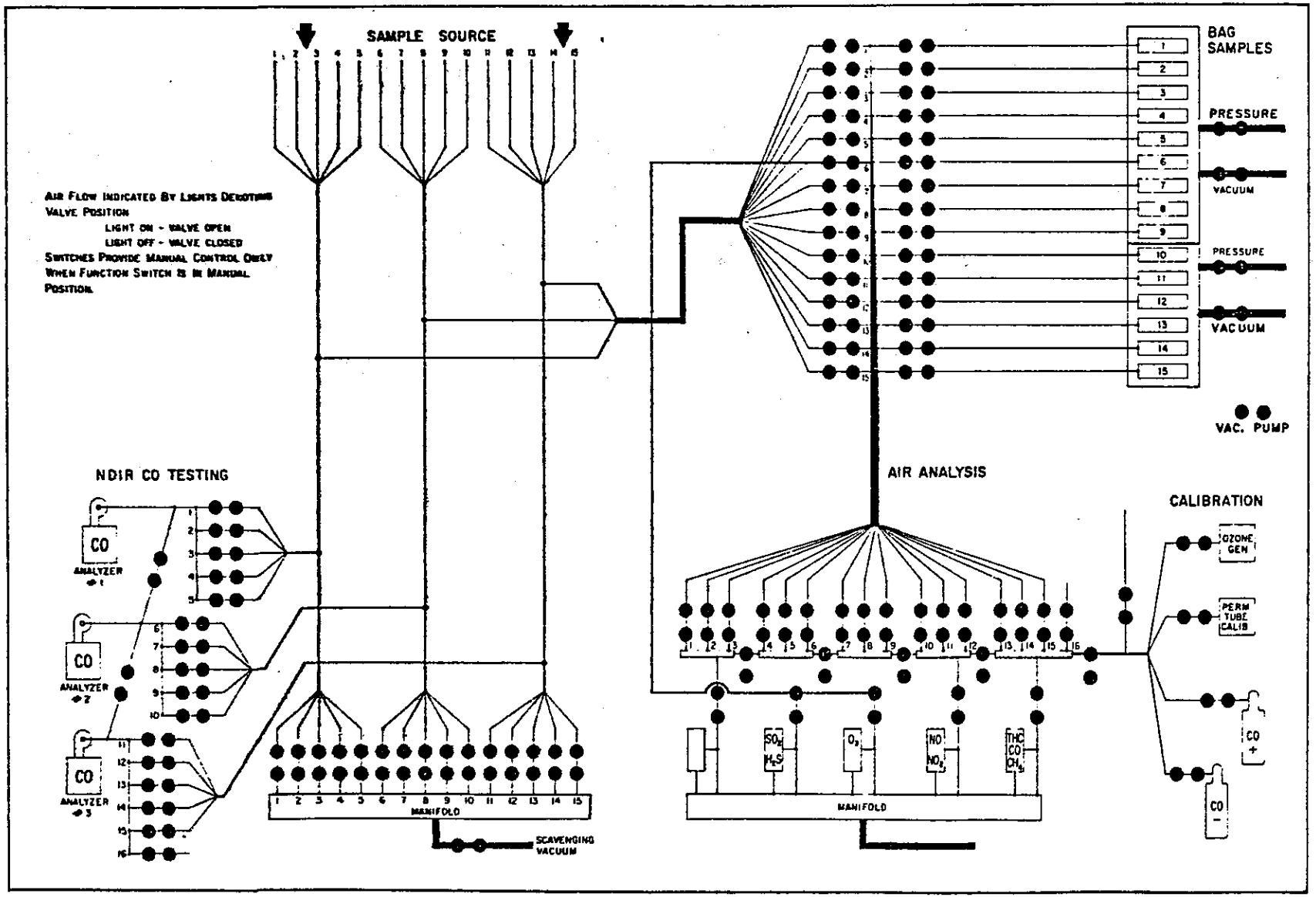

Figure I.

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Figure 1. These valves may be operated manually for testing purposes (Figure 2) or automatically controlled by a small computer located in the van. During routine sampling, this computer not only controls valving but also regulates analyzer operation and stores all acquired data (including meteorological) on magnetic tape (Figure 3).

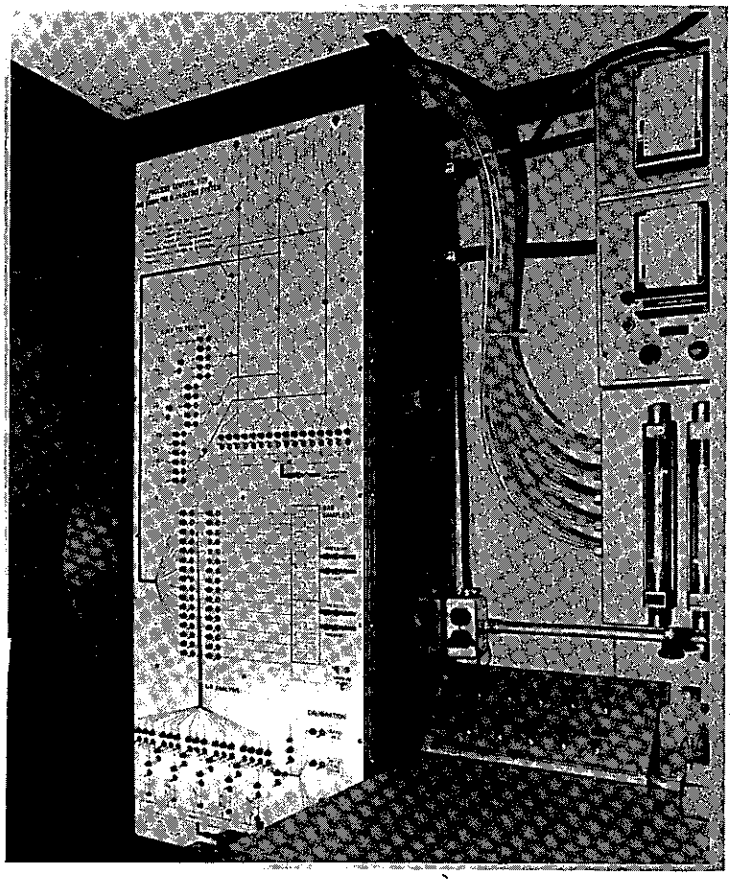

Figure 2. Control panel for manual operation of valves in sampling system. Lights on panel indicate when valves are open.

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Figure 3. The computer system, immediately to the right of teletype at center, controls valving and stores all acquired data.

The CO analyzers operate continuously, drawing air samples from whatever inlet line to which they are connected. In routine sampling the valves are actuated in a manner such that each analyzer samples from a particular inlet line for 1 minute. With all 15 inlet lines and 3 CO analyzers in operation, every inlet line is sampled every 5 minutes.

Air samples are drawn into the bags within the bag sampling chamber ("bagbox") by applying a vacuum to the interior of the chamber. As the interior pressure of the bagbox drops below the pressure level within the inlet lines, air is drawn into the sampling bags located in the bagbox. These bags are filled gradually over a 15 minute period, at the end of which time the bagbox is pressurized and air samples are pumped out of the bags, one bag at a time, into any or all of the remaining

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analyzers. Each individual bag is evacuated and its contents analyzed over a 5 minute interval. The total time required for analyzing all 15 bags would be 75 minutes. The total bagbox cycle time, including both filling and analyzing, is 90 minutes for all 15 bags. In actual practice, all 15 bags have never been used simultaneously in a sampling operation, and the bagbox has been split into two compartments (9 and 6 bags) which may be operated individually when fewer bag samples are needed. The bagbox is depicted in Figures 4 and 5.

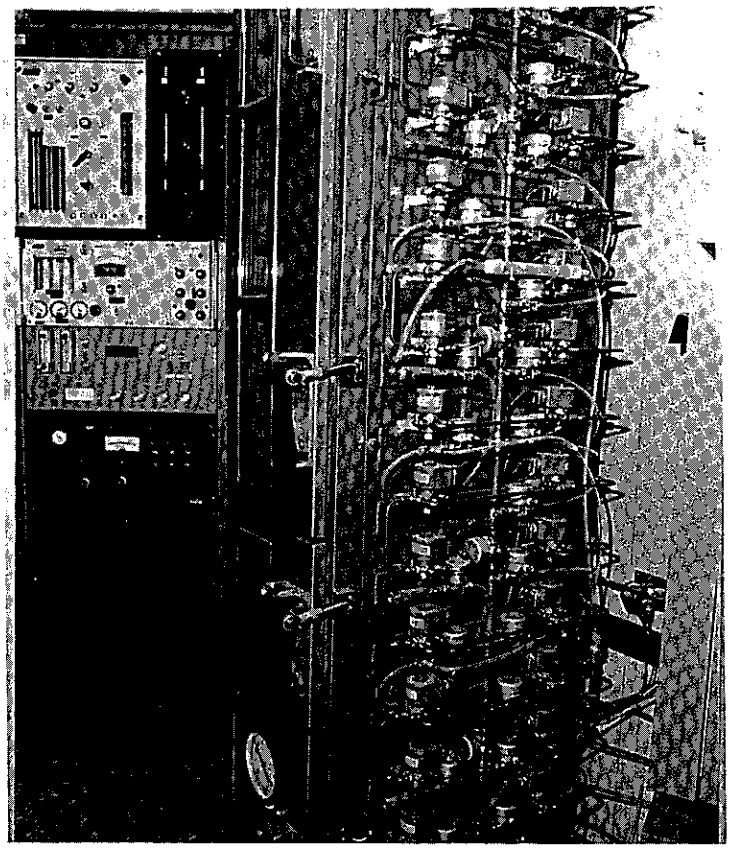

Figure 4. Bag sampling chamber, with valve system mounted on side. The upper and lower sections of the chamber contain 9 and 6 bags respectively, and each section may be operated independently.

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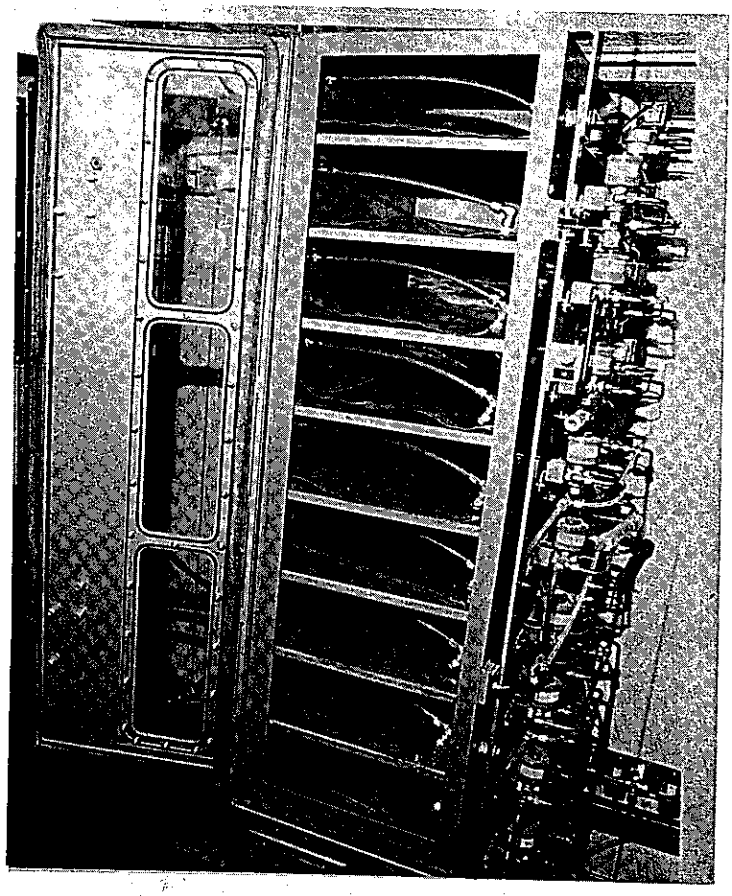

Figure 5. Interior view of upper section of bag sampling chamber. A teflon bag may be seen on each shelf.

This research van presented some unique air sampling and analysis problems since the analytical instruments on board are subjected to relatively unusual conditions, ones not found in typical stationary monitoring systems. As a consequence, it was decided to carry out a testing program to determine how these conditions affect analytical results, if at all.

At the time this testing program was undertaken, the Caltrans research van was situated in a mixed single-multiple family dwelling residential neighborhood in Los Angeles, in an open,

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unshaded lot adjacent to the Santa Monica Freeway at 4th Avenue. The van is equipped with air conditioning and a small heater, but it was felt that the interior temperature might possibly fluctuate excessively. The van was serviced with city power, but line voltage fluctuations were observed through the course of the day as local consumer use varied. Air samples were drawn into the van through 15 teflon-tubing inlet lines of various lengths up to more than 600 feet (182.88 meters), with glass-fiber filters attached to the tubing inlets (sampling inlet locations shown in Figure 6).

In view of all these characteristics and methods of operation, it was deemed necessary to determine what effects they had, if any, on air quality data. Specifically, the variables of concern were: (1) van interior temperature, (2) line voltage fluctuation, (3) cleanliness of the tubing inlet filters, (4) length of inlet lines (teflon tubes), and (5) sample retention time in the bagbox.

Limited research had previously been done concerning the effects of these variables on gases and analyzers; therefore, a series of tests were made to determine the significance of the variables in terms of altering analytical instrument readings from the actual pollutant levels at the points being sampled. Assistance in this study was provided by personnel from the California Department of Health's Air and Industrial Hygiene Laboratory.

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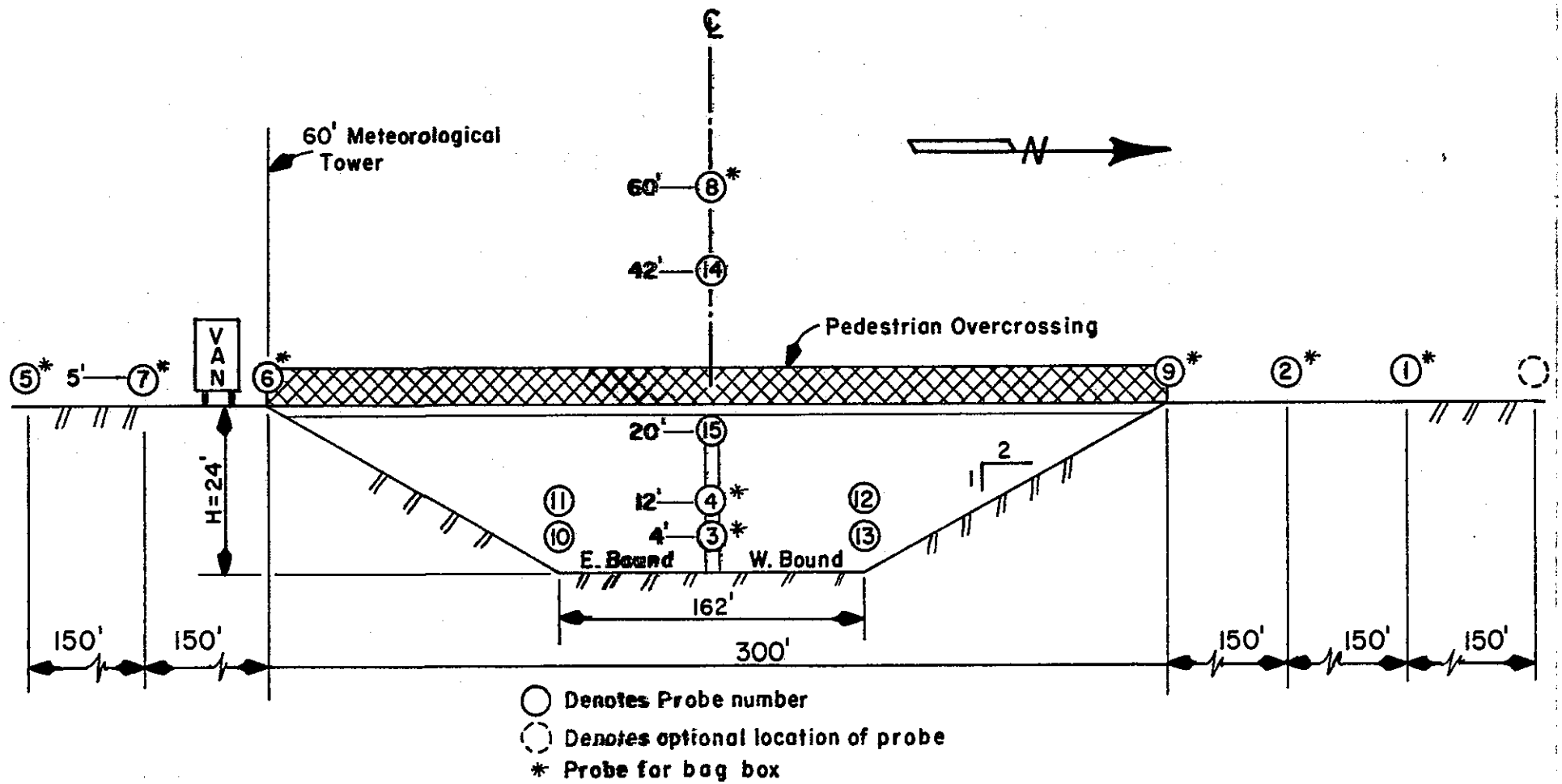
SANTA MONICA FWY. AT 4th AVE. P.O.C.
SAMPLING INLET LOCATIONS



June, 1977

Figure 6

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CONCLUSIONS AND RECOMMENDATIONS

Three different system variables were found to significantly alter pollutant concentration within the sampling train and/or affect instrument response. These findings were primarily based upon regression analysis techniques. First, the response of the Beckman 315BL CO analyzer was determined to be sensitive to fluctuations in the interior temperature of the research van. Secondly, ozone was found to decay with time while stored in the bagbox. Finally, the length of the sample intake line affected the SO_2 concentrations as indicated by the Tracor 250H analyzer.

The indicated ozone levels on the Rem 612 analyzer fluctuated excessively when samples were drawn through the long Teflon intake lines, although the sampled ozone concentrations were constant. This fluctuation was of such magnitude that the van sampling train, as originally designed, was considered unsatisfactory for ozone sampling and analysis. The fluctuation has since been eliminated by drawing samples directly into the ozone analyzer through a teflon tube approximately 15 feet (4.57 meters) in length. This limits ozone sampling to the immediate area of the research van location.

Regression equations were developed for each instrument which closely estimated actual pollutant concentrations, based upon instrument response and any system variables which were determined to be significant.

Since the experiments in this study utilized interference-free test gases, it is recommended that further testing be conducted using ambient air. A limited amount of testing has already been performed to study the interactive effects of ambient NO, NO_2 and ozone within the sampling train. However, much more data

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is required to accurately determine the extent of the reactions between these gases from the time they enter the inlet lines until they reach the analyzers. Some aspects to be considered are the oxidation of NO to NO_2, the reduction of ozone, the effects of line length, and storage time in the bagbox.

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IMPLEMENTATION

The information obtained in this study has been applied in the data reduction phase of this research project. The air quality data collected during the research project monitoring operations was input to the regression equations developed in this reqport. The use of these regression equations provided more accurate determinations of actual ambient air quality than the raw data alone.

In addition, the ozone monitoring system used was modified as a result of this study. The original monitoring system, as described in this report, was found to give rise to serious fluctuation in the response of the analytical instrument. A simplified system was substituted which corrected the problem.

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EXPERIMENT DESIGN

Because of the complexities involved in the study, Dr. Kenneth Kerri*, Professor of Civil Engineering at California State University, Sacramento, was engaged as a consultant to assist in the statistical design of the experiment on which the study was based. These data obtained in the experiment would be used to formulate empirical equations capable of predicting the changes (if any) in indicated concentrations of air pollutants from the point of sampling to actual readout of sample analyzed, given any specific set of values for the variables which we are considering. It was initially determined that a full Analysis of Variance (ANOVA) would provide the information desired, but would be unfeasible in view of the great amount of time and expense required to collect all the samples. Instead of the ANOVA, an abbreviated experimental design was developed by Dr. Kerri, based upon modified text book methods(1,2). These methods involved the randomized reduction of the replications that would have been required for a complete ANOVA.

*Dr. Kenneth Kerri is presently a consultant to the Transportation Laboratory through a State funded contract to assist Caltrans in the areas of statistical design and regression analysis applied to aerometric data.

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The air quality instruments considered in this experiment were as follows:

Pollutant Analyzed	Analytical Instrument	Principle of Instrument Operation
Carbon Monoxide (CO)	Beckman 315BL (3 instruments)	Non-Dispersive Infrared Spectroscopy (NDIR)
Ozone (O_3)	Rem 612	Chemiluminescent Method
Total Hydrocarbons, Methane, Carbon Monoxide (THC, CH_4, CO)	Beckman 6800	Gas Chromatography (FID)
Nitric Oxide, Nitrogen Dioxide, Oxides of Nitrogen (NO, NO_2, NO_x)	Bendix 8101B	Chemiluminescent Method
Sulfur dioxide, Hydrogen Sulfide (SO_2, H_2S)	Tracor 250-H	Gas Chromatography (Flame Photometry)

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The CO analyzers were the subject of the first stage in Dr. Kerri's experimental design. The variables in this design were voltage to the analyzer, van temperature, length of tubing, CO concentration at the sampling inlet, and flow rate of the gas sample through the CO analyzer. Due to the inherent stability of CO, it was the general consensus of the Caltrans engineers involved in this project that soiling of the inlet filters would not affect CO analysis results; consequently, this variable was not included in the CO experiment design. Given three different values for each of these 5 variables (i.e., 3 flow rates, 3 tubing lengths, etc.) and 3 different analyzers, a response surface of 3×3^5 or 729 possible data points exists. Using Hicks'(1) example of "One-third Replication of a 3^3 factorial", Dr. Kerri's design reduced the number of data points to 54 in a random selection process. The resulting design is shown in Appendix A. Using the same design, the experiments for the remaining analytical instruments were comprised of only 18 data points (Appendix A). The variables considered for these instruments were line voltage, length of tubing, filter (clean or dirty), pollutant gas concentration, and van temperature. Except for the condition of the filter, for which only 2 values were considered, 3 values were assigned to each variable. Separate tests were also planned for the effects of sample retention time in bags.

The ultimate goal of this experimental design was to develop an equation, based on the analysis of experimental data, taking the following form:

$$Y = b_o + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_5 x_5 \pm \text{a confidence interval}$$

where: Y = actual concentration of pollutant at sampling point

x_1 through x_5 = values of the variables considered (e.g. line length in feet, van temperature in °F, etc.)

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b_o = constant

$b_1, b_2 \ldots b_k$ = partial regression coefficients.

Interaction terms might also be added if deemed appropriate or significant. A different equation would be developed for each different analyzer.

From our initial 54 data points for the 3 CO analyzers and 18 data points for each of the remaining analyzers, multiple regression analysis techniques would be used to determine the significance of the experimental variables. If some significance was then apparent or if the number of data points appeared inadequate, the experimental design could be modified and/or expanded as necessary.

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DATA ACQUISITION

A. CO Analyzers

The first instruments for which data were acquired were the Beckman Model 315 BL NDIR CO analyzers (Figure 7). Using the 54 data point experimental design, variable values were obtained in the following manner:

1. Three lengths of tubing (sample intake lines) were selected from the available lines extending from the research van to various sampling points. During this phase of the study, the shortest inlet line was 175 feet (53.34 meters) in length, so this was selected as being representative of a "short" line length. In addition, 225 and 600 foot (68.58 and 182.88 meters) lengths were selected to represent "medium" and "long" lengths.

2. Three known CO concentrations were provided at the inlets of the sampling lines (probes) by connecting the inlets to different bottles of dry nitrogen - CO mixtures. The three CO concentrations were selected as being representative of low, moderate and high CO levels found within Southern California freeway right-of-ways. The CO concentrations in the 3 bottles used for this experiment were verified by the California Department of Health in Berkeley. The low, medium and high concentrations were 11.0, 33.0 and 62.5 ppm respectively.

3. Voltage to the analyzers was varied by use of a transformer (in parallel with a voltmeter) connected to the appropriate terminals in the circuit breaker box of the research van. Three voltage levels were chosen as being representative of the largest foreseeable voltage fluctuation range: 105, 110 and 120 volts.

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4. Sample flow rates through the CO analyzers were varied by the use of rotameters which are permanently mounted at the sample inlets of the 3 analyzers. Values of 0.5, 1.0 (the recommended flow rate for these analyzers) and 1.5 litres/minute (.0177, .0353 and .0530 cu ft/min) were used. The 0.5 and 1.5 litres/minute (0.0177 and .0530 cu ft/min) flows were considered the most extreme deviations from the recommended flow that could occur as a result of incorrect rotameter adjustment.

5. Van temperatures were regulated by use of the air conditioners. The small heater in the van was rarely needed because of the heat output from the electronic equipment within the van. The normal interior van temperature maintained during monitoring operations is about 75°F (24°C). Since the maximum expected temperature fluctuation in the van was ± 10°F (5.6°C), the three temperatures chosen for this test were 65°, 75° and 85°F (18°, 24° and 29°C). Van temperatures were held at the specified levels for approximately 2 hours prior to actual testing.

The 54 data points obtained in this procedure are detailed in Appendix B.

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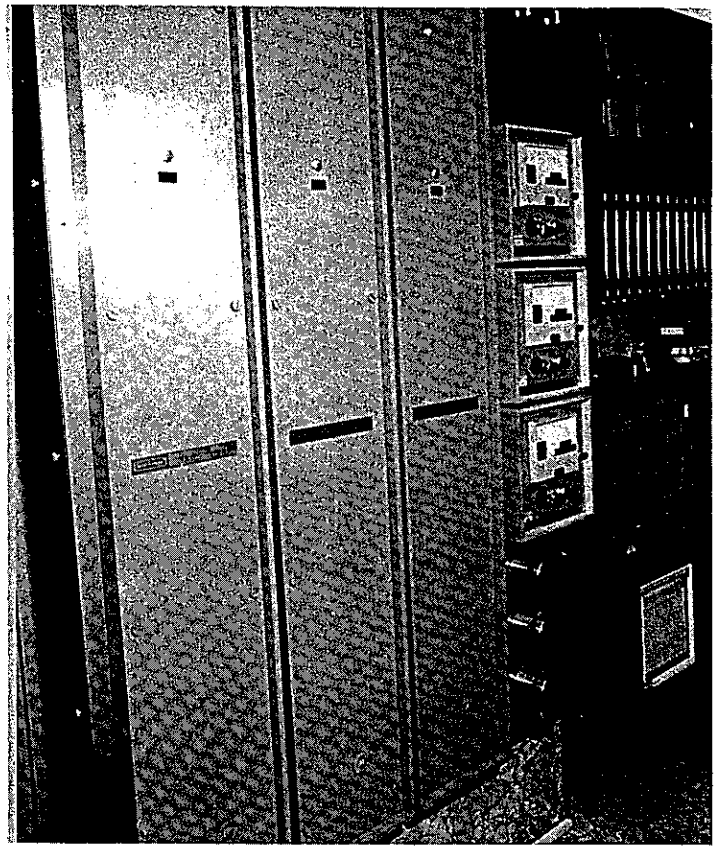

Figure 7. Beckman 315 BL NDIR analyzers. The three large boxes on the left are the sample and reference cell chambers, and the accompanying electronic units with meter readouts are immediately to the right of the chambers.

B. O_3 Monitor

The next instrument to be checked was the Rem 612 ozone analyzer, shown in Figure 8. The variable values for this instrument were obtained as follows:

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1. Three lengths of tubing were selected from among the available inlet lines: 150, 225 and 600 feet (45.7, 68.58 and 182.88 meters). By this stage of the experiment, a new 150 foot (45.7 m) inlet line had been added to the research van sampling train. The 150 foot (45.7 m) tubing was used in this test instead of the 175 foot (53.3 m) length that had been used during the CO analyzer experiment. This was done to provide a larger differential between the "short" and "medium" (225 foot (68.58 m)) lengths of tubing.

2. Voltage to the analyzer was varied by use of a transformer connected to a voltmeter and the analyzer power input. Voltages used were 110, 115 and 120 V. This voltage range differed from the one used during the CO analyzer checkout (105, 115 and 120 V) because it was feared that voltages much less than 110 V could possibly damage the Rem analyzer. In addition, the city line voltage was never observed to drop below 110 V when it was monitored during peak demand periods.

3. The condition of the inlet filters (substituted for the "flow rate" parameter used with the CO analyzer) was varied by using either new filters, defined as "clean", or heavily soiled "dirty" filters which had previously been in use for an entire 16-hour sampling day.

4. Van temperatures and method of temperature regulation were the same as those used in the CO analyzer study.

5. Ozone concentrations at the sampling line inlets were regulated by means of an ozone generation system operated by personnel from the California Department of Health. Ambient air was drawn through a series of scrubbers to remove all background ozone and oxides of nitrogen, and then through an ozone generator which could be adjusted to any ozone concentration over a range of values (Figure 9). The ozonized air stream was

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thoroughly mixed and then distributed through a multi-port manifold. One port led to the sampling line probe connected to the research van, and another was connected to a Dasibi ozone analyzer (Model 1003-AH) which was used to continually monitor the concentration of ozone in the airstream. Both the Dasibi and the Rem analyzers were calibrated by the Department of Health immediately prior to this test, using the Neutral Buffered Potassium Iodide California reference method. The three ozone concentrations used were approximately 11, 26 and 43 pphm (exact concentrations indicated in Appendix B). These particular ozone concentrations were selected as being representative of low, moderate and high concentrations generally found in this area.

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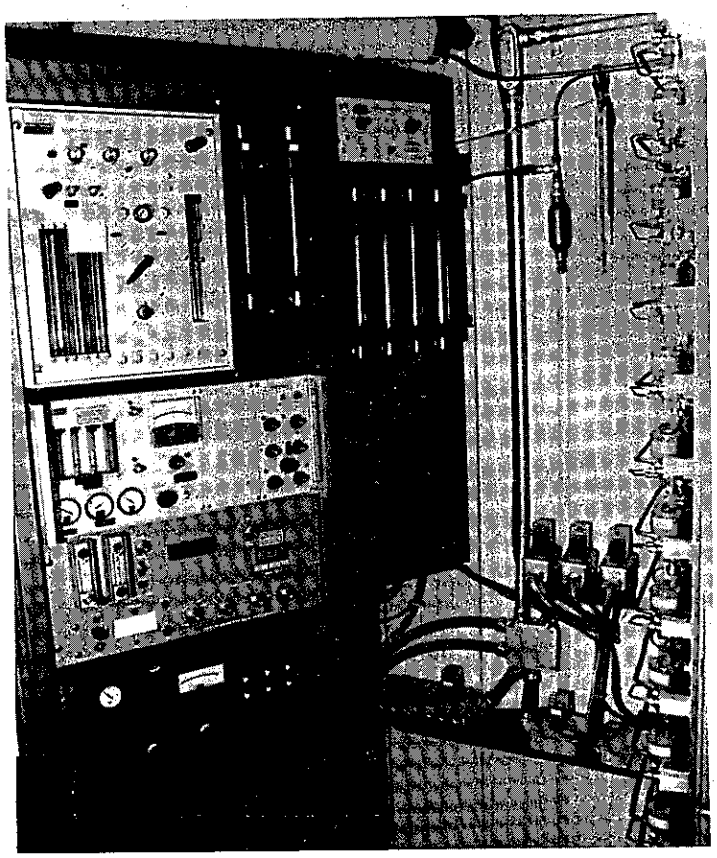

Figure 8. Shown from top to bottom are the Tracor SO_2 and H_2S permeation standard, the Tracor 250-H SO_2 and H_2S analyzer, the Rem 612 ozone analyzer and the Bendix 8101B $NO-NO_2-NO_x$ analyzer.

When air samples were being drawn in through the intake lines, the ozone concentrations indicated on the face of the Rem analyzer fluctuated continuously, sometimes over a relatively wide range, e.g. 1.2 to 6.4 pphm, with an actual input concentration of 10.5 pphm. Average readings were obtained by recording 25 to 35 values at 5 second intervals and then computing the arithmetic mean of the values. An example of readout variation is shown in Figure 10.

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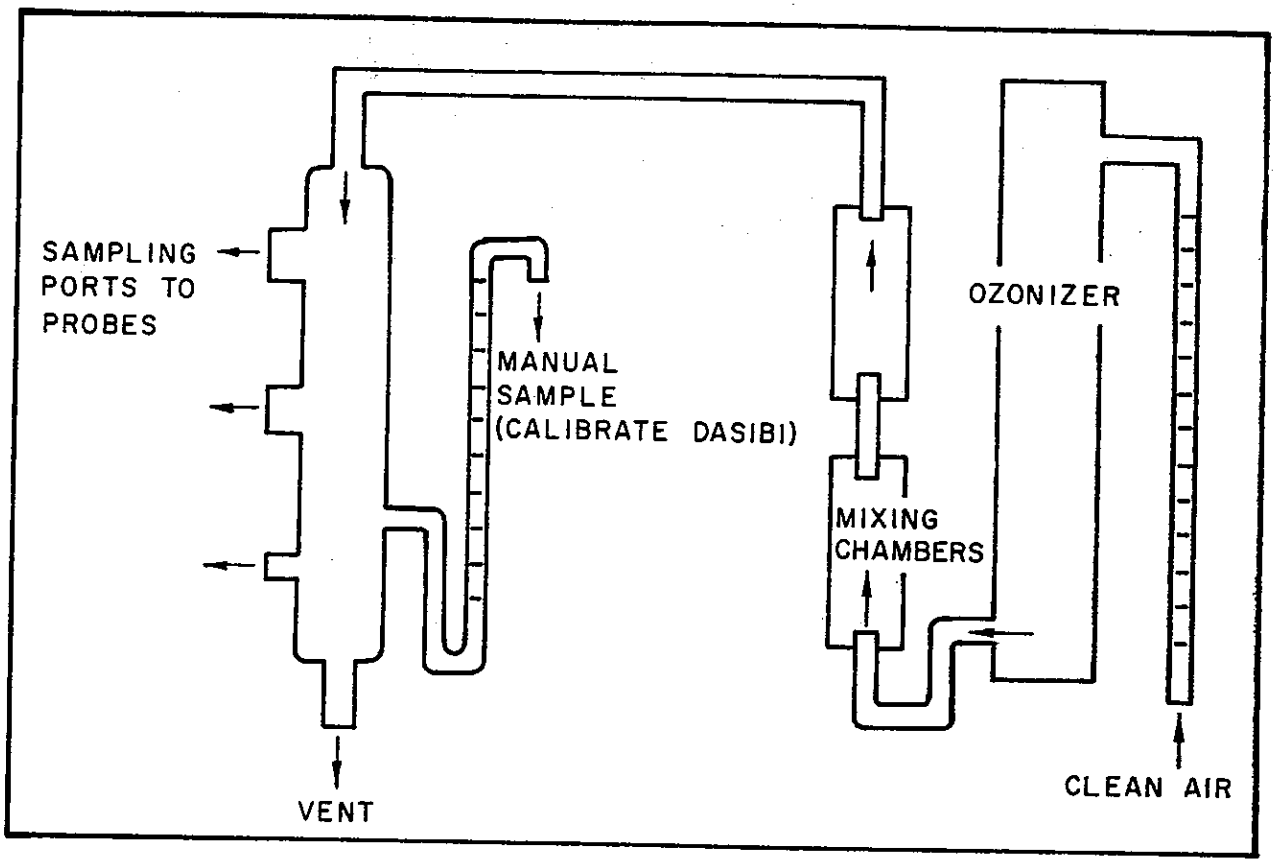
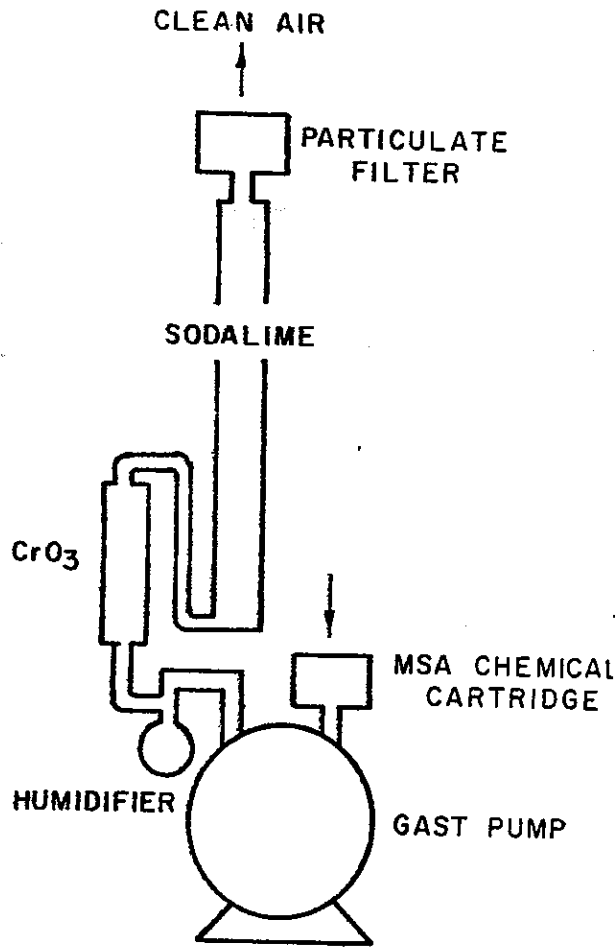
OZONE GAS GENERATION SYSTEM



DILUTION PANEL



CLEAN AIR GENERATION

Figure 9

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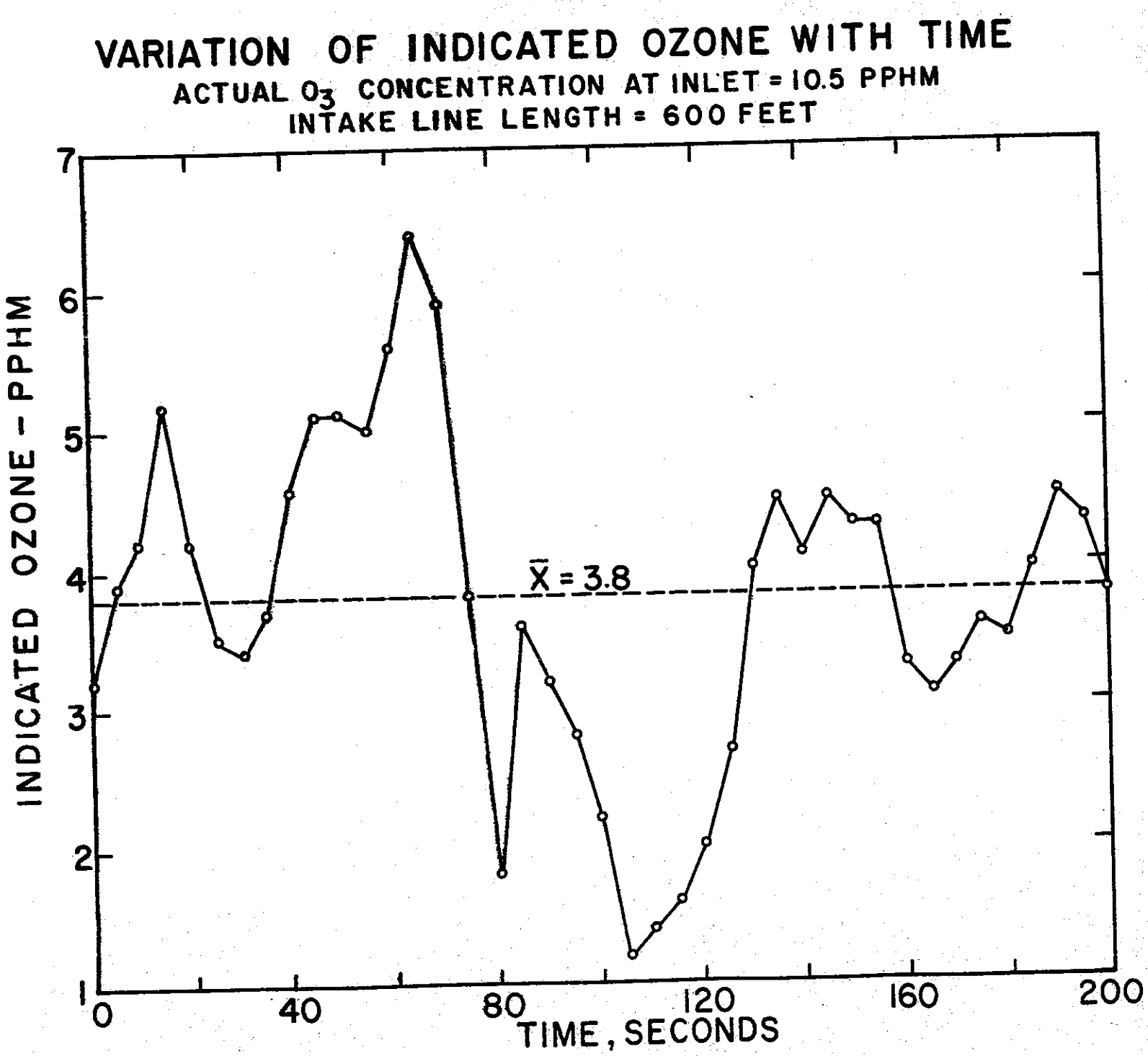

Figure 10

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After obtaining the 18 data points as described in the original experimental design, a cursory analysis of the data indicated that more data points would be required for a multiple regression analysis. When using this type of analysis, larger quantities of data significantly reduce the probability of erroneous results. Upon consultation with Dr. Kerri, it was decided to modify the original- experimental design with the addition of 18 more data points, for a total of 36. This design modification is described in Appendix A. The effects of bag storage on ozone concentrations as well as on the concentrations of other gases will be discussed later.

C. NO_x Analyzer

The Bendix model 8101 B NO_x analyzer (Figure 8) was tested in much the same way as the Rem O_3 analyzer. Except for the test gases fed through sample inlet lines, all parameters and their values were identical with those used in the Rem experiment. The NO_x stream was produced from bottled NO gas, diluted with scrubbed air from which all NO_x and O_3 had been removed (Figure 11). Using the previously mentioned ozone generator, ozone could be added to the diluted NO gas whenever a pre-determined concentation of NO_2 in the sample stream was desired. Following dilution with air and the addition of ozone, if needed, the NO_x stream was thoroughly mixed and then distributed through a multi-port manifold, as in the O_3 generation system. One port was directly connected to a Bendix NO_x analyzer which served as a monitor for the NO_x stream being produced, and another port was joined to the sample inlet probe connected to the research van. This latter NO_x analyzer and the one located in the van were calibrated by the Department of Health immediately prior to this test, utilizing the Saltzman California reference method.

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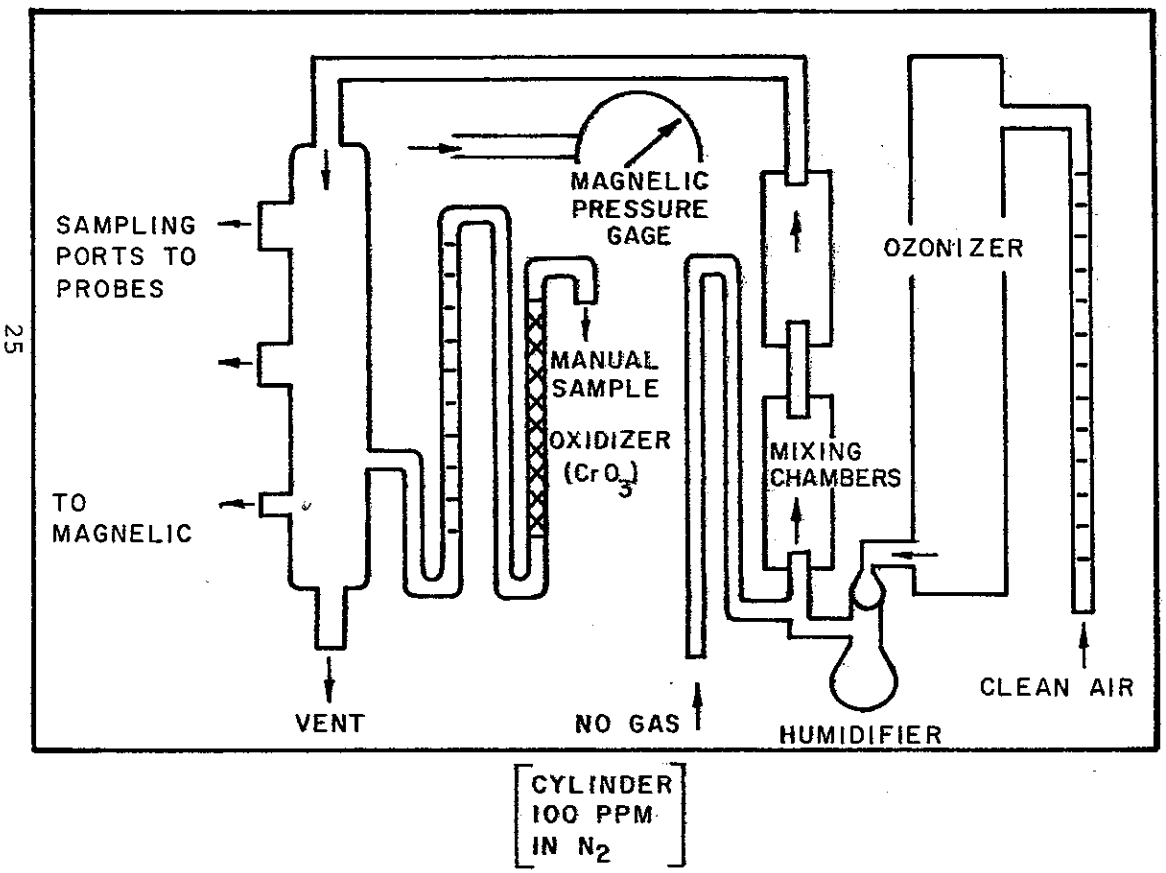
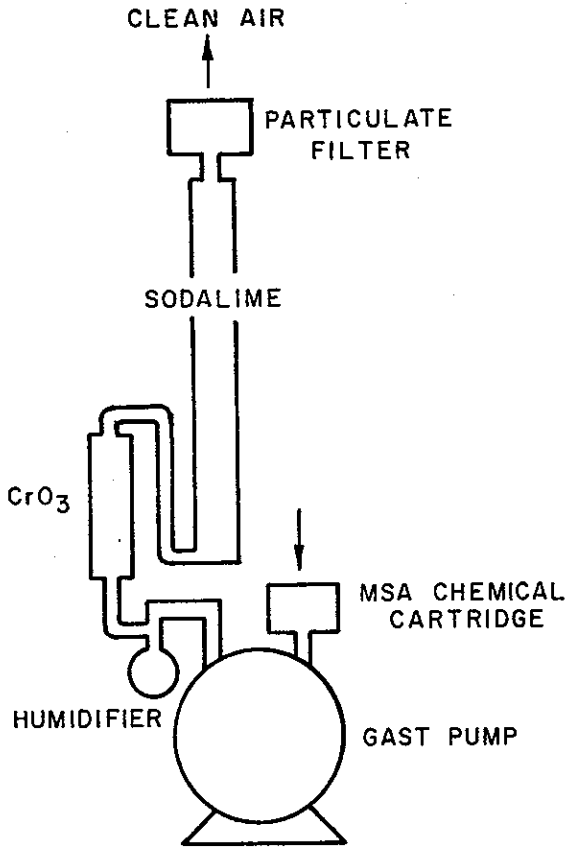
NO-NO_2 GAS GENERATION SYSTEM



DILUTION PANEL



CLEAN AIR GENERATION

Figure 11

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D. HC Analyzer

The Caltrans engineers concerned with this experiment felt that an abbreviated test procedure would be adequate for the checkout of the Beckman 6800 analyzer. The reason for this judgement is that the Beckman 6800 (Figure 12) is known to be stable under varying external conditions, and ambient hydrocarbons are relatively non-reactive over a short term in the absence of sunlight. The test parameters were limited to filter condition, gas concentration, and line length, with two values of each parameter (see Appendix B for actual design of experiment and test results). The two different gases used in the test contained known concentrations of methane, propane and carbon monoxide in synthetic air. The concentrations of each component in both gases were verified by the Department of Health. These concentrations were as follows (all figures in parts per million):

Concentration Classification	CO	Methane (CH_4)	Total Hydrocarbons (THC)
Low	33	4.7	10.1
High	40	12.0	43.7

The hydrocarbon concentrations in these 2 gas mixtures were chosen as representative of low and high ambient concentrations found in the test area. The gases were contained in two pressurized tanks which were connected directly to the sample inlet probes and probe filters. A total of 8 data points were collected in this test.

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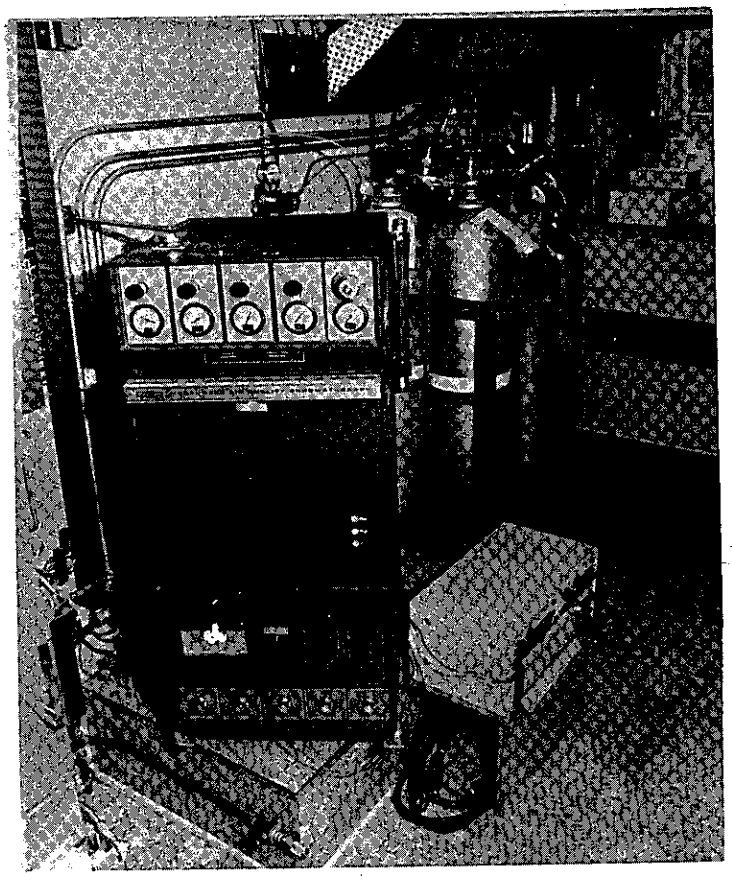

Figure 12. Beckman 6800 gas chromatograph for analyzing methane, total hydrocarbons and carbon monoxide.

E. Sulfur Analyzer

An abbreviated test also was used in the checkout of the Tracor Sulfur Analyzer (Figure 8), since the concentrations of sulfur compounds (SO_2 and H_2S, specifically) were expected to be minimal in the geographical areas to be sampled. Since highway-generated emissions of H_2S are negligible, this pollutant was not considered during the checkout of the Tracor analyzer. Consequently, only the analyzer response to SO_2 was investigated. The SO_2 test

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parameters were gas concentration, filter condition and line length. Gas concentrations were regulated by Department of Health personnel using a tank of compressed SO_2. Gas from the tank was diluted to the desired concentration with ambient air, thoroughly mixed, and fed into the sample inlet probes leading to the van (Figure 13). The SO_2 concentrations used in this experiment were approximately 0.1, 0.2 and 0.4 ppm, the latter figure approaching the California 1-hour health standard. The SO_2 stream was continually monitored at the source using the Conductimetric California reference method to ensure that the desired concentration was entering the inlet line. A total of 18 test points were collected.

F. Bag Sampling

Originally it had been planned that CO (as measured by the Beckman 6800), O_3, SO_2, hydrocarbons, and oxides of nitrogen concentrations would all be measured in air samples that had been temporarily stored in inert (teflon or Tedlar) bags, as mentioned previously. In current sampling operations, Ozone and SO_2 concentrations are being determined from air samples pulled through a single short line extending only a few feet outside the van. Air samples for CO analysis by the NDIR instruments are drawn through the sample inlet lines and pumped directly into the NDIR analyzers.

In view of the diminished likelihood that SO_2 and O_3 concentrations would ever be determined from bag samples, and because of the apparent stability of hydrocarbons, abbreviated tests were used for the checkout of instrument response to these bag stored gases. An abbreviated test also was selected for checking the effects of bag storage on the indicated concentration of $NO-NO_x$, since further research was already being planned in this area (see page 42 for more details regarding this research).

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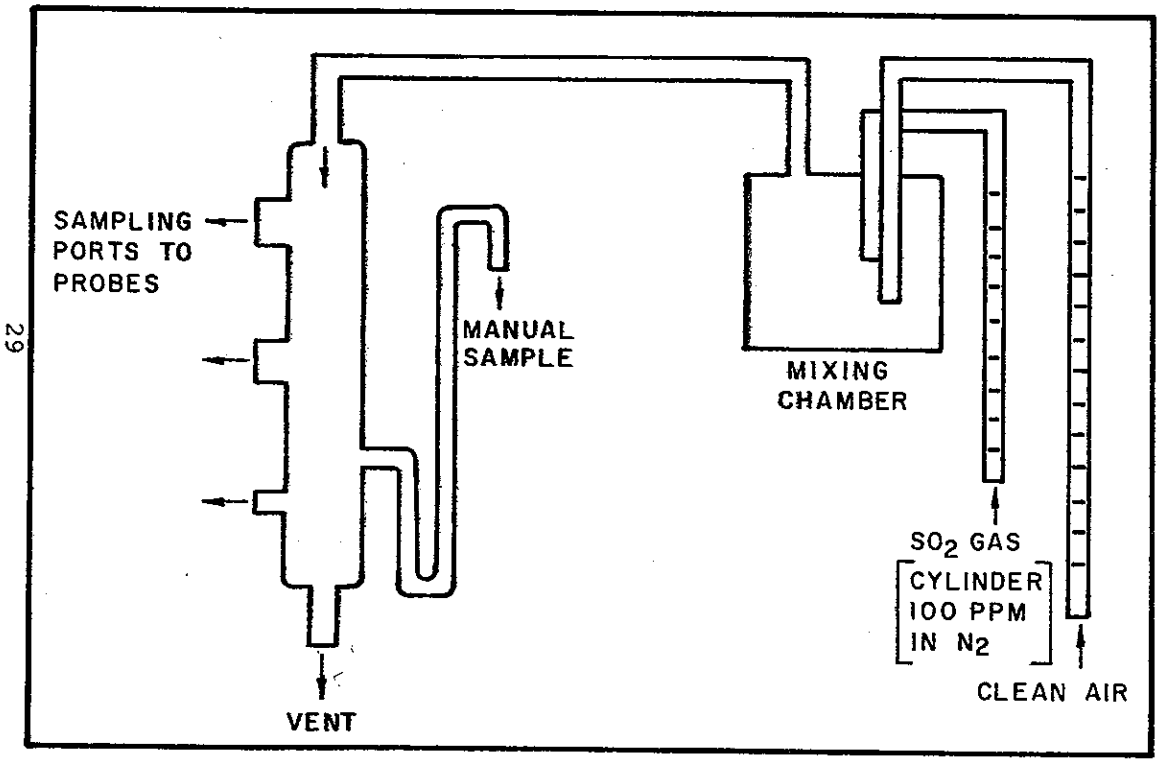
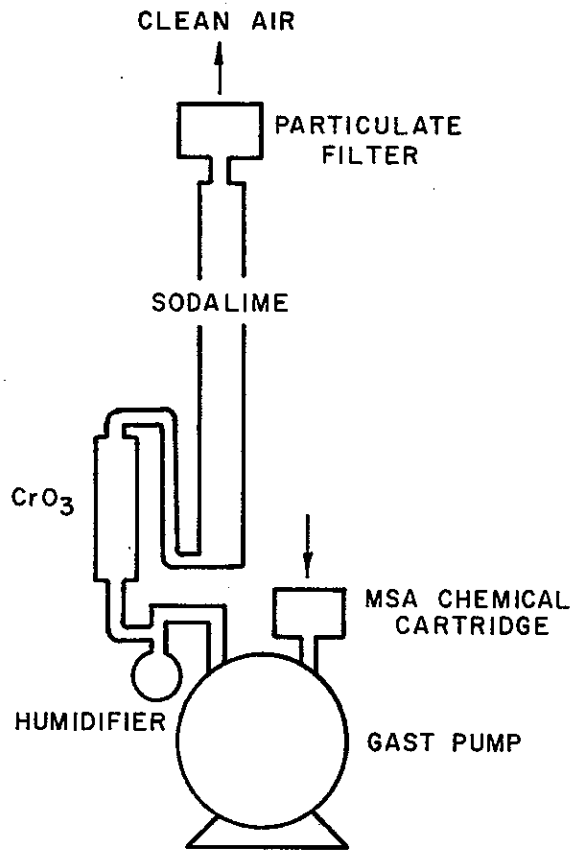
SULFUR DIOXIDE GAS GENERATION SYSTEM



DILUTION PANEL



CLEAN AIR GENERATION

Figure 13

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The parameters considered in these abbreviated tests were retention time in the bags and gas concentration. Three retention times (15, 30 and 60 minutes) were used for all of the tests, and three concentrations of all gases except hydrocarbons were used. Only two methane-propane-CO gas mixtures were used when checking the Beckman 6800 response. The experimental designs and test results are detailed in Appendix B.

Sampling Line Exposure

The exposure of the transparent teflon inlet lines to sunlight was another system variable with potential impact on O_3 samples. Ozone is known to breakdown rapidly in the absence of sunlight, but the significance of this reaction in the sampling train was not fully understood. Since most of the inlet lines were shielded from the sun, instrument response could conceivably be affected. The effects of this line exposure were investigated by sampling O_3 through a 150 foot (45.7 m) section of new teflon tubing. The O_3 was generated by Department of Health personnel using the system shown in Figure 9, and the O_3 concentration was measured at the opposite end of the tubing section with the Rem analyzer in the van. This test was conducted in both "dark" and "light" conditions, using three different O_3 concentrations under each condition. Darkness was simulated by coiling the tubing and placing it inside an opaque box during O_3 sampling. Sampling was then repeated with the tubing straightened out and completely exposed to the bright, warm, early afternoon sunlight. The results of this experiment are discussed in the following section and tabulated in Appendix B.

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ANALYSIS OF DATA

The principal method used in the analysis of the data obtained in these experiments was a stepwise multiple linear regression computer program entitled "STPREG"[3]. This program considered each variable individually and tested its significance in predicting a dependent variable (actual gas concentrations in this case). If any or all independent variables were significant in this regard they were automatically included in a regression equation describing the relationship of the dependent variables with the independent variable, similar to the equation form on page 14 . The significance of an independent variable was based upon the partial F-ratio computed for that variable as used in the regression equation. If this partial F-ratio did not exceed a pre-established level (e.g., 0.05), the computer automatically rejected that variable from the regression equation, considering it not significant. The partial F-ratio is not an absolute measure of significance in this example, but an indicator of significance. The pre-established partial F-ratio level for inclusion was set so low that only the most insignificant variables would be rejected outright by the computer. The final decision to include a variable in the regression equation was not made by the computer, but was based upon t-statistic of the variable and the overall F-ratio and multiple correlation coefficients of the regression equation which includes the respective variable. These statistical parameters were included in the STPREG printouts.

Detailed descriptions of these analytical procedures follow:

A. Beckman 315-BL CO Analyzers

Prior to running a STPREG program with all 54 items of data,

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a quick check was made to determine if there was a significant difference between the 3 analyzers tested. These data used for this check were the analyzer meter deflections (which approximate indicated CO levels) for an actual input CO concentration of 33.0 ppm. The first step was to compare the variances of the 3 analyzers, using Bartlett's Test(2, pp. 160-162).

This test is used in lieu of the F test whenever more than 2 variances are being compared. To test the null hypothesis that there is no significant difference between the variances of the 3 analyzers, the calculated and critical X^2 values were compared as shown below. These data were separated according to the actual CO concentrations input to the analyzers.

Concentration, ppm	x^2 calc.	x^2 critical (5% level of significance)
11	5.55	5.99
33	8.66	"
62.5	4.43	"

Since x^2 calc. > x^2 crit. at the 33 ppm concentration, the null hypothesis was rejected and it was assumed that the variances between analyzers were different. This nonhomogeneity was most likely due to a "noisy" analyzer, which still furnished accurate readings.

The t-test could not be used to compare the data means from each analyzer because a condition for this test is that all analyzer variances be the same. As an alternative, a test was used in which the ratio of the standard deviations of two sample means,

$$\frac{S_{\bar{x}_1}}{S_{\bar{x}_2}} = \text{Tan } \Theta$$

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is considered in determining the significance of the difference of the means(2, pp. 150-152). The difference $\bar{x}_1 - \bar{x}_2$ is considered significant if

$$\frac{\bar{x}_1 - \bar{x}_2}{S^2_{\bar{x}_1} - S^2_{\bar{x}_2}} \geq d_{crit.},$$

where $d_{crit.}$ is based upon Θ, upon the level of significance, and upon the number of degrees of freedom. The null hypothesis for this test was that there was no significant difference between the data means of any 2 analyzers, given the same initial CO concentration. The results of this test are shown below:

Analyzers Compared	CO Conc.	$d_{calc.}$	$d_{crit.}$ (@5% level of sig.)
1-2	11	.52	2.44
1-2	33	.30	"
1-2	62.5	.97	"
1-3	11	1.49	"
1-3	33	1.04	"
1-3	62.5	.69	"
2-3	11	1.43	"
2-3	33	.68	"
2-3	62.5	1.71	"

Since $d_{calc.} < d_{crit.}$ for all cases, it was assumed that there was no significant difference between the data means from the different analyzers, thus accepting the null hypothesis. As a consequence, all the data could be lumped together for STPREG analysis.

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The output from the STPREG program is tabulated below:

Variable	t value	$t_{crit.}$ (=.05)	r	F	Sy
Meter Deflection	154	2.0	.9989	23840	.977
Temperature	-5.33	"	.9993	18219	.790
Voltage	1.79	"	.9993	12671	.773
Flow Rate	-1.46	"	.9994	9721	.765
Line Length	- .88	"	.9994	7740	.767

The values for the above variables comprised the input to the STPREG program; these variables are listed in the order in which they entered the regression equation. Each t value is indicative of the significance of the respective variable at the time it entered the regression equation. Since only the t values for the meter deflection and temperature variables are greater than the critical t value, these are the only significant regression coefficients at the 5% level.

The value "r" represents the correlation coefficient between actual CO values and the estimated values calculated by the regression equation. The correlation coefficients shown are cumulative, meaning that they are applicable to the regression equation which includes the corresponding variable plus all preceeding variables listed. These coefficients are all highly significant ($r_{crit.} \approx 0.4$ @ the 5% level of significance), and increase only slightly after the meter deflection variable has been introduced to the regression equation.

The F ratios shown are also cumulative and are all well in excess of the critical F value of 24 at the 5% level of significance.

The high F values indicate that the regression equations incorporating these variables are highly significant in terms of estimating actual CO values.

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Sy, the standard error of the estimate, is also a cumulative parameter. The smaller the Sy parameter is, the more accurate is the regression equation in estimating the actual CO concentration. There is very little change in Sy after the introduction of the temperature variable.

Based primarily upon the significance of their calculated t values, meter deflection and temperature were judged to be the only statistically significant variables as used in the regression equation. The regression equation which includes these variables, as calculated by the STPREG program is the following:

$$CO(ppm) = 4.30 - .070(Temp.\ °F) + .937(\%\ Meter\ Deflec.) \pm 1.58\ ppm$$

The confidence interval at the end of the equation equals $\pm$ 2 Sy, where Sy = .790.

Although statistically significant, the temperature variable actually has only a small effect on the regression equation. This is illustrated by the relatively small increase in the correlation coefficient of the equation when this variable is introduced. In addition, the interior temperature of the van in the field has been consistently maintained at 75°F $\pm$ 5° (24°C $\pm$ 2.7°) during its many months of operation since this study was conducted. Consequently, any temperature effect on the CO analyzer performance would be minimal, and could generally be ignored. The exclusion of this variable leaves only the NDIR instrument output value as the basis for determining the actual CO value.

The Beckman-supplied calibration curves indicate that the relationship between NDIR instrument response and actual CO values is slightly curvilinear. Since STPREG only calculates

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linear regression equation coefficients, and only one input variable was very significant in determining actual CO concentrations (instrument response), a polynomial equation would more accurately describe the relationship between that variable and actual CO concentrations. A computer program entitled "POLFIT"[3] was used to determine this polynomial equation, based upon data collected in a second experiment.

In the second experiment, 5 different CO concentrations were used, all of them verified by the California Department of Health. These concentrations were 0, 11.0, 33.0, 62.5 and 82.5 ppm, the first value being used to zero the instrument, and the latter ones to set the instrument span. Since the data acquisition system in the research van receives signals from the CO analyzers in the form of output voltage, these voltage values were used as measures of instrument response rather than meter deflection, the two not always being precisely equal. The system variables which had earlier been found to have no significant effect on instrument response (voltage, line length and flow rate) were held constant. The van interior temperature was maintained at 75°F (24°C). The response of all three analyzers to each of the gases was recorded, and the resulting data were input to the POLFIT program.

By use of the least squares method, POLFIT is capable of fitting the data to a polynominal equation of any degree up to n-1, where n is the number of data points. Equations of several different degrees were computed for each of the three CO analyzers and the polynominals selected as being the most representative of the CO concentration and voltage output relationship were those of the third degree.

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The equations selected are as follows:

CO Analyzers	CO vs. Analyzer Voltage Output*
#1	$CO\ (ppm) = .06+20.38V+.01V^2-.05V^3 \pm .38$ ppm
#2	$CO\ (ppm) = .02+19.36V+.31V^2-.08V^3 \pm .14$ ppm
#3	$CO\ (ppm) = -.05+18.82V+.81V^2-16V^3 \pm .32$ ppm

The choice of the most representative equation was based upon the standard error and F-ratio parameters, listed below.

CO Analyzer	Degree	Standard Error	F-Ratio**
1	1	.71	9593
	2	.21	56453
	3	.19	42664
2	1	.55	15636
	2	.27	32630
	3	.07	501505
3	1	.60	13033
	2	.51	9194
	3	.16	63505

*The confidence intervals used in these equations are actually ± 2 times the standard.

**These F ratios are all well in excell of $F_{crit.}$ at the 5% level of significance ($F_{crit.} \approx 6.4$). This means that all of these equations are highly significant models of actual CO concentrations, based upon voltage output.

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A check was made to ascertain whether the maxima, minima and inflection points of the 3rd order equations were above or below the 0-5V range. This range is the entire span of the CO analyzer output. The maxima and minima points of the three selected equations were determined by setting the first derivatives of these equations equal to zero and solving for V. The inflection points were determined by setting the second derivative equal to zero and solving for V. The following table shows that all these points are indeed outside the 0-5V range:

Analyzer	Equation Maximum	Equation Minimum	Equation Inflection Point
1	11.8 V	-11.6 V	-0.07 V
2	10.8 V	-8.2 V	-1.3 V
3	8.2 V	-4.8 V	-1.7 V

In conclusion, the third order equations developed for each analyzer by the POLFIT program were found to be the best equations for estimating actual CO concentrations, assuming that the van interior temperature remains at approximately 75°F (24°C).

B. Rem 612 Ozone Analyzer

1. Inlet Line System

The original experimental design for the ozone analyzer test provided 18 data points. These data were input to the STPREG program and the output is summarized below:

Variables	t value (18 data points)	$t_{crit.}$ (=.05)	r	F	Sy
Indicated Ozone	13.3	2.11	.9578	178	3.99
Line Length	.87		.9599	87.9	4.02
Voltage	.49		.9606	55.7	4.13
Temperature	.20		.9607	38.9	4.28
Filter Condition	F-Level too low for computation		-	-	-

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These variables are listed in the order in which they entered the regression equation. Since only the t value for the indicated ozone variable is greater than $t_{crit.}$, indicated ozone is the sole variable used in the regression equation which is significant at the 5% level. The correlation coefficient r is significant for the indicated ozone variable ($r_{crit.} \approx 0.6$ @the 5% level) and changes only very slightly as additional variables are introduced to the regression equation. This latter characteristic stresses the insignificance of these additional variables in estimating actual ozone concentration. The F ratios, in the above table are all in excess of the critical F value of 3.1, meaning that the equations containing the respective variables are significant in terms of estimating actual O_3 values, although all these equations contain the indicated ozone variable as well as the additional variable(s) entered. The values of Sy are shown to increase as variables other than indicated ozone enter the regression equation, indicating further that nothing is really gained by the inclusion of these other variables.

At this point it was decided that 18 additional data points would give a better understanding of the factors involved in fluctuations of the readout on the Rem instrument, mentioned earlier. It was still felt that variables such as filter condition or line length might still be determined significant, given more data for analysis. STPREG analysis of the combined 36 data points is summarized in the following table.

Variable	t value (36 data points)	$t_{crit.}$ (=.05)	r	F	Sy
Indicated Ozone	8.77	2.03	.8329	77	7.44
Line Length	1.38		.8489	43	7.22
Filter Condition	-.84		.8524	28	7.25
Temperature	-.32		.8529	21	7.36
Voltage	-.17		.8531	16	7.47

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Once again, indicated ozone is the only variable of significance in the regression equation at the 5% level. But more important the values of r and F decreased and the values of Sy increased in comparison with the output from the 18 data point STPREG analysis. What this means is that the regression equation based upon the 36 data points cannot estimate actual ozone concentrations as accurately as the original 18 data point regression equation could.

The reason for this decrease in accuracy was that ozone readings on the face of the Rem analyzer were markedly more erratic and the fluctuations larger than when the first 18 data points were collected. The same averaging method was used as before to arrive at a single indicated O_3 value to compare against the actual O_3 concentration entering the intake line. There was no malfunction or loss of calibration by the Rem instrument, as verified by Department of Health personnel who checked the analyzer out completely before each set of data was collected. It was theorized that, during routine sampling, certain gases or aerosols in the sampling stream had been adsorbed on the inner walls of the sampling lines, and that these adsorbates were somehow capable of affecting ozone concentrations within the lines. Ambient air from above and adjacent to the Santa Monica Freeway had been sampled through these lines for a cumulative time span of approximately 800 hours between ozone data set collections. This latter factor may explain the greater readout fluctuations when the second data set was being collected.

In order to verify the theory that the used intake line was affecting the ozone concentrations, a 150 foot (45.7 m) length of new teflon tubing was temporarily substituted for one of the older lines, and known ozone concentrations were pumped through the tubing to the Rem Analyzer at the standard flow rate of 10 litres/minute (.35 cu.ft./min.). This test

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was performed with the tubing exposed to sunlight and then repeated with the tubing in total darkness. The O_3 readings on the Rem Analyzer were very steady and the indicated values were quite close to the actual O_3 concentrations provided (see Appendix B). It also was apparent that a relatively short darkness residence time (approximately 20 seconds) did not decrease O_3 concentration significantly; in fact, concentrations appeared to increase very slightly in the dark condition, but this could be attributed to normal instrument error.

2. O_3 Bag Storage

As would be expected, the ozone concentration in air samples stored in teflon bags deteriorated significantly with time. The decay rates appeared to be approximately 10-20% for 15 minutes, 33% for 30 minutes and 50% for 60 minutes. Since only a limited amount of ozone bag storage data were collected, a regression analysis of this data was not feasible. Nevertheless, it is quite apparent that ozone breaks down rapidly when stored for even short periods of time in relatively inert materials.

In summary, it appears that ambient ozone concentrations cannot be accurately determined by sampling through the long inlet line and bagbox system. Not only does ozone appear to treak down rapidly in bag storage, but ozone readings on the Rem analyzer fluctuate excessively when samples are drawn through the inlet lines. This fluctuation characteristic apparently becomes more pronounced the longer the inlet lines are in service.

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C. Bendix 8101B NO - NO_x Analyzer

1. Inlet Line System

The 36 test point experimental design that was used for the REM O_3 Analyzer also was used for the Bendix instrument. The data were input to the STPREG PROGRAM, with NO, NO_2 and NO_x each being considered separately for purposes of regression analysis. A summary of the STPREG output is shown below.

Gas	Variable	t value	$t_{crit.}$ (=.05)	r	F	Sy
NO	Indicated NO	56.5	2.03	.9947	3198	.097
	Filter Condition	1.8		.9952	1714	.094
	Line Length	- 0.6		.9953	1120	.095
	Temperature	0.2		.9953	816	.096
	Voltage	F level too low for computation		-	-	-
NO_2	Indicated NO_2	40.0	2.03	.9895	1602	.084
	Filter Condition	1.9		.9906	863	.081
	Temperature	1.4		.9911	594	.080
	Voltage	0.4		.9912	434	.081
	Line Length	0.3		.9912	338	.082
NO_x	Indicated NO_x	51.1	2.03	.9936	2613	.099
	Filter Condition	1.1		.9938	1311	.099
	Voltage	0.4		.9938	853	.100
	Length	0.4		.9938	623	.101

The only t values which exceed $t_{crit.}$ are those for the indicated NO, NO_2 and NO_x variables. Consequently, these are the only significant variables in the regression equations which estimate the actual concentrations of NO, NO_2, and NO_x. This is reinforced by the fact that r does not increase measurably after the indicated NO, NO_2 or NO_x variable has been introduced; similarly, there is little change in Sy after the introduction of the indicated NO, NO_2, or NO_x variable to the respective regression equations.

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Since only the indicated gas concentrations were significant, an additional computer program was utilized to determine whether the y-intercept and slope of the regression line were significantly different from 0 and 1 respectively. This computer program, developed by Frazier[3], is a linear regression program entitled LINREG. The output from LINREG is summarized below.

NO Regression Equation: $y = -.03+1.11x \pm .20$*, where y is actual NO concentration (ppm) and x is the indicated NO concentration.

	95% Confidence Limits	
y-intercept:	-.08 ,	.02
Slope:	1.07 ,	1.15

NO_2 Regression Equation : $y = -.09+1.12x \pm .20$*, where y is the actual NO_2 concentration (ppm) and x is the indicated NO_2 concentration.

	95% Confidence Limits	
y-intercept:	-.15 ,	-.04
Slope:	1.06 ,	1.18

NO_x Regression Equation: $y = -.03+1.11x \pm .18$ppm*, where y is the actual NO_x concentration (ppm) and x is the indicated NO_x concentration.

	95% Confidence Limits	
y-intercept:	-.08 ,	.02
Slope:	1.07 ,	1.15

*The confidence intervals included after each regression equation are plus or minus 2 times the standard error of the mean.

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Since the 95% confidence limits for the slopes of these regression equations do not fall on either side of 1.0, the slopes of these equations are significantly different from unity. The 95% confidence limits for the y-intercepts of the NO and NO_x regression equations do encompass zero, so the intercept terms may be dropped from these two equations. The net results is as follows:

1. NO(ppm) = 1.11(Indicated NO, ppm) $\pm$ .20 ppm
2. NO_2(ppm) = -.09 ppm + 1.12 (Indicated NO_2,ppm) $\pm$ .20 ppm
3. NO_x(ppm) = 1.11 (Indicated NO_x, ppm) $\pm$ .18 ppm

2. NO_x Bag Storage

The effects of storage time in teflon bags on synthesized NO_x concentrations (i.e., interference-free gases) proved to be minimal. Use of the STPREG program showed that the only significant variable for estimating actual ambient concentrations was the indicated NO, NO_2, or NO_x concentration. At this point the LINREG program was used to determine whether the y-intercept and slope of the regression equation were significantly different from 0 and 1 respectively. The output from this analysis is summarized below:

NO Regression Equation (Bagbox): $y = -.005+1.04x \pm .12$ppm*, where y is the actual NO Concentration (ppm), and x is the indicated NO concentration.

	95% Confidence Limits		
y-intercept:	-.08	,	.09
Slope:	.98	,	1.09

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NO_2 Regression Equation (Bagbox): $y = -.005+1.02x \pm .08$ppm*, where y is the actual NO_2 concentration (ppm) and x is the indicated NO_2 concentration.

	95% Confidence Limits		
y-intercept:	-.06	,	.05
Slope:	.96	,	1.07

NO_x Regression Equation (Bagbox): $y = -.01+.99x \pm .07$ppm*, where y is the actual NO_x concentration (ppm) and x is the indicated NO_x concentration.

	95% Confidence Limits		
y-intercept:	-.04	,	.06
Slope:	.96	,	1.03

Since the 95% confidence limits for the y-intercepts and slopes of these regression equations lie on either side of 0 and 1 respectively, it can be assumed that they are not significantly different from 0 and 1, and the regression equations are superfluous. It can also be assumed that the indicated gas concenxrations are not different from the actual gas concentrations which entered the bags. When the entire sampling line-bagbox system is utilized, only the three numbered regression equations on the previous page need be utilized to estimate actual NO, NO_2 and NO_x concentrations, given the indicated concentrations.

*The confidence intervals included after each regression equation are plus or minus 2 times the standard error of the mean.

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The NO gas used as a sample source during this testing program was partially oxidized with O_3 to form NO_2. Some effects of continued oxidation of NO in the sample inlet lines were noted in these data. This brought up the possibility of NO oxidation in the intake lines during routine sampling, due to ambient ozone. The performance analysis of the Bendix instrument was generally conducted under ideal conditions, with all interfering gases removed from the sample stream. It was decided that a complete analysis must also include realistic conditions, such as sampling the ambient air "soup", or mixture of normal atmospheric gases plus pollutants.

Research has been initiated to study the interactive effects of ambient ozone and nitric oxide within the sampling system. The goal of this study is to be able to predict the change in the ambient NO/NO_2 ratio from the time it enters the intake line until it reaches the analyzer inside the research van. This ratio change would prospectively be a function of ambient ozone concentration, line length, retention time in the bagbox and/or other possible parameters.

The testing procedure for this particular study involves measuring NO, NO_2, NO_x and O_3 concentrations in the ambient air adjacent to inlets of the research van sampling lines. These ambient concentrations are then correlated with the NO, NO_2 and NO_x values indicated by the Bendix 8101B $NO-NO_x$ analyzer.

These data collected thus far indicate that relatively little NO is oxidized to NO_2 within the sampling train, although these data are admittedly limited. During the course of this study, ambient ozone levels ranged from zero to .06 ppm. Oxides of nitrogen concentrations were at a maximum (0.2-0.4 ppm) in the early morning when no ambient ozone could be

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detected, but $NO-NO_x$ levels were approaching the minimum detectable (.02-.04 ppm) by the time O_3 concentrations peaked in the afternoon. There were no significant changes in NO, NO_2 or NO_x concentrations in ambient air samples which were stored in the bagbox for periods of up to 16 hours.

D. Beckman 6800 Gas Chromatograph

1. Inlet Line System

The response of the Beckman Analyzer to the variables considered was as expected - indicated CO and hydrocarbon concentrations (as indicated by output voltage) were nearly indentical to actual concentrations in all respects. The STPREG program was not utilized since there was so little fluctuation in gas concentrations through the system that it was obvious by inspection of these data that neither filter condition nor line length had any significant effect. The largest fluctuations noted were with total hydrocarbons, but at no time did the indicated THC concentrations deviate from the actual by more than 7%. Even this deviation was quite possibly due to instrument error. For all practical purposes, the gas concentrations indicated by the Beckman 6800 analyzer could be considered as identical to the actual concentrations entering the intake line.

2. HC Bag Storage

There was no discernable decay in either CO or hydrocarbon concentrations after air samples had been stored in the bagbox for periods of up to 60 minutes. The maximum indicated reduction in the concentration of a stored gas was less than 5%, which could be explained by instrument error. Since any concentration changes during storage appeared negligible by inspection, the STPREG program was not used to analyze these test data.

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E. Tracor 250-H Sulfur Analyzer

1. Inlet Line System

Data from the Tracor experiment were input to the STPREG program and the output is summarized below:

Variable	t value	$t_{crit.}$ (=0.5)	r	F	Sy
Indicated SO_2	21.2	2.11	.983	449	.023
Line Length	3.7		.991	413	.017
Filter Condition	F level too low for computation		-	-	-

The t values for both the indicated SO_2 and line length variables are greater than $t_{crit.}$, verifying that these two variables are significant at the 5% level as used in the regression equation. Filter condition is insignificant. The regression equation which includes the significant variables is as follows:

$$\text{Actual } SO_2(\text{ppm}) = 1.32\ [\text{Indicated } SO_2(\text{ppm})] + .00008\ [\text{Line Length (ft.)}] \pm .03\text{ppm}^*$$

2. SO_2 Bag Storage

The highly abbreviated test of SO_2 decay in teflon bags indicated very little decrease in SO_2 concentration even when samples were stored in the bags for 60 minutes (Appendix B). There were far too few test points to perform an adequate statistical analysis of these data, but it appears that the decay of SO_2 (in interference-free air samples) is negligible when samples are stored in teflon bags.

*The confidence interval used in this equation is ± 2 times the standard error of the mean.

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V. SUMMARY

The following sampling variables were determined through regression analysis to be significant in estimating actual ambient pollutant concentrations:

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VARIABLES IN THE REGRESSION ANALYSIS SIGNIFICANT IN ESTIMATING ACTUAL POLLUTANT CONCENTRATION

ANALYZER TYPE	INTAKE LINE SYSTEM	BAG STORAGE SYSTEM
Beckman 315-BL-carbon monoxide	Output voltage, van temperature[1]	--
Rem 612 - Ozone	Indicated Concentration[2]	Indicated concentration, retention time in bags.
Beckman 6800 - Total Hydrocarbons, Methane, CO	Indicated concentration (Proportional to output voltage)	Indicated concentration (proportional to output voltage).
Bendix 8101B-NO, NO_2, NO_x	Indicated concentration, satisfactory	Indicated concentration
Tracor 250H- SO_2	Indicated concentration, intake line length	Indicated concentration[3]

1. Temperature can be ignored as a factor if analyzers are exposed to a relatively constant temperature level (i.e., 75°F ± 5°) (24°C ± 2.7°).
2. Indicated concentrations of O_3 fluctuated excessively during sampling through the intake line system, a feature which makes this system unreliable for O_3 sampling.
3. Conclusion based on limited test data.

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The NDIR carbon monoxide analyzers function well within the sampling system, provided internal research van temperatures are maintained at a fairly constant level (75°F ± 5°) (24°C ± 2.7°). The output, in voltage form, must be used in a polynominal expression to estimate the actual CO concentration. The actual concentration is estimated with a high degree of accuracy by this expression.

Based on independent studies of O_3 decay in the intake lines and the bagbox, it was determined that ozone could not be routinely sampled through the long intake line system or the bagbox due to excessive fluctuations in the indicated concentrations. In actual practice, ozone was sampled through a very short (15 feet) (4.6 m) inlet line and pumped directly into the analyzer. This method eliminated fluctuation problems.

Using interference-free test gases, the indicated NO, NO_2 and NO_x concentrations were used as the independent variables in regression equations which provide very good estimates of actual concentrations.

The output from the Beckman 6800 analyzer (indicated concentration) for CO and HC was not significantly different from the actual gas concentrations input to the system, and these data could be used without modification.

Although there is evidence of considerable decay of SO_2 through the intake lines, the regression equation developed for SO_2 is capable of estimating actual concentrations from the indicated values. No decay of SO_2 in the bagbox was apparent in these very limited data collected.

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REFERENCES

1. Hicks, C. R., Fundamental Concepts in the Design of Experiments, Holt, Rinehart & Winston, Inc., N.Y., 1964.

2. Neville, A. M., and Kennedy, J. B., Basic Statistical Methods for Engineers and Scientists, International Textbook Co., Scranton, Pa., 1964.

3. Program written by Charles A. Frazier of the Transportation Laboratory, California Department of Transportation.

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APPENDIX A

EXPERIMENT DESIGNS

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1. Experimental Design for CO Analyzers

Treatment No.	Temp., °F*	Voltage	CO Conc. ppm	Flow Rate** litres/min.	Line Length** ft.
1	65	120	11	1.0	600
2	75	110	11	1.4	175
3	85	105	11	0.5	225
4	65	120	33	0.5	175
5	75	110	33	1.0	225
6	85	105	33	1.4	600
7	65	120	62.5	1.4	225
8	75	110	62.5	0.5	600
9	85	105	62.5	1.0	175
10	65	120	11	0.5	225
11	75	105	11	1.0	600
12	85	120	11	1.4	175
13	65	120	33	1.0	225
14	75	105	33	0.5	175
15	85	110	33	1.4	600
16	65	120	62.5	1.0	175
17	75	105	62.5	1.4	225
18	85	110	62.5	0.5	600

* °C = (°F -32) x 5/9

** cu.ft./min = litres/min x 0.03532

*** m = ft x 0.30480

Repeat above treatments for each of 3 analyzers for a total of 54 data points.

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2. Experimental Design for Analyzers Other than CO (Initial 18 Points)

Treatment No.	Temp., °F*	Voltage	Gas Conc.	Filter Cond.	Line Length** Ft.
1	65	120	med.	clean	600
2	75	115	high	dirty	150
3	85	110	low	clean	225
4	65	120	low	dirty	150
5	75	115	med.	clean	225
6	85	110	high	dirty	600
7	65	120	high	clean	225
8	75	115	low	dirty	600
10	65	120	low	dirty	225
11	75	110	med.	clean	600
12	85	115	high	dirty	150
13	65	120	med.	clean	225
14	75	110	low	dirty	150
15	85	115	high	clean	600
16	65	120	med.	dirty	150
17	75	110	high	clean	225
18	85	115	low	dirty	600

*°C = (°F -32) x 5/9

** m = ft. x 0.30480

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3. Modified Experimental Design for Analyzers Other than CO (Additional 18 Points)

Treatment No.	Temp., °F*	Voltage	Gas Conc.	Filter Cond.	Line Length** Ft.
19	85	120	low	dirty	150
20	65	115	low	clean	225
21	75	110	low	clean	600
22	65	120	med.	clean	150
23	75	115	med.	dirty	225
24	85	110	med.	dirty	600
25	75	120	high	clean	150
26	85	115	high	clean	225
27	65	110	high	dirty	600
28	75	120	low	clean	150
29	85	110	low	dirty	225
30	65	115	low	dirty	600
31	75	120	med.	dirty	150
32	65	110	med.	clean	225
33	85	115	med.	clean	600
34	65	120	high	dirty	150
35	75	110	high	dirty	225
36	85	120	high	clean	600

*°C = (°F −32) x 5/9

** m = ft. x 0.30480

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4. Abbreviated Experiment Design for Hydrocarbon Analyzer (8 points)

Treatment No.	Temp., °F*	Gas Conc.	Filter Condition	Line Length,** Ft.
1	75	high	clean	225
2	↓	low	clean	225
3	↓	high	dirty	225
4	↓	low	dirty	225
5	↓	high	clean	600
6	↓	low	clean	600
7	↓	high	dirty	600
8	↓	low	dirty	600

Note: Analyzer operated at unmodified line voltage levels.

* 75°F = 24°C

** 225 ft = 68.6 m and 600 ft = 182.9 m

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5. Abbreviated Experiment Design for Sulfur Analyzer (18 points)

Treatment No.	Temp., °F*	Gas Conc	Filter Condition	Line Length,** Ft.
1	75	high	clean	150
2		med.	clean	
3		low	clean	
4		high	dirty	
5		med.	dirty	
6		low	dirty	
7		high	clean	225
8		med.	clean	
9		low	clean	
10		high	dirty	
11		med.	dirty	
12		low	dirty	
13		high	clean	600
14		med.	clean	
15		low	clean	
16		high	dirty	
17		med.	dirty	
18		low	dirty	

* 75°F = 24°C

** 150 ft = 45.7 m., 225 ft = 68.6 m. and 600 ft = 182.9 m.

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The following pages list the instrument response in terms of meter or voltage readings for each respective treatment number. The combination of variables comprising each treatment number was described in Appendix A.

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APPENDIX B

TEST RESULTS

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1. CO Analyzer Test Results (54 Data Points)

Treatment No.	Meter Readings, % Full Scale Analyzer #1	Analyzer #2	Analyzer #3
1	10.7	11.8	9.6
2	11.8	11.3	11.0
3	12.5	11.1	11.8
4	32.3	33.3	31.5
5	34.7	34.3	34.0
6	35.2	33.7	34.7
7	63.6	65.2	63.0
8	65.0	65.2	64.6
9	65.8	65.1	65.4
10	10.5	11.6	9.9
11	12.1	11.8	11.0
12	12.5	11.2	12.0
13	32.7	33.7	31.9
14	34.5	33.7	33.2
15	35.2	33.7	34.7
16	63.6	65.1	63.0
17	65.0	66.0	65.0
18	65.5	64.8	65.1

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2. CO Analyzer Results - Actual Concentration versus Voltage Output

Actual CO Conc. (ppm)	Analyzer No.	Output Voltage*
0	1	0.00
0	2	0.00
0	3	0.00
11.0	1	0.53
11.0	2	0.56
11.0	3	0.58
33.0	1	1.63
3.0	2	1.68
33.0	3	1.67
62.5	1	3.13
62.5	2	3.20
62.5	3	3.16
82.5	1	4.22
82.5	2	4.30
82.5	3	4.25

*Range of Output Voltage = 0-5.0 volts.
CO Analyzer set on 0-100 ppm scale.

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3. Ozone Analyzer Test Results

Treatment No.	Actual O_3 Concn. (pphm)	Avg. Indicated O_3 Conc. (pphm)
1	26.0	12.5
2	42.5	28.3
3	10.9	6.2
4	11.0	6.2
5	26.0	16.2
6	43.0	30.0
7	43.0	34.3
8	10.5	3.8
9	26.0	15.0
10	11.0	4.6
11	31.2	9.7
12	43.0	26.9
13	26.0	14.0
14	10.4	7.6
15	43.0	35.1
16	26.0	14.9
17	43.0	37.4
18	11.0	3.7
19	11.0	7.2
20	11.0	1.3
21	11.6	4.9
22	26.0	8.4
23	26.0	9.2
24	26.0	9.3
25	43.0	22.9
26	43.0	31.2
27	43.0	19.6
28	11.0	7.3
29	11.0	7.9
30	11.0	1.3
31	26.0	17.7
32	26.0	4.4
33	26.0	2.1
34	43.0	28.9
35	43.0	21.2
36	43.0	5.8

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4. Effect of Bag Storage on Ozone

	Low O_3 Concentration		
Storage Time	15 min.	30 min	105 min
Actual Conc.	10	10	10
Indic. Conc.	7.5	6.7	2.3

	Medium O_3 Concentration		
Storage Time	15 Min.	30 min.	60 min.
Actual Conc.	26	25	26
Indic. Conc.	22	18	18

	High O_3 Concentration		
Storage Time	15 min.	30 min.	60 min.
Actual Conc.	51	51	50
Indic. Conc.	48	33	22

Note: Interior van temperature was approximately 75°F during test. All concentrations are in units of parts per hundred million (pphm). "Actual concentrations" are those initially stored in the bags, and "indicated concentrations" are those indicated by the analyzer in the van when bag samples are analyzed at the end of the specified storage time.

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5. Effect of Unused Teflon Tubing on Ozone

Note: O_3 was sampled through 150 feet (457 m) of previously unused tubing in both dark and light conditions.

Light Condition	O_3 Conc., Actual (pphm)	O_3 Conc., Indic. (pphm)
light	11	12
dark	11	12.5
light	26	25
dark	24	26
light	51	49
dark	50	54

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6. $NO-NO_2-NO_x$ Analyzer Test Results

Note: All concentrations are in parts per million (ppm). Two concentrations are given for each component gas (NO, NO_2 and NO_x): the first figure represents the concentration in the non-ozonized sample and the second figure represents the concentration in the ozonized sample.

Treatment No.	Actual or Indicated Concentrations	NO w/o O_3*	NO with O_3	NO_2 w/o O_3	NO_2 with O_3*	NO_x w/o O_3*	NO_x with O_3
1	Actual	.75	.16	0	.54	.75	.73
	Indic.	.72	.08	0	.58	.73	.65
2	Actual	2.49	1.10	.04	1.30	2.50	2.40
	Indic.	2.10	.97	0	1.13	2.10	2.05
3	Actual	.23	.07	0	.14	.23	.22
	Indic.	.23	.02	0	.21	.23	.22
4	Actual	.24	.03	0	.20	.24	.23
	Indic.	.22	0	0	.24	.24	.23
5	Actual	.89	.16	.01	.70	.90	.87
	Indic.	.88	.08	0	.80	.88	.86
6	Actual	2.3	.63	0	1.64	2.30	2.35
	Indic.	2.1	.58	0	1.53	2.10	2.20

Treatment No.	Actual or Indicated Concentrations	NO w/o O_3*	NO with O_3	NO_2 w/o O_3	NO_2 with O_3*	NO_x w/o O_3*	NO_x with O_3
7	Actual	2.20	.77	0	1.36	2.20	2.20
	Indic.	2.25	.80	0	1.48	2.20	2.20
8	Actual	.27	.06	0	.20	.27	.26
	Indic.	.27	0	0	.29	.27	.28
9	Actual	.67	.10	.01	.55	.68	.66
	Indic	.61	.03	0	.58	.60	.60
10	Actual	.26	.04	0	.22	.26	.26
	Indic.	.28	0	0	.25	.27	.23
11	Actual	.86	.14	0	.66	.86	.82
	Indic.	.79	.09	0	.75	.80	.82
12	Actual	2.40	.82	.04	1.54	2.40	2.40
	Indic.	2.00	.67	0	1.30	2.00	2.00
13	Actual	.74	.16	.01	.55	.74	.72
	Indic.	.74	.08	0	.70	.76	.75
14	Actual	.13	.03	0	.09	.13	.12
	Indic.	.14	0	0	.12	.14	.12
15	Actual	2.43	.70	.03	1.65	2.43	2.35
	Indic.	2.30	.70	0	1.47	2.25	2.20
16	Actual	.68	.10	0	.56	.68	.68
	Indic.	.62	.02	0	.59	.62	.60

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Treatment No	Actual or Indicated Concentrations	NO w/o O_3*	NO with O_3	NO_2 w/o O_3	NO_2 with O_3*	NO_x w/o O_3*x	NO_x with O_3
17	Actual	2.50	.90	.03	1.60	2.55	2.55
	Indic.	2.36	.87	0	1.59	2.36	2.35
18	Actual	.31	.10	0	.20	.31	.30
	Indic.	.30	.05	0	.26	.31	.31
19	Actual	.19	.05	0	.14	.19	.19
	Indic.	.18	.01	0	.17	.20	.18
20	Actual	.26	.03	0	.20	.26	.24
	Indic.	.28	0	0	.25	.29	.24
21	Actual	.27	.09	0	.17	.27	.26
	Indic.	.26	.03	.02	.24	.29	.27
22	Actual	.72	.13	0	.55	.72	.69
	Indic.	.64	.04	0	.59	.64	.61
23	Actual	.78	.20	0	.58	.78	.80
	Indic	.78	.17	0	.65	.78	.82
24	Actual	.80	.17	0	.62	.80	.80
	Indic.	.74	.09	0	.67	.73	.74
25	Actual	2.49	1.06	.04	1.28	2.50	2.40
	Indic.	2.12	1.00	0	1.16	2.10	2.05

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Treatment No	Actual or Indicated Concentrations	NO w/o O_3*	NO with O_3	NO_2 w/o O_3	NO_2 with O_3*	NO_x w/o O_3*x	NO_x with O_3
26	Actual	2.35	.72	0	1.72	2.35	2.50
	Indic.	2.20	.62	0	1.72	2.20	2.30
27	Actual	2.40	.85	.02	1.46	2.40	2.38
	Indic.	2.00	.78	0	1.26	2.00	1.95
28	Actual	.11	.03	0	.07	.11	.10
	Indic.	.11	0	.01	.11	.12	.11
29	Actual	.23	.07	0	.15	.23	.23
	Indic.	.22	.03	0	.20	.23	.23
30	Actual	.23	.04	0	.20	.23	.24
	Indic.	.23	0	0	.22	.26	.21
31	Actual	.83	.17	.02	.66	.84	.84
	Indic.	.78	.08	0	.72	.78	.78
32	Actual	.72	.16	.02	.55	.74	.72
	Indic.	.81	.07	0	.71	.79	.76
33	Actual	.85	.16	.01	.66	.85	.83
	Indic.	.81	.10	0	.71	.82	.80
34	Actual	2.30	.53	.02	1.64	2.30	2.20
	Indic.	1.95	.48	0	1.58	1.95	2.00

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Treatment No	Actual or Indicated Concentrations	NO w/o O_3*	NO with O_3	NO_2 w/o O_3	NO_2 with O_3*	NO_x w/o O_3*	NO_x with O_3
35	Actual	2.40	1.16	.03	1.20	2.43	2.35
	Indic.	2.25	1.11	0	1.10	2.20	2.25
36	Actual	2.43	.70	.03	1.65	2.43	2.35
	Indic.	2.30	.70	0	1.47	2.25	2.25

*Figures used in regression analysis.

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7. Effect of Bag Storage on Oxides of Nitrogen

a. Low $NO-NO_2-NO_x$ Concentrations

Storage Time	Indic. or Actual conc.	NO w/o O_3	NO with O_3	NO_2 w/o O_3	NO_2 with O_3	NO_x w/o O_3	NO_x with O_3
15 min.	Actual	.28	.16	0	.19	.28	.35
	Indic.	.25	.16	0	.16	.27	.33
30 Min.	Actual	.275	.16	0	.19	.275	.35
	Indic.	.23	.15	.02	.20	.26	.36
60 min.	Actual	.30	.16	0	.19	.30	.35
	Indic.	.26	.13	0	.19	.26	.335

b. Medium $NO-NO_2-NO_x$ Concentrations

Storage Time	Indic. or Actual conc.	NO w/o O_3	NO with O_3	NO_2 w/o O_3	NO_2 with O_3	NO_x w/o O_3	NO_x with O_3
15 min.	Actual	.90	.29	0	.63	.90	.93
	Indic.	.91	.29	0	.64	.90	.93
30 min.	Actual	.90	.28	.02	.63	.92	.92
	Indic.	.92	.29	0	.64	.93	.95
60 min.	Actual	.92	.28	.01	.63	.93	.92
	Indic.	.92	.29	0	.64	.94	.96

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c. High $NO-NO_2-NO_x$ Concentrations

Storage Time	Indic. or Actual conc.	NO w/o O_3	NO with O_3	NO_2 w/o O_3	NO_2 with O_3	NO_x w/o O_3	NO_x with O_3
15 min.	Actual	2.63	.63	.03	1.52	2.65	2.15
	Indic.	2.60	.69	0	1.42	2.60	2.10
30 min.	Actual	2.30	.64	.02	1.48	2.32	2.15
	Indic.	2.20	.69	0	1.50	2.25	2.20
60 min.	Actual	2.30	.64	.02	1.48	2.32	2.15
	Indic.	2.10	.70	0	1.48	2.20	2.10

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8. Hydrocarbon Analyzer Test Results

Note: The term "volts" refers to the analyzer output signal voltage.

Treatment No.	Actual or Indicated Conc. or Voltage	THC conc. ppm	THC volts	CH_4 conc. ppm	CH_4 volts	CO conc. ppm	CO volts
1	Actual	43.7	4.33	12.0	1.17	40	1.97
	Indicated	44.6	4.42	11.9	1.16	40	1.96
2	Actual	10.1	1.00	4.7	.42	33	1.47
	Indicated	9.7	.96	4.8	.43	33	1.48
3	Actual	43.7	4.33	12.0	1.17	40	1.97
	Indicated	43.6	4.32	12.0	1.17	40	1.96
4	Actual	10.1	1.00	4.7	.42	33	1.47
	Indicated	10.0	.99	4.8	.43	33	1.49
5	Actual	43.7	4.33	12.0	1.17	40	1.97
	Indicated	43.2	4.28	12.0	1.17	40	1.97
6	Actual	10.1	1.00	4.7	.42	33	1.47
	Indicated	9.5	.94	4.9	.44	33	1.50
7	Actual	43.7	4.33	12.0	1.17	40	1.97
	Indicated	43.8	4.34	12.1	1.18	40	1.97
8	Actual	10.1	1.00	4.7	.42	33	1.47
	Indicated	9.4	.93	4.9	.44	33	1.49

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9. Effect of Bag Storage on Hydrocarbons

Note: All concentrations are in parts per million (ppm). "Voltage" refers to the analyzer output signal voltage.

Low Gas Concentration

	THC	CH_4	CO
Actual Conc. (ppm)	10.1	4.7	33
Actual Voltage	1.00	0.42	1.47

Retention Time	THC Indic. Voltage	THC Indic. Conc.	CH_4 Indic. Voltage.	CH_4 Indic. Conc.	CO Indic. Voltage	CO Indic. Conc.
15 min.	1.03	10.4	0.41	4.6	1.42	32
30 min.	1.01	10.1	0.42	4.7	1.42	32
60 min.	1.01	10.1	0.43	4.8	1.44	32

High Gas Concentration

	THC	CH_4	CO
Actual Conc (ppm)	43.7	12.0	40
Actual Voltage	4.33	1.17	1.97

Retention Time	THC Indic. Voltage	THC Indic. Conc.	CH_4 Indic. Voltage	CH_4 Indic. Conc.	CO Indic. Voltage	CO Indic. Conc.
15 min.	4.24	42.8	1.15	11.8	1.91	39
30 min.	4.23	42.7	1.15	11.8	1.90	39
60 min.	4.29	43.3	1.18	12.1	1.96	40

10. Sulfur Analyzer Test Results

Treatment No.	SO_2 Conc. Actual (pphm)	SO_2 Conc. Indicated (pphm)
1	35	25
2	20	15
3	7.0	5.3
4	35	25
5	20	15
6	7.0	5.0
7	40	32
8	19	12
9	9.5	5.5
10	40	29
11	19	12
12	9.5	5.0
13	35	22
14	20	11
15	10	5.5
16	35	22
17	20	13
18	10	5.5

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11. Effect of Bag Storage on Sulfur Dioxide

SO_2 Conc., Actual (pphm)	SO_2 Conc. Indicated (pphm)	Retention Time (min.)
7.6	7.6	30
7.6	7.6	60
21	18	15
17	14	30
35	36	15

Note: Interior temperature of van was approximately 75°F (24°C) at time of test.

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