

FINAL REPORT

May 8, 1970 through May 8, 1972

FIELD EVALUATION OF NEW AIR POLLUTION MONITORING SYSTEMS

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FOREWORD

This final report describes the results of a field evaluation of ambient air analyzers conducted by the Research Triangle Institute for the Environmental Protection Agency under Contract CPA 70-101 during the period May 8, 1970 to May 8, 1972. During this study, a mobile laboratory was located in Los Angeles for three months and in St. Louis for six months. Interim reports describing the three phases of this instrument evaluation program have been prepared and are available from the Environmental Protection Agency.

The work on this project was performed by the Instrumentation, Measurements and Device Research Department, Engineering Division, Research Triangle Institute for the Field Methods Development Section, Division of Chemistry and Physics, Environmental Protection Agency. Mr. R. K. Stevens, EPA, was Project Monitor. Mr. C. E. Decker and Dr. L. F. Ballard served as Project Leaders. Mr. J. B. Tommerdahl, Mr. T. M. Royal, Mr. R. W. Murdoch, and Mrs. L. K. Matus participated in the field evaluation program.

The Research Triangle Institute wants to acknowledge the cooperation and assistance provided throughout the evaluation program by Messrs. Stevens, O'Keeffe, Hodgeson, Clark, and others of the Field Methods Development Section, Division of Chemistry and Physics, Environmental Protection Agency.

Appreciation is also expressed to the Los Angeles County Air Pollution Control District and the St. Louis County Air Pollution Control Office for providing the respective sites for the evaluation program.

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1.0 INTRODUCTION

1.1 Objectives

The purpose of this program was to conduct a full scale field evaluation of ambient air analyzers in different geographical areas to determine the effects of typical combinations of urban environment pollutants on the instrument performance level. The aim was to establish on both an absolute and comparative basis the degree to which the instruments evaluated meet the needs of control agencies for reliable and accurate measurements. This study was also intended to determine if newly developed instrumentation can adequately measure pollutant concentrations in ambient air and to compare them to the reference methods.

As a result of the tremendous growth in pollution monitoring instrumentation, it was also very important that techniques for rapidly evaluating the performance level of a large number of instruments under identical field conditions be conceived and implemented. Automatic calibration techniques and electronic data acquisition and analysis were considered to be necessary ingredients for this accomplishment in terms of accuracy, time, and economy. As a pioneer program in combining all these features, the procedures that have been used may serve as guidelines for broader application.

The instrument evaluation program conducted over the past two years was divided into three separate studies. The first study was conducted in Los Angeles [1], where the major source of pollution is the internal combustion engine, during the period September 4 to

December 1, 1970. St. Louis was selected for the additional tests because of its varied industrial activities, which are typical of many urban environments in the United States and which introduce a large number of organic and inorganic pollutants into the atmosphere. Phase I [2] in St. Louis was conducted during the period May 13 to August 17, 1971. Phase II [3] in St. Louis was conducted during the period October 7 to December 20, 1971. In each of the three studies the performance of classical measurement principles for ambient air pollutants were compared with new analytical techniques.

Gas analyzers were included in the instrument evaluation program for measuring SO_2 , O_3 , O_x , NO , NO_2 , H_2S , THC , CH_4 , CO , and non-methane hydrocarbons. Meteorological instruments were included for supporting measurements of wind speed and direction, temperature, solar radiation, and dewpoint.

Several of the ambient air analyzers evaluated during these studies were prototype instruments based on newly-developed measurement techniques or first production models. Mechanical and electrical problems were frequently encountered with these systems which hindered their performance. An important aspect of this evaluation program was to identify weaknesses in the monitoring principle and design and to make appropriate adjustment where possible.

1.2 Experimental Approach and Description of Facilities

An environmentally controlled mobile laboratory was considered to be the most realistic vehicle to both transport and house the instruments, data acquisition system, and supporting laboratory equipment. Figure 1.1 shows two internal views of the mobile laboratory on location adjacent to the St. Louis County air monitoring station at 55 Hunter Road, Clayton, Missouri. Figure 1.2 is a diagram of the mobile laboratory showing the location of the monitoring instruments evaluated during Phase II in St. Louis, the data acquisition system, and gas sampling manifold. During the Los Angeles Study (Sept. 4-Dec. 1, 1970), the trailer was located adjacent to the Los Angeles County Air Pollution Control District's research facility on San Pedro Street in downtown Los Angeles.

The gas analyzers evaluated during each study are listed in Section 2.0. Instrument descriptions and operation summaries for each evaluation period are presented in three Interim Reports [1,2,3] and are not duplicated here. The calibration schedule consisted of a zero air and span calibration every two (2) days and a multi-point calibration on alternating weekends. Calibration procedures used during this study are given in Section 3.0.

Meteorological sensors are described in Section 4.0 and the data acquisition system in Section 5.0. In addition to the data storage function, the overall system was designed to automate the communication between the laboratory operator and the data processing and analysis facility.

The data handling programs used to process all data are given in Section 6.0. These programs provide air quality data, cross correlation

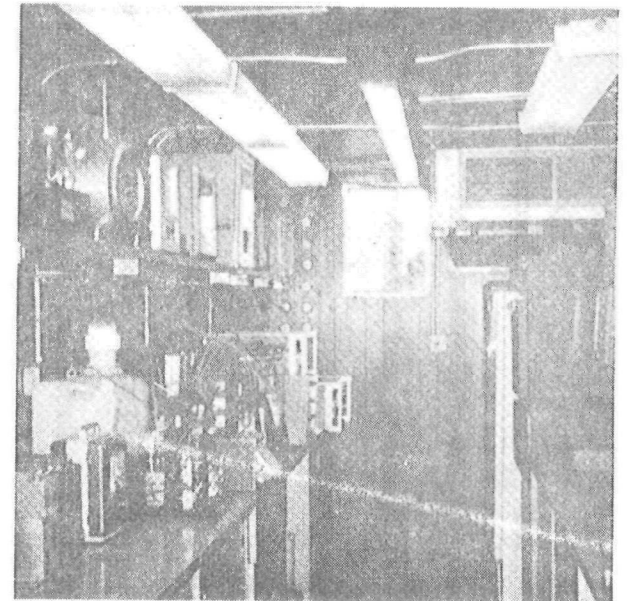
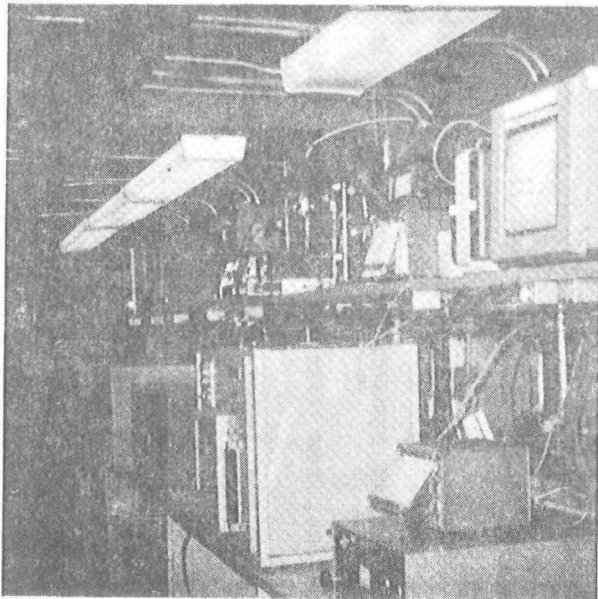
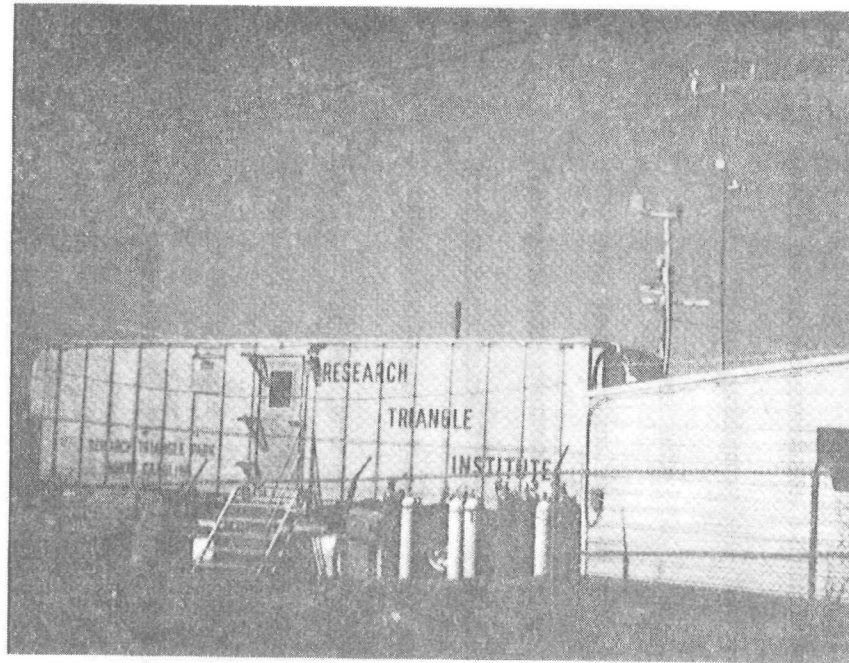
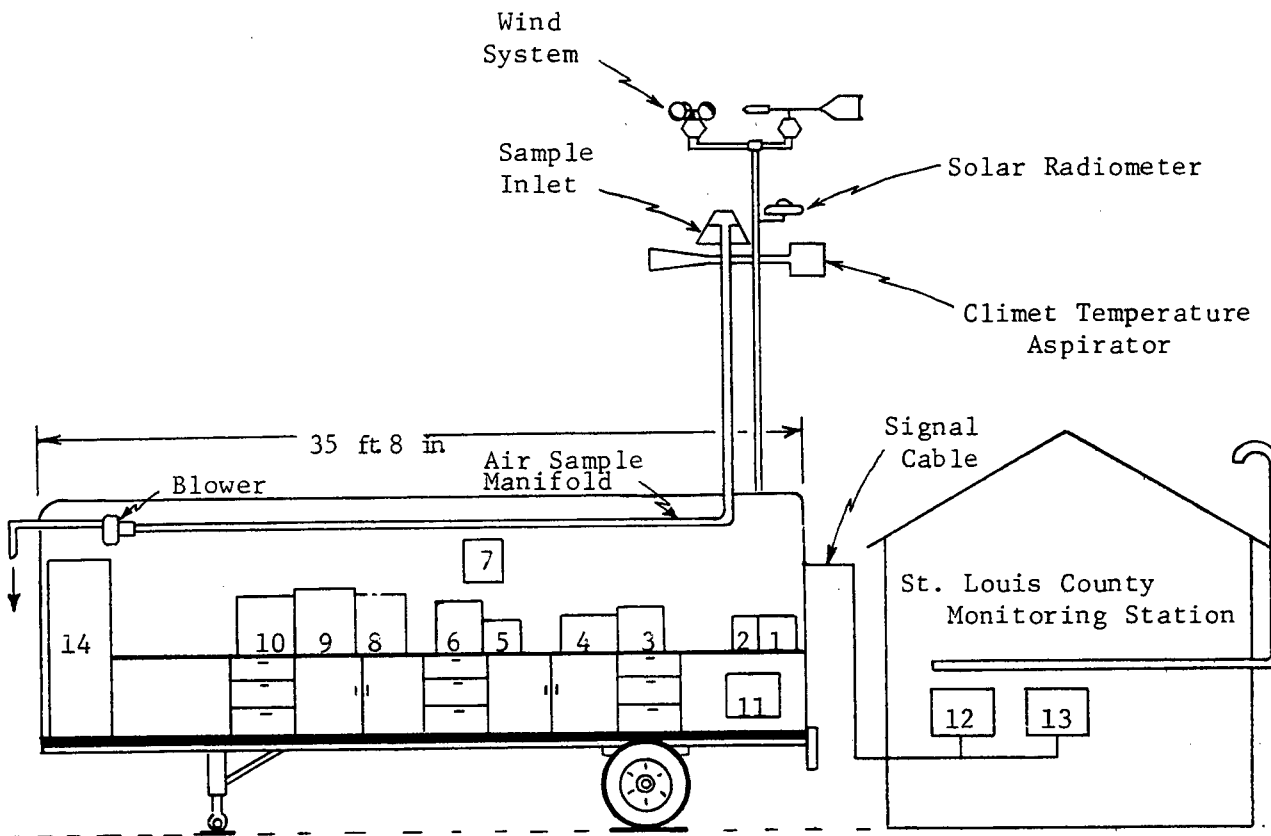


FIGURE 1.1. Mobile Field Laboratory



- | | |
|---|--|
| 1 Tracor SO ₂ , H ₂ S | 8 Thermo Electron NO, NO _x |
| 2 Melpar SO ₂ | 9 Aerochem NO |
| 3 Philips SO ₂ | 10 Beckman NO ₂ |
| 4 Pollution Mon. SO ₂ | 11 Beckman - THC, CH ₄ , CO |
| 5 Bendix O ₃ | 12 Power Design Pacific THC |
| 6 Technicon O _x | 13 MSA NDIR CO |
| 7 Mast O _x | 14 Data Acquisition System |

FIGURE 1.2 Diagram of Air Sampling System and Location of Continuous Ambient Air Analyzers in the Mobile Laboratory

between various instruments and statistical data on the stability and overall performance of each instrument. Summaries of these results are given in Section 7.0 and 8.0.

2.0 GAS ANALYZERS

The instrumentation and measurement methods evaluated in the field program in Los Angeles and St. Louis (Phase I and Phase II) are summarized in Tables 2.1, 2.2, and 2.3. The principle of operation of these instruments and measurement methods have previously been described in the literature. For further information refer to the three interim reports [1,2,3] or the additional references provided.

TABLE 2.1 INSTRUMENTATION AND MEASUREMENT METHODS
EVALUATED IN THE LOS ANGELES STUDY

<u>Pollutant</u>	<u>Analyzer or Method</u>	<u>Principle of Operation</u>	<u>References</u>
Ozone	RTI O ₃	Chemiluminescent	4
	EPA O ₃ (Prototype)	Chemiluminescent	5
Oxidant	Mast O _x	Coulometric	6
	Technicon O _x	Colorimetric	7
Nitrogen Dioxide	Technicon NO ₂	Colorimetric	8,9
Sulfur Dioxide	Melpar SO ₂	Flame Photometric	10,11
	Philips SO ₂	Coulometric	3
	L&N SO ₂	Conductometric	2
	Tracor GC-SO ₂	GC-Flame Photometric	12
	Technicon SO ₂	Colorimetric	1
Hydrogen Sulfide	Tracor GC-H ₂ S	GC-Flame Photometric	12
	Technicon H ₂ S	Colorimetric	13

TABLE 2.2 INSTRUMENTATION AND MEASUREMENT METHODS
EVALUATED IN THE ST. LOUIS STUDY: PHASE I

<u>Pollutant</u>	<u>Analyzer or Method</u>	<u>Principle of Operation</u>	<u>References</u>
Ozone	RTI O ₃	Chemiluminescent	4
	Bendix Environmental O ₃	Chemiluminescent	5
	Dasibi O ₃	UV-Absorption	2
Oxidant	Mast O _x	Coulometric	6
	Beckman 908 O _x	Coulometric	2
	Technicon IV O _x	Colorimetric	7
Nitrogen Dioxide	Beckman 910 NO ₂	Coulometric	2
Nitric Oxide	Beckman 909 NO	Coulometric	2
	Aerochem NO	Chemiluminescent	14
Sulfur Dioxide	Melpar SO ₂	Flame Photometric	10,11
	Philips SO ₂	Coulometric	3
	Beckman 906A SO ₂	Coulometric	2
	L&N SO ₂	Conductometric	2
	Tracor GC-SO ₂	GC-Flame Photometric	12
	Pollution Monitors SO ₂	Colorimetric	2
Hydrogen Sulfide	Tracor GC-H ₂ S	GC-Flame Photometric	12
Carbon Monoxide	MSA CO	NDIR	2
	Beckman 6800 CO	GC-FID	15,16
Total Hydrocarbons	Power Design Pacific	FID	2
	Beckman 6800	GC-FID	15,16
Non-Methane Hydrocarbons	Beckman 6800	GC-FID	15,16

TABLE 2.3 INSTRUMENTATION AND MEASUREMENT METHODS
EVALUATED IN THE ST. LOUIS STUDY: PHASE II

<u>Pollutant</u>	<u>Analyzer or Method</u>	<u>Principle of Operation</u>	<u>References</u>
Ozone	Bendix Process O ₃	Chemiluminescent	3
Oxidant	Mast O _x	Coulometric	6
	Technicon IV O _x	Colorimetric	7
Nitrogen Dioxide	Beckman 910 NO ₂	Coulometric	2
	Thermo Electron NO ₂ *	Chemiluminescent	17
	Technicon NO ₂	Colorimetric	8,9
	Jacobs-Hochheiser	Manual-Colorimetric	18
Nitric Oxide	Aerochem NO	Chemiluminescent	14
	Thermo Electron NO	Chemiluminescent	17
Sulfur Dioxide	Melpar SO ₂	Flame Photometric	10,11
	Tracor GC-SO ₂	GC-Flame Photometric	12
	Philips SO ₂	Coulometric	3
	Pararosanine	Manual-Colorimetric	19
Hydrogen Sulfide	Tracor GC-H ₂ S	GC-Flame Photometric	12
Carbon Monoxide	Beckman 6800 CO	GC-FID	15,16
	MSA CO	NDIR	2
Total Hydrocarbons	Beckman 6800	GC-FID	15,16
	Power Design Pacific	FID	2
Non-Methane Hydrocarbons	Beckman 6800	GC-FID	15,16

*Modified to measure both NO and NO_x.

3.0 CALIBRATION PROCEDURES

3.1 Calibration Techniques

Dynamic calibration techniques were used to calibrate the monitoring systems evaluated during these studies and are outlined in Table 3.1. Multipoint calibrations were performed bi-weekly with zero and span checks every two days. These data were used to provide updated transfer equations for input into the computer for data reduction. For additional information regarding calibration procedures, refer to the three interim reports [1,2,3] or the references cited. Diagrams of these calibration systems are included in Figures 3.1, 3.2, and 3.3.

TABLE 3.1 CALIBRATION TECHNIQUES

<u>Pollutant</u>	<u>Calibration Technique</u>	<u>References</u>
Ozone/Oxidant	UV-Ozone generator referenced to Manual KI	20
Nitrogen Dioxide	Permeation Tube & NO-NO ₂ Conversion System	21,22
Nitric Oxide	Cylinder-dilution	22
Sulfur Dioxide	Permeation Tube	21,23
Hydrogen Sulfide	Permeation Tube	3
Carbon Monoxide	Cylinder	3
Total Hydrocarbons	Cylinder	3
Non-Methane Hydrocarbons	Cylinder	3

3.2 Ambient Air Sampling System

In order to avoid eddy currents and street pollution, the sample inlet was located five feet above the trailer. A 1" I.D. TFE

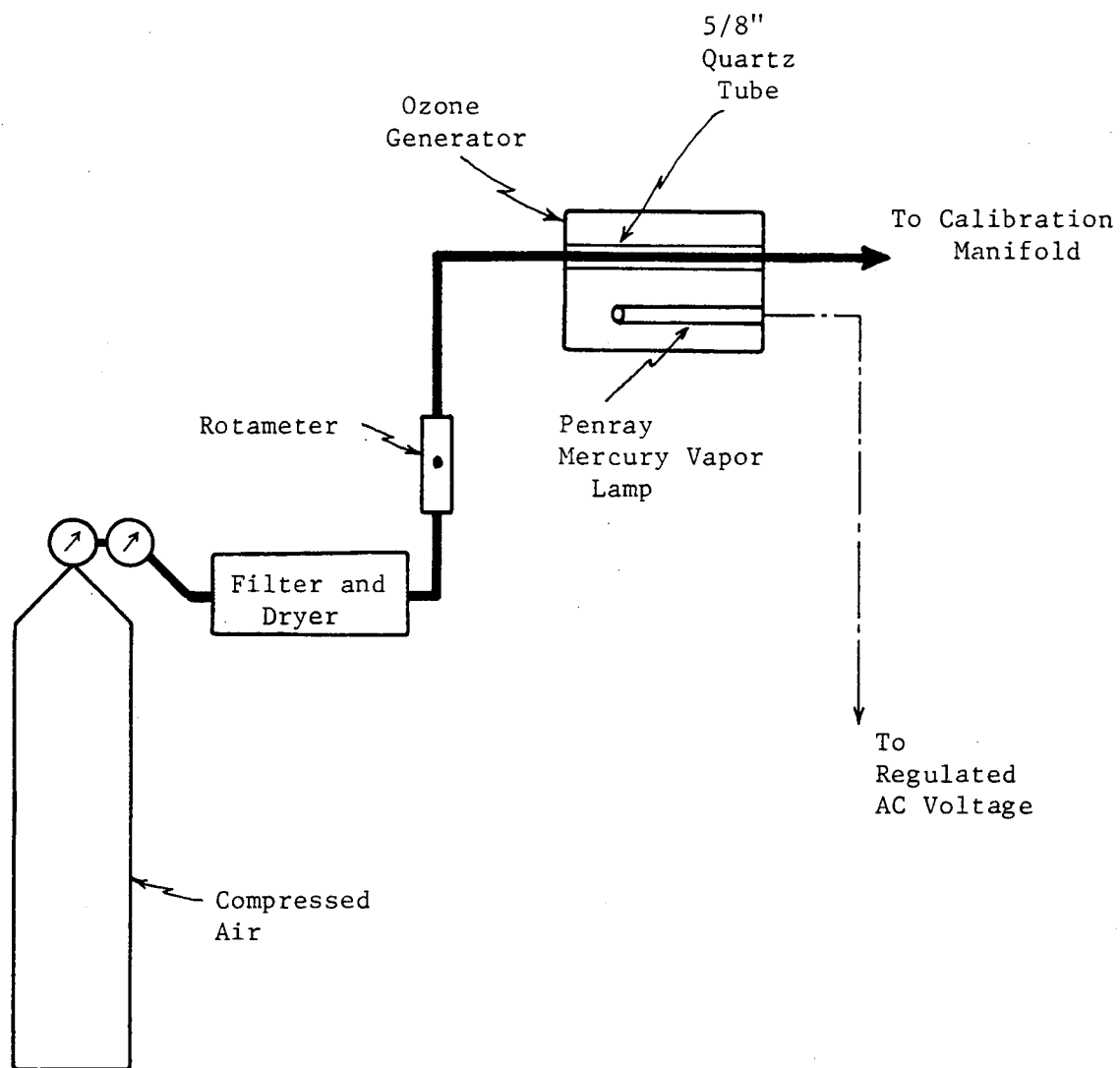


Figure 3.1 Ozone Calibration System

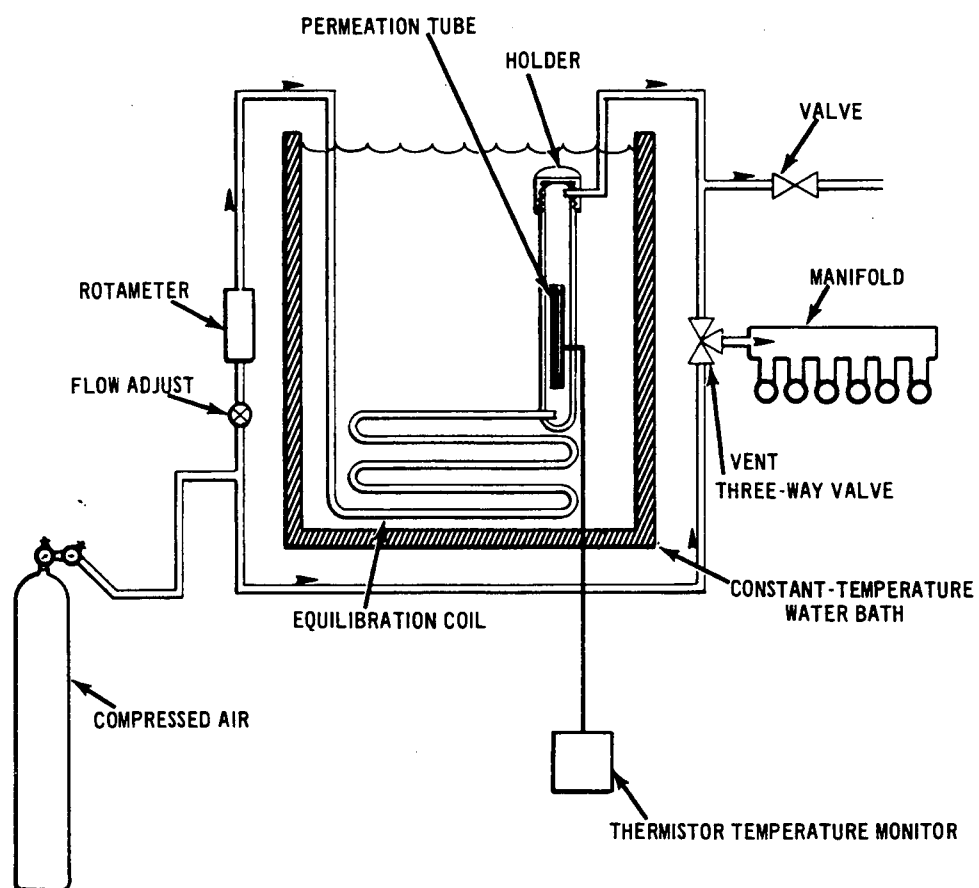


Figure 3.2 Permeation Tube Calibration System

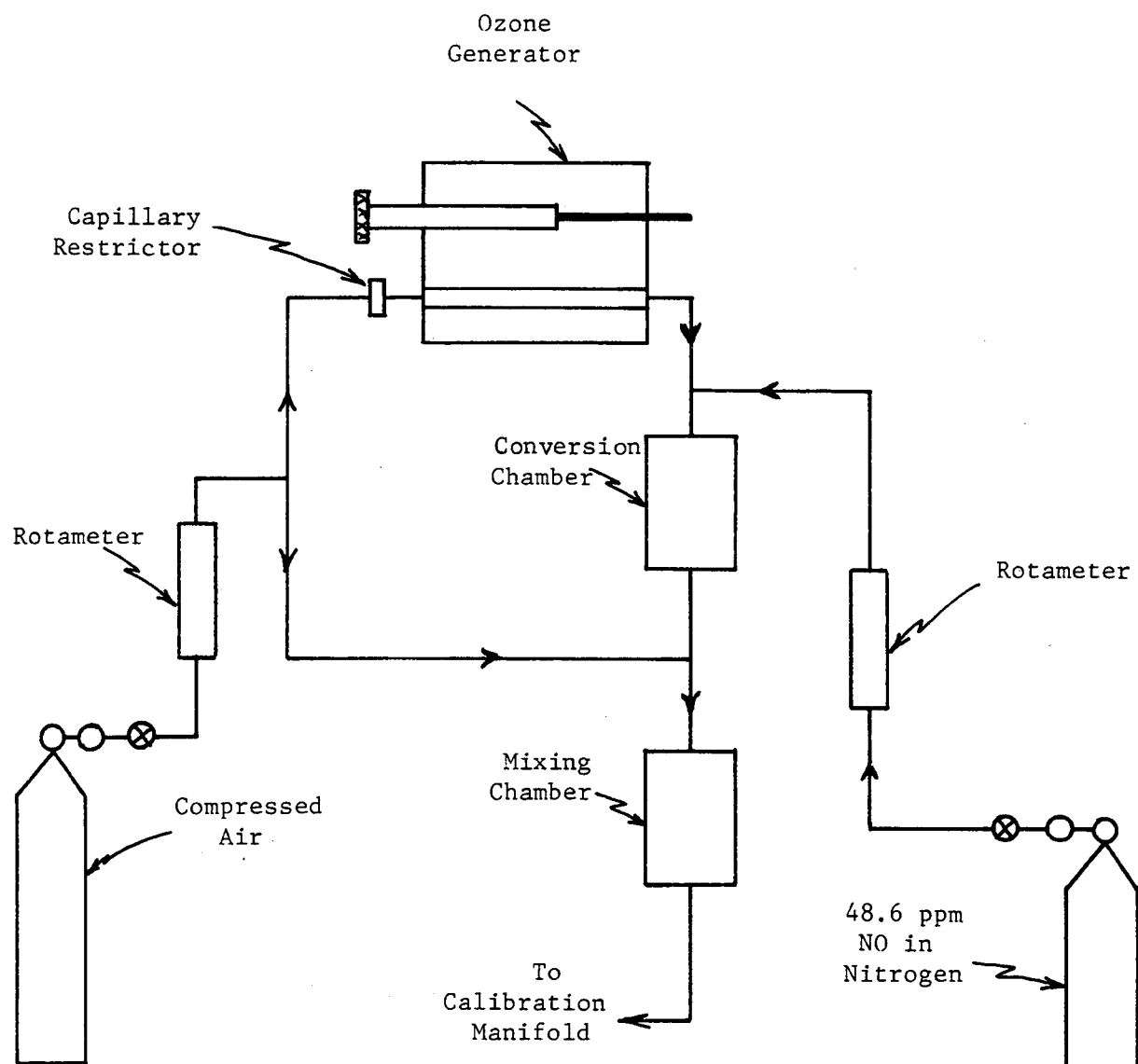


Figure 3.3 Nitric Oxide and Nitrogen Dioxide Calibration System.

teflon tube extended from the sample holder located on the meteorological tower to the trailer where it connected to a 1" O.D. pyrex glass manifold which extended behind the air monitoring systems. This arrangement is shown in Figures 3.4, 3.5, and 3.6. A glass flower pot protected the sample inlet and prevented moisture and settleable particulates from entering the sample line. Sample air was aspirated via a blower through the teflon line and glass manifold at a rate of 3 CFM. Sampling ports made of 12/5 ball and socket joints were used for easy hook-up of instrument sample inlet lines.

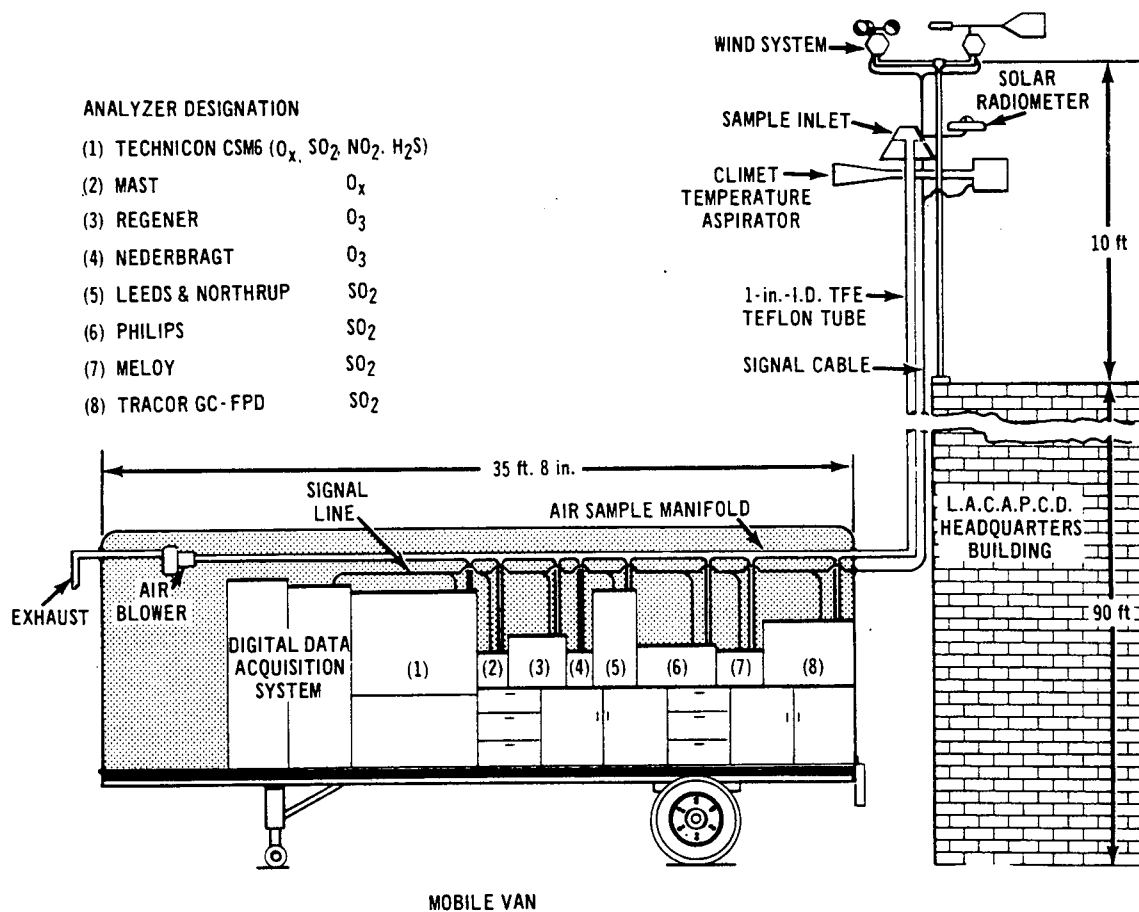


Figure 3.4 Diagram of Air Sampling System and Sulfur Dioxide and Ozone Monitors in Mobile Laboratory

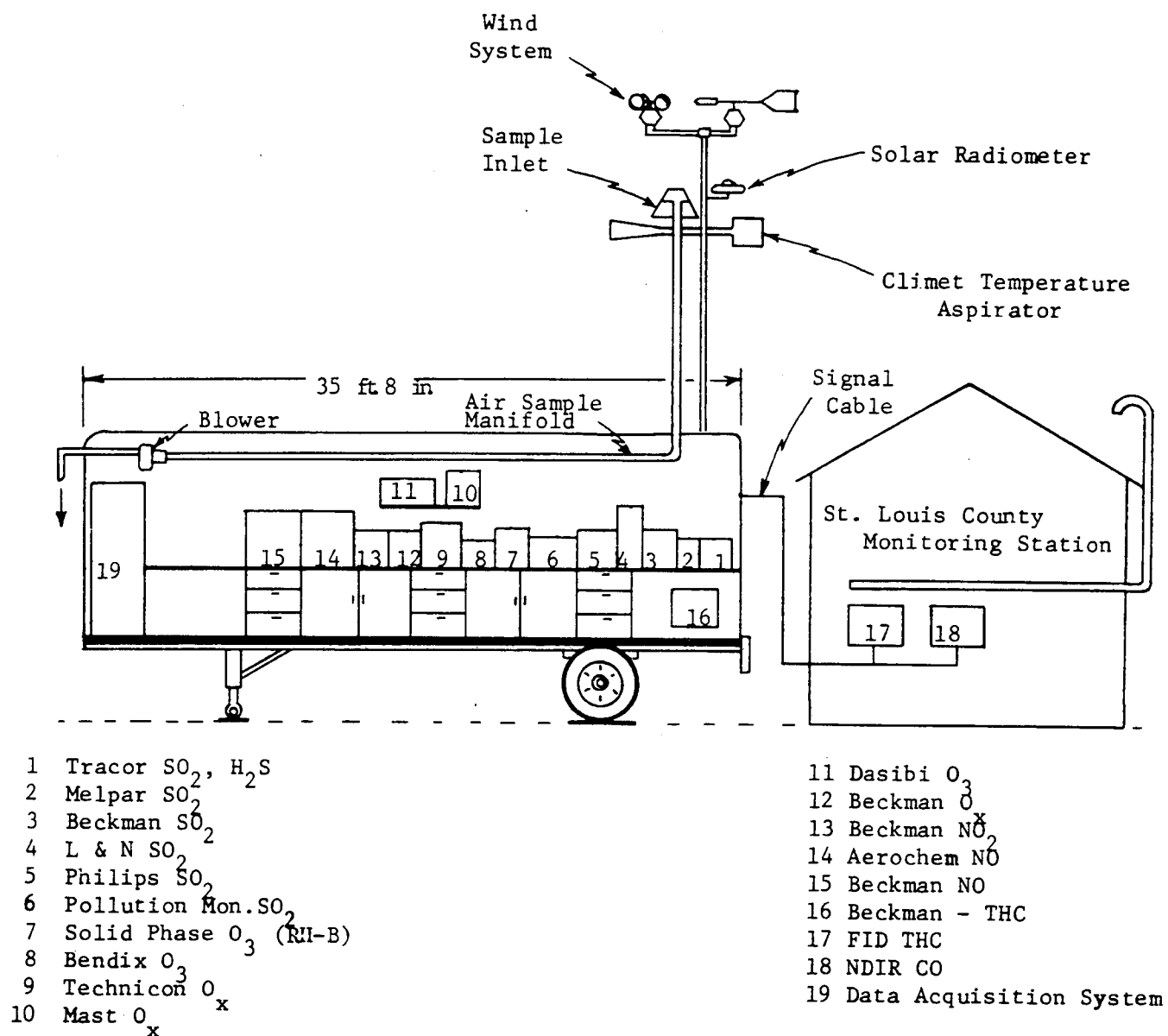
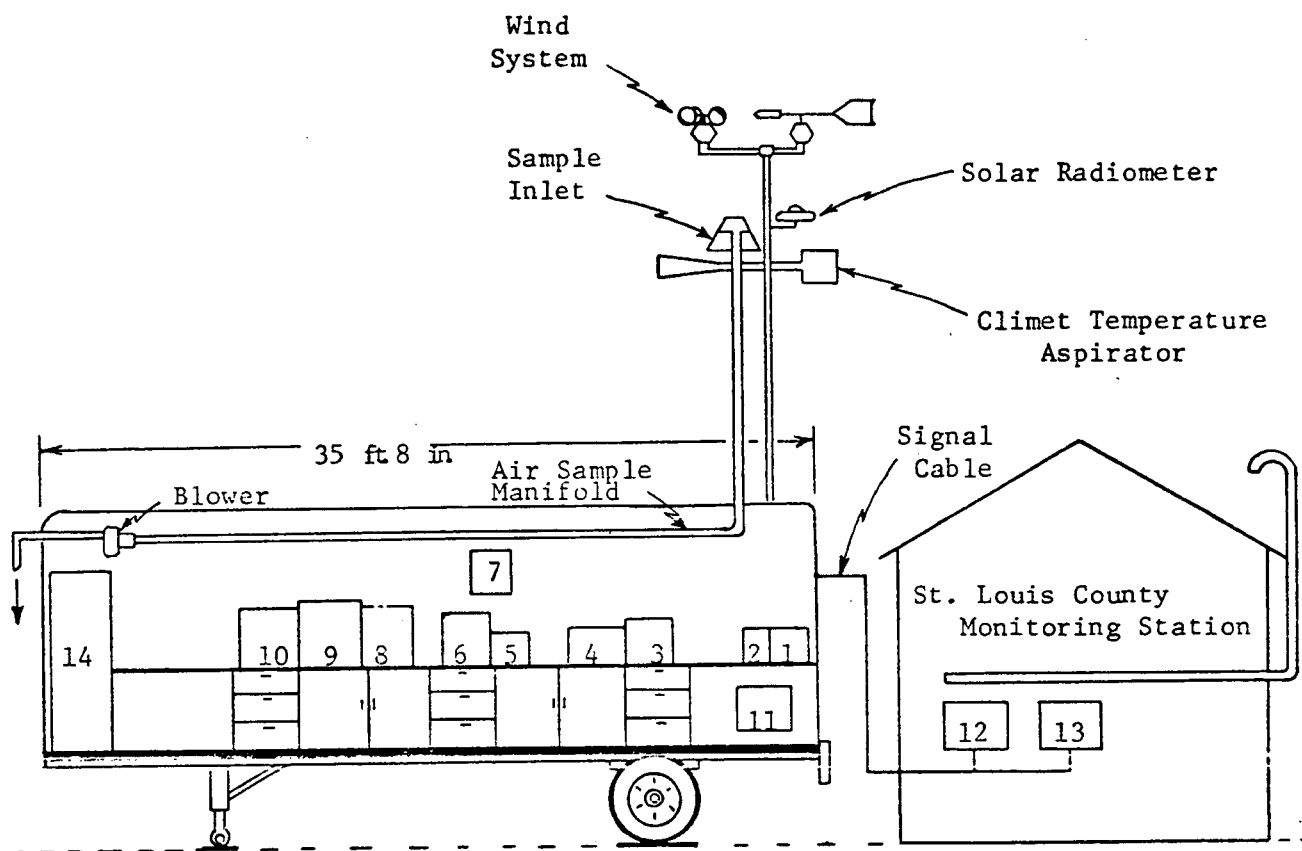


FIGURE 3.5 Diagram of Air Sampling System and Location of Continuous Ambient Air Analyzers in the Mobile Laboratory



- | | |
|---|--|
| 1 Tracor SO ₂ , H ₂ S | 8 Thermo Electron NO, NO _x |
| 2 Melpar SO ₂ | 9 Aerochem NO |
| 3 Philips SO ₂ | 10 Beckman NO ₂ |
| 4 Pollution Mon. SO ₂ | 11 Beckman - THC, CH ₄ , CO |
| 5 Bendix O ₃ | 12 Power Design Pacific THC |
| 6 Technicon O _x | 13 MSA NDIR CO |
| 7 Mast O _x | 14 Data Acquisition System |

FIGURE 3.6 Diagram of Air Sampling System and Location of Continuous Ambient Air Analyzers in the Mobile Laboratory

4.0 METEOROLOGICAL SENSORS

The following meteorological parameters were monitored throughout the duration of the field evaluation program: wind speed and direction, ambient air temperature, relative humidity and solar radiation. Sensors for monitoring these parameters were mounted on a small tower which was attached to the top of the mobile van. The tower as assembled for checkout is shown in Figure 4.1. The instrumentation used to monitor these meteorological parameters is outlined in Table 4.1.

TABLE 4.1 METEOROLOGICAL INSTRUMENTATION

<u>Parameter</u>	<u>Instrument or Method</u>	<u>Reference</u>
Wind Speed & Direction	Modified Bendix Aerovane	3
Temperature	Thermistor in Aspirated Temperature Shield	3
Dewpoint	Foxboro Dewcell	3
Solar Radiation	Kipp & Zonen Solarimeter	3

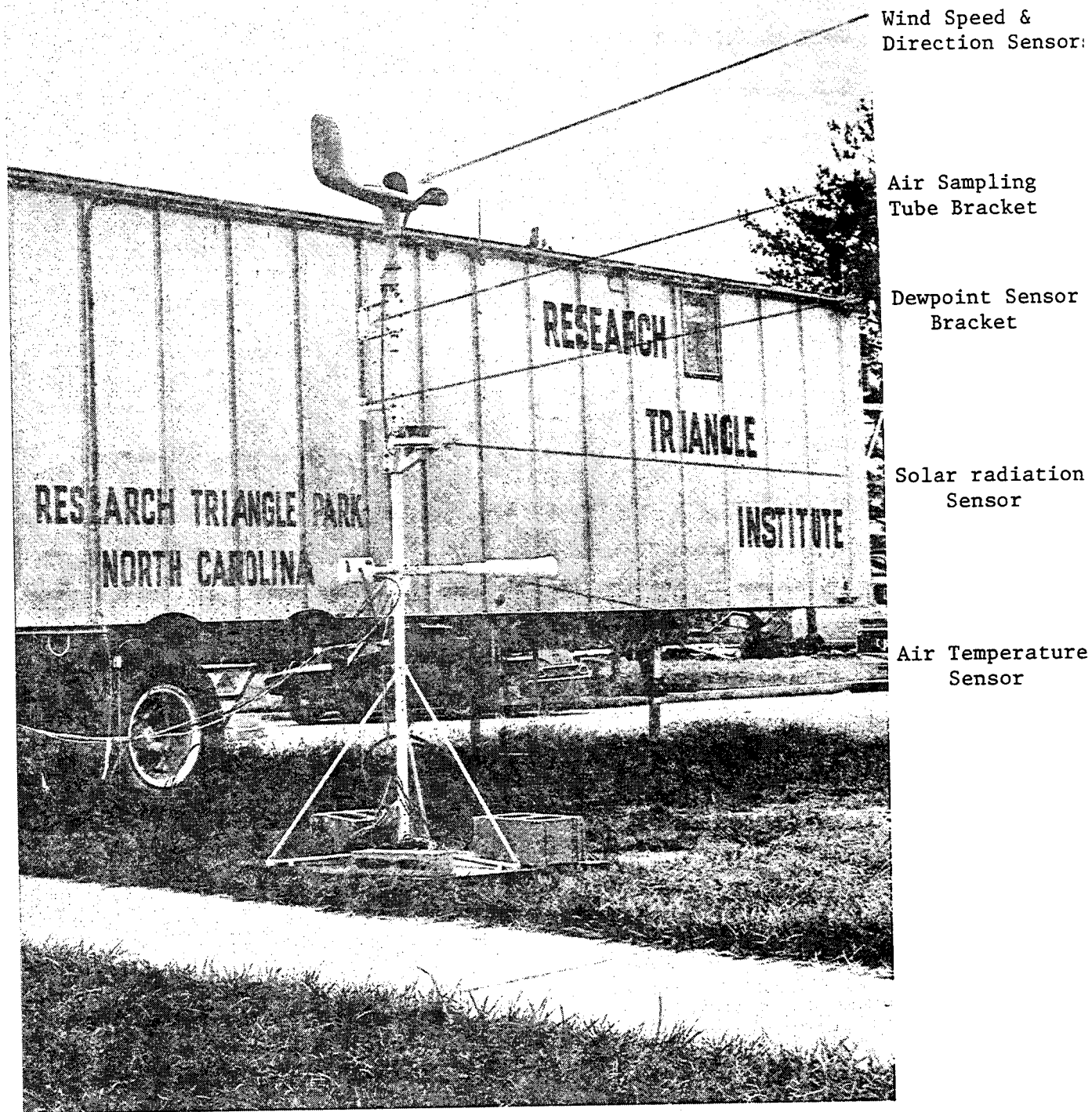


Figure 4.1 Meteorological Sensor Tower

5.0 DATA ACQUISITION SYSTEM

5.1 General System Description

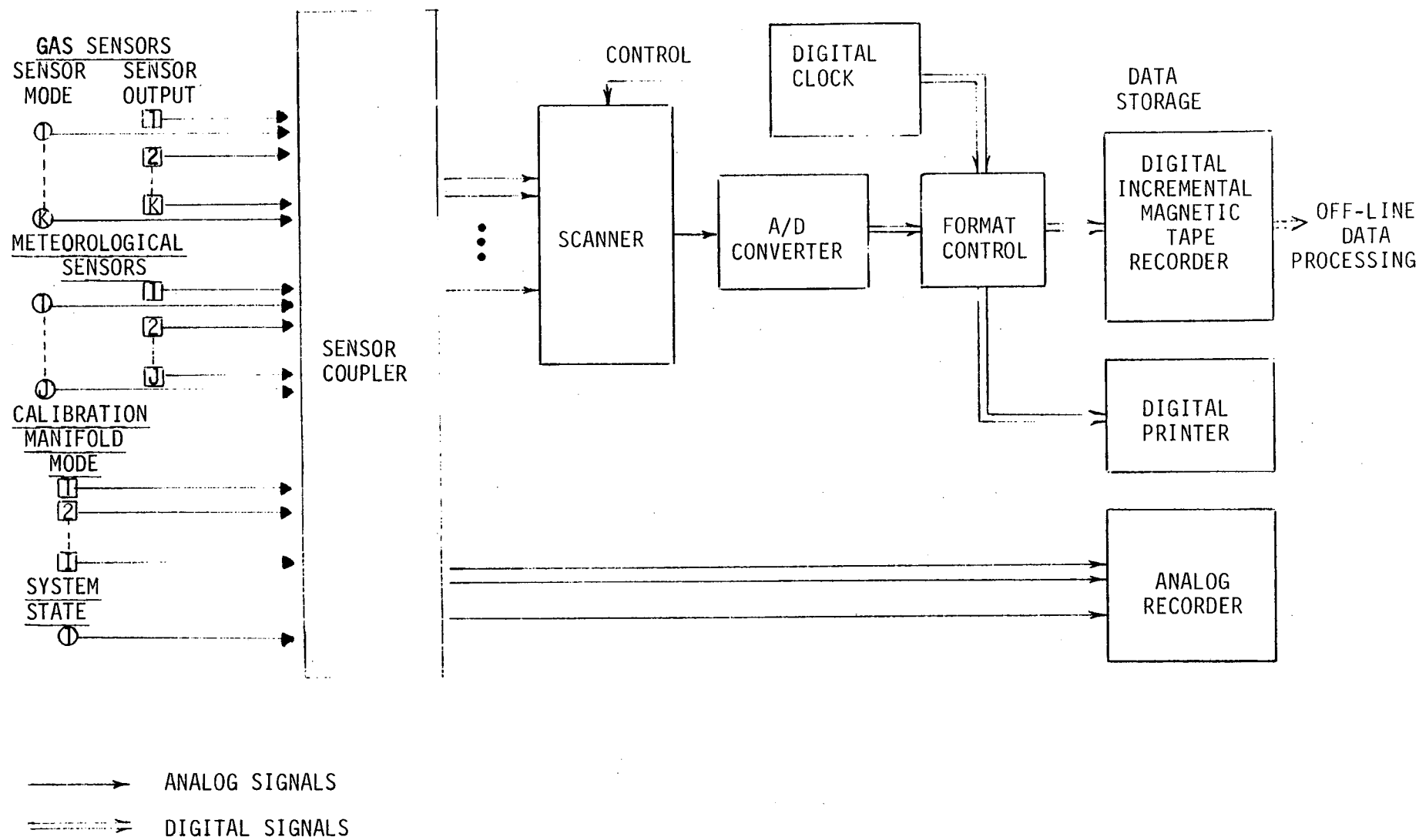
The basic purpose of the data acquisition system was to automatically acquire and record in digital form the output signals derived from the air monitoring instruments, meteorological sensors and manual data. The data acquisition system consists basically of the signal conditioning circuitry, on-line digital and analog recording systems and power supply units. The off-line data processing was an important consideration in nearly all aspects of the design of the data acquisition system.

A block diagram illustrating the functional relationships between the various subsystems which comprise the data acquisition system and a photo of the data acquisition system are shown in Figures 5.1 and 5.2. The system was so designed that data channels could be added or deleted without disturbing the digital recording system. The data was sampled in sequence once every 5 minutes and required approximately 12 seconds for a complete scan.

Manual data such as instrument mode or status were introduced into the system via the manual data entry channels. By utilizing codes the status or operational mode information was placed in the respective channels and utilized in the data processing phase to indicate the status of the respective sensors for each scan.

5.2 Automatic Calibration Technique

When evaluating a large number of air monitoring analyzers simultaneously, it is highly desirable to employ an automatic calibration system. The manual data entry modes shown in Table 5.1 were used to



MODE SWITCHES

DATA INPUTS

FIGURE 5.1 FUNCTIONAL DIAGRAM OF DATA ACQUISITION SYSTEM

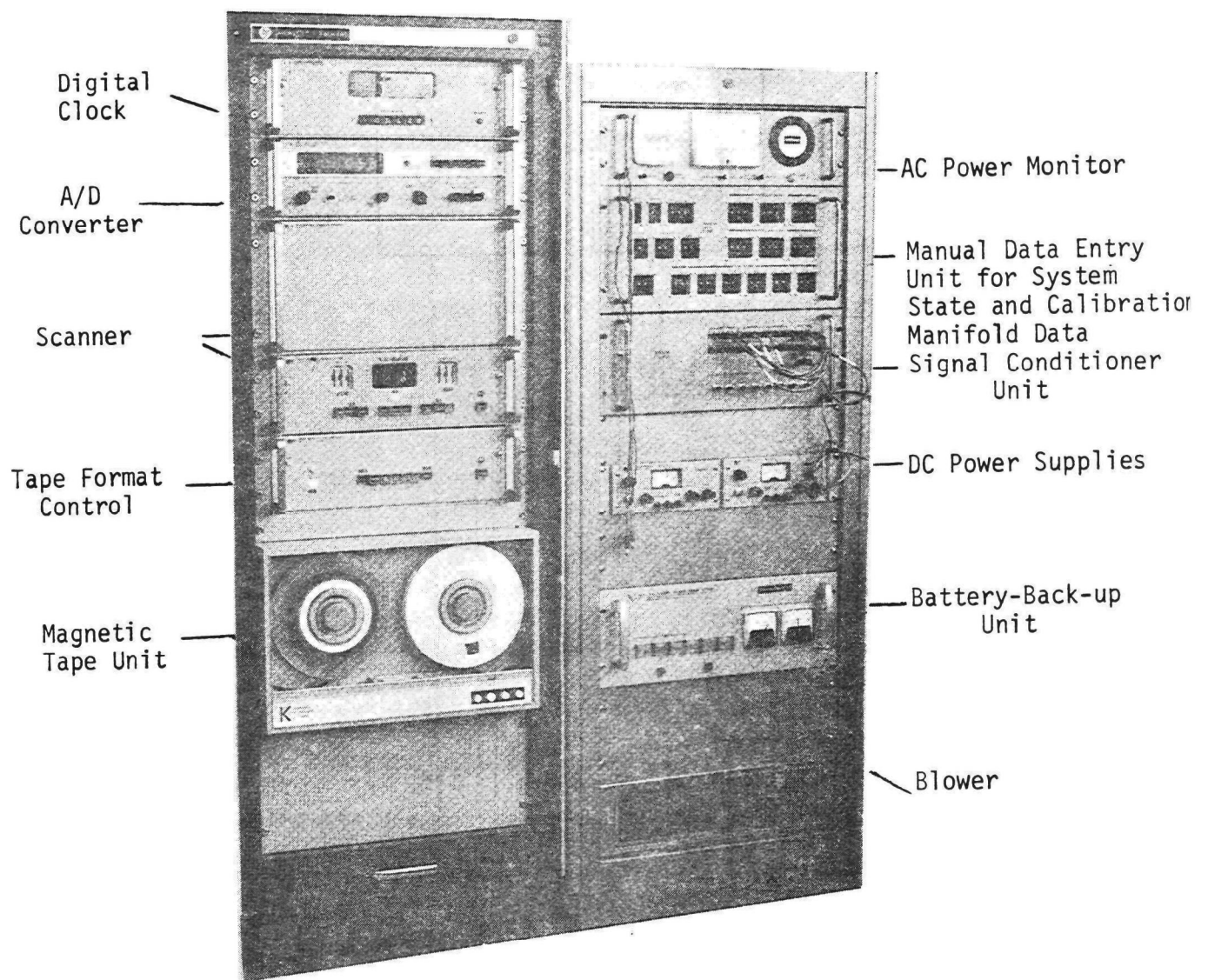


Figure 5.2 Data Acquisition System

indicate the different phases of calibration such as stabilizing, zero averaging and multi-point averaging. The concentration levels were set to the appropriate calibration values and simultaneously placed in the respective calibration channels and utilized in data processing to determine a best fit calibration curve for both linear and non-linear instrument response.

TABLE 5.1 INSTRUMENT OPERATIONAL MODES

<u>Output Symbol</u>	<u>Mode Switch Setting</u>	<u>Operating Condition</u>
	0	Measure - - - Valid Ambient Data
C	1	Calibration - Stabilizing
A	2	Calibration - Zero Averaging
B	3	Calibration - Multi-point Averaging
T	4	Routine Test Procedures
X	5	Offline - - - Not Set-up or Available
Q	6	Awaiting Repair
R	7	Repair
L	8	Awaiting Maintenance
M	9	Maintenance
99999		Data Not Available

A typical stripchart recording of the calibration technique is shown in Figure 5.3 and can be used to demonstrate the calibration procedure. Looking at the bottom of the stripchart recording the calibration is begun by changing the operational mode switch from "0" position to "1" position and introducing zero air into the ozone calibration manifold. Mode 1 is maintained while the instrument response is reaching equilibrium. The mode switch is now set to Mode 2 to indicate that the data is valid for determining V_0 , the instrument output voltage for zero air. The instrument is returned to Mode 1 completing the zero calibration. In the meantime, an ozone concentration of 0.055 ppm has been introduced into the calibration manifold. The voltage of the manual data entry channel for ozone is adjusted to read 0.055 volts using a 10-turn potentiometer and a digital voltmeter. After the analyzer reaches equilibrium the mode switch is set to "3" to indicate that the data is valid for determining V_1 in the transfer function described in Section 6.1 corresponding to $Y_1 = 0.055$ ppm. After several scans at this concentration level the mode switch is returned to position "1". These values establish one calibration point. The same procedure is repeated for concentrations of 0.097, 0.130, and 0.170 ppm of ozone and the analyzer is returned to the ambient air manifold. During the data processing this portion of the raw data was used to establish a new transfer function and to eliminate zero and span adjustments to fit a given voltage versus concentration response curve. Analyzer zero and span adjustments were made if the intercept (zero-level) or a slope of the transfer function changed by approximately 20 percent from the original transfer function. A computer printout demonstrating the automatic calibration procedure is shown in Figure 5.4.

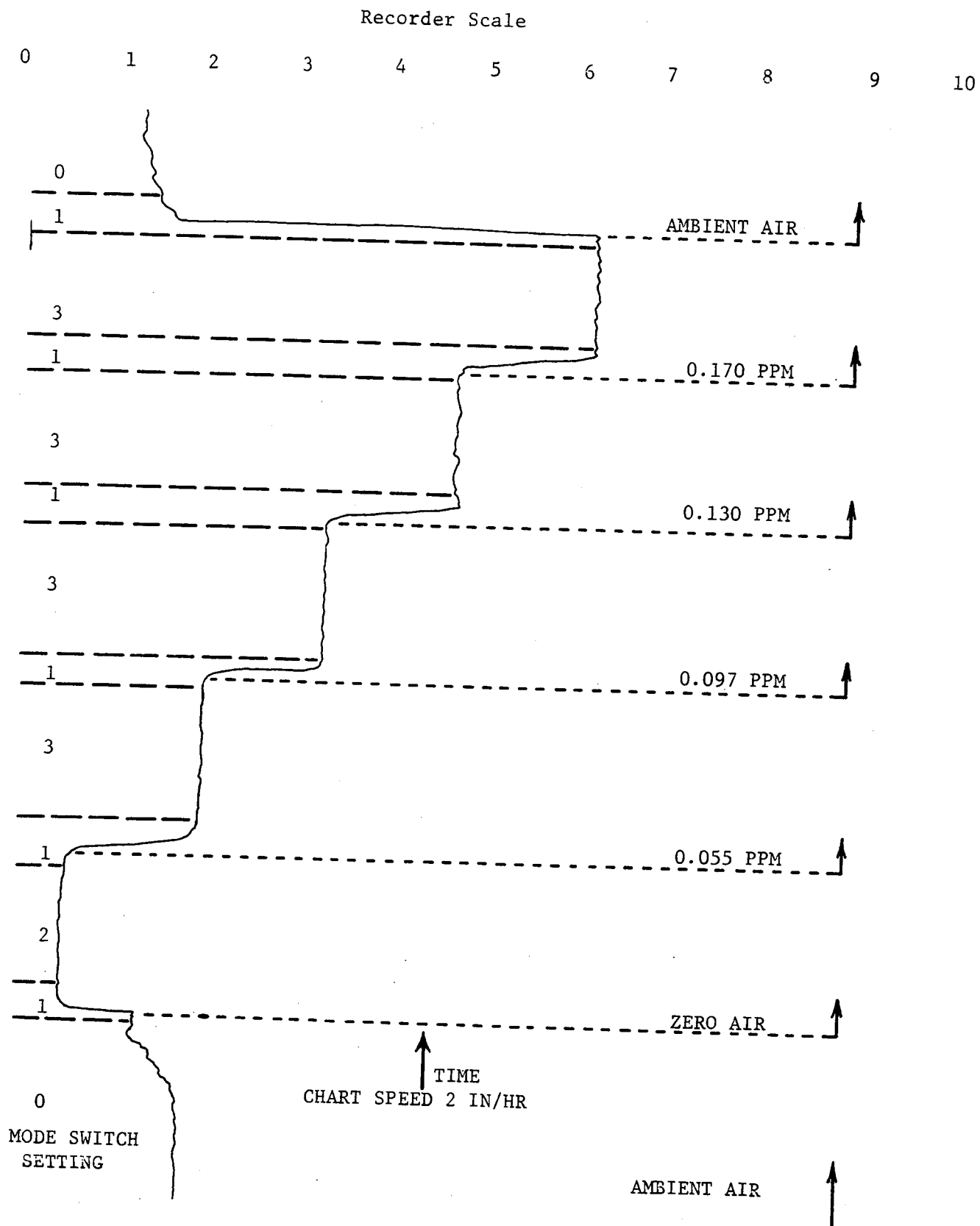


FIGURE 5.3. Automatic Calibration Procedure Showing Mode Switch Settings

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TIME (CST)	***** OZONE (PPM) *****		***** OXIDANT (PPM) *****			*****	
	CHEM1		COLOR	COUL1	AVG	(ADJ) COLOR	(ADJ) COUL1
1000	.000C	{ Stabilizing	.003C	.000C	99.999	99.999	99.999
1005	-.000C		.003C	0.000C	99.999	99.999	99.999
1010	-.000A	{ Zero Averaging	.002A	0.000A	99.999	99.999	99.999
1015	-.000A		.002A	.000A	99.999	99.999	99.999
1020	-.000A	{ Note: No zero drift since last calibration	.002A	0.000A	99.999	99.999	99.999
1025	.097C		.045C	.103C	99.999	99.999	99.999
1030	.100C	{ Stabilizing	.100C	.105C	99.999	99.999	99.999
1035	.101C		.104C	.105C	99.999	99.999	99.999
1040	.101C	{ Multi-point Averaging	.105C	.107C	99.999	99.999	99.999
1045	.102B		.106B	.107B	99.999	99.999	99.999
1050	.102B	{ 0.097 ppm Ozone	.108B	.109B	99.999	99.999	99.999
1055	.103B		.107B	.106B	99.999	99.999	99.999
1100	.016C	{ Note: Average drift since last calibration = +0.0053 ppm	.047C	.016C	99.999	99.999	99.999
1105	.015C		.023C	.015C	99.999	99.999	99.999
1110	.013		.022	.013	.018	99.999	99.999
1115	.012		.021	.013	.017	99.999	99.999
1120	.010		.020	.012	.016	99.999	99.999
1125	.007		.019	.011	.015	99.999	99.999
1130	.007		.017	.009	.013	99.999	99.999
1135	.006		.017	.010	.014	99.999	99.999
1140	.007		.017	.011	.014	99.999	99.999
1145	.007		.018	.011	.014	99.999	99.999
1150	.009		.018	.012	.015	99.999	99.999
1155	.010		.023	.013	.018	99.999	99.999

TIME (CST)	**** NITROGEN DIOXIDE ****			* OXIDES OF NITROGEN *		***** NITRIC OXIDE *****			
	COUL	UV	AVG	NOX	NOX-NO	UV	CHEM1	CHEM2	AVG
1000	.025	99.999X	.025	.037	.022	99.999X	.010	.015	99.999X .013
1005	.027	99.999X	.027	.039	.025	99.999X	.010	.014	99.999X .012
1010	.028	99.999X	.028	.044	.032	99.999X	.004	.012	99.999X .008
1015	.030	99.999X	.030	.048	.028	99.999X	.013	.020	99.999X .016
1020	.030	99.999X	.030	.056	.036	99.999X	.014	.021	99.999X .018
1025	.030	99.999X	.030	.049	.038	99.999X	.003	.011	99.999X .007
1030	.029	99.999X	.029	.048	.024	99.999X	.016	.025	99.999X .020
1035	.029	99.999X	.029	.046	.029	99.999X	.008	.017	99.999X .013
1040	.028	99.999X	.028	.030	.022	99.999X	.004	.008	99.999X .006
1045	.025	99.999X	.025	.033	.023	99.999X	.006	.011	99.999X .008
1050	.023	99.999X	.023	.038	.028	99.999X	.007	.010	99.999X .009
1055	.023	99.999X	.023	.032	.023	99.999X	.004	.008	99.999X .006
1100	.023	99.999X	.023	.029	.021	99.999X	.000	.008	99.999X .004
1105	.015C	99.999X	99.999	-.004C	99.999	99.999X	.000	-.002C	99.999X .000
1110	.005C	99.999X	99.999	-.004C	99.999	99.999X	.005	-.003C	99.999X .005
1115	.002C	99.999X	99.999	-.004C	99.999	99.999X	.003	-.002C	99.999X .003
1120	.001C	99.999X	99.999	-.003C	99.999	99.999X	.003	-.002C	99.999X .003
1125	.001A	99.999X	99.999	-.004A	99.999	99.999X	.004	-.002C	99.999X .004
1130	.000A	99.999X	99.999	-.003A	99.999	99.999X	.002	-.002C	99.999X .002
1135	.000A	99.999X	99.999	-.003A	99.999	99.999X	.005	-.002C	99.999X .005
1140	-.001C	99.999X	99.999	.113C	99.999	99.999X	.005	-.001C	99.999X .005
1145	.004C	99.999X	99.999	.313C	99.999	99.999X	.004	.001C	99.999X .004
1150	.023C	99.999X	99.999	.326C	99.999	99.999X	.009	.003C	99.999X .009
1155	.001C	99.999X	99.999	.329C	99.999	99.999X	.007	.003C	99.999X .007

FIGURE 5.4 Automatic Calibration Printout

6.0 COMPUTER PROCESSING OF FIELD DATA

6.1 General Data Processing Programs

Field data can be processed by computer either by real time monitoring of the instrument output or by the method of temporarily storing the data on magnetic tape and later processing the tapes. In this program, data stored on magnetic tapes were received weekly from the mobile laboratory in the form of digital voltages. The flow diagram in Figure 6.1 describes the treatment of the data from the time they were received on magnetic tape reels until they were printed in the various useful forms.

The calibration data for each instrument were programmed as a transfer equation [$y = M(V-V_0)$ or $y = M(V-V_0)^n$] to convert the voltages to appropriate physical units. The current calibration curves are automatically updated in this program when the calibration modes are switched by the operator. The five-minute data with respective manual entry operational modes and hourly averages are printed out with two hours of data per page.

6.2 Data Output

Average values, frequency distributions, and maximum hourly averages per day are calculated for all data output from Program 6.6. The diurnal averages and standard deviations for each analyzer were calculated from the 5-minute data output. These diurnal averages for each sensor were plotted against time with the standard deviation and case count included on each plot.

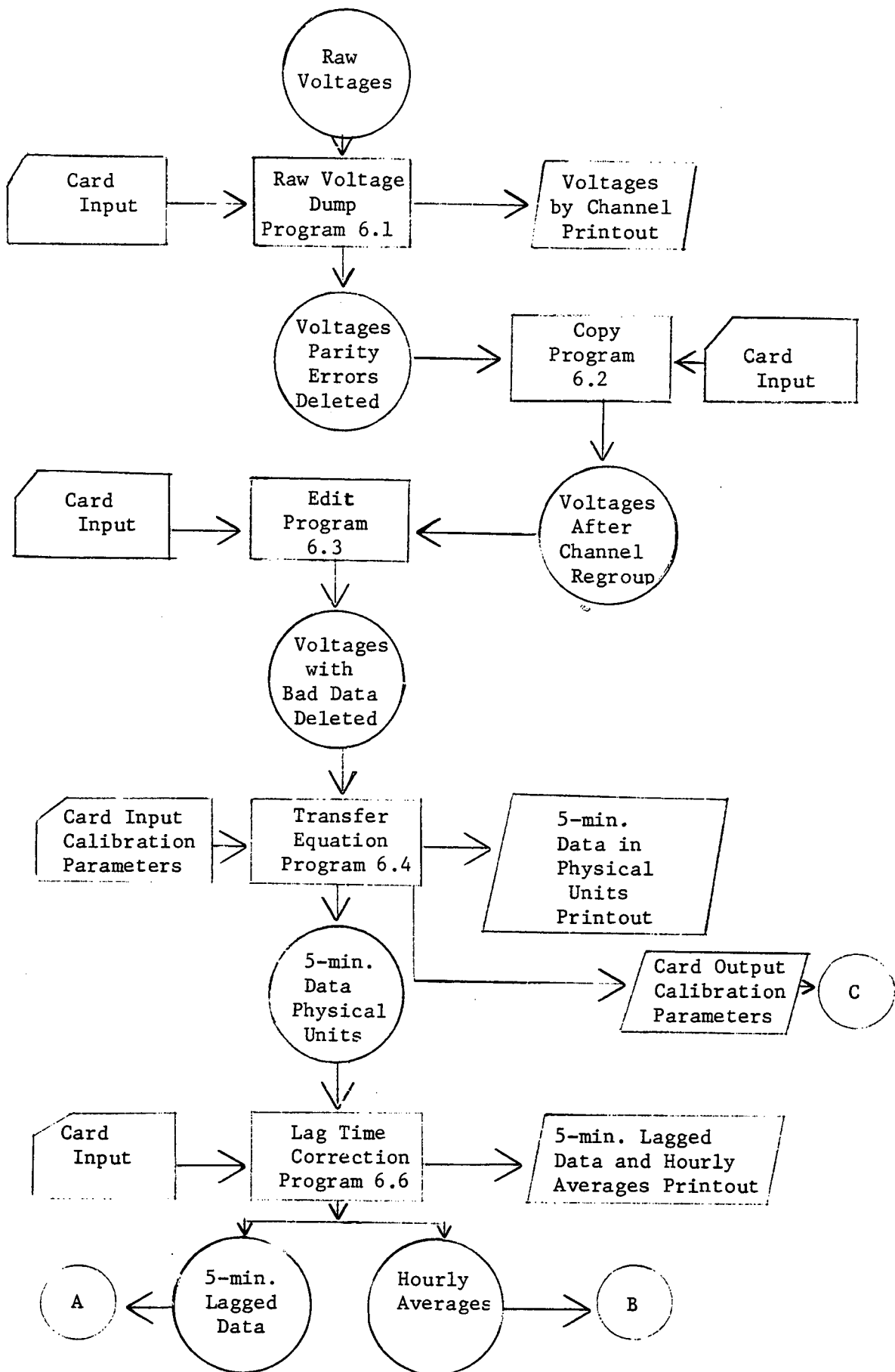


FIGURE 6.1 (a). Data Processing Flow Chart

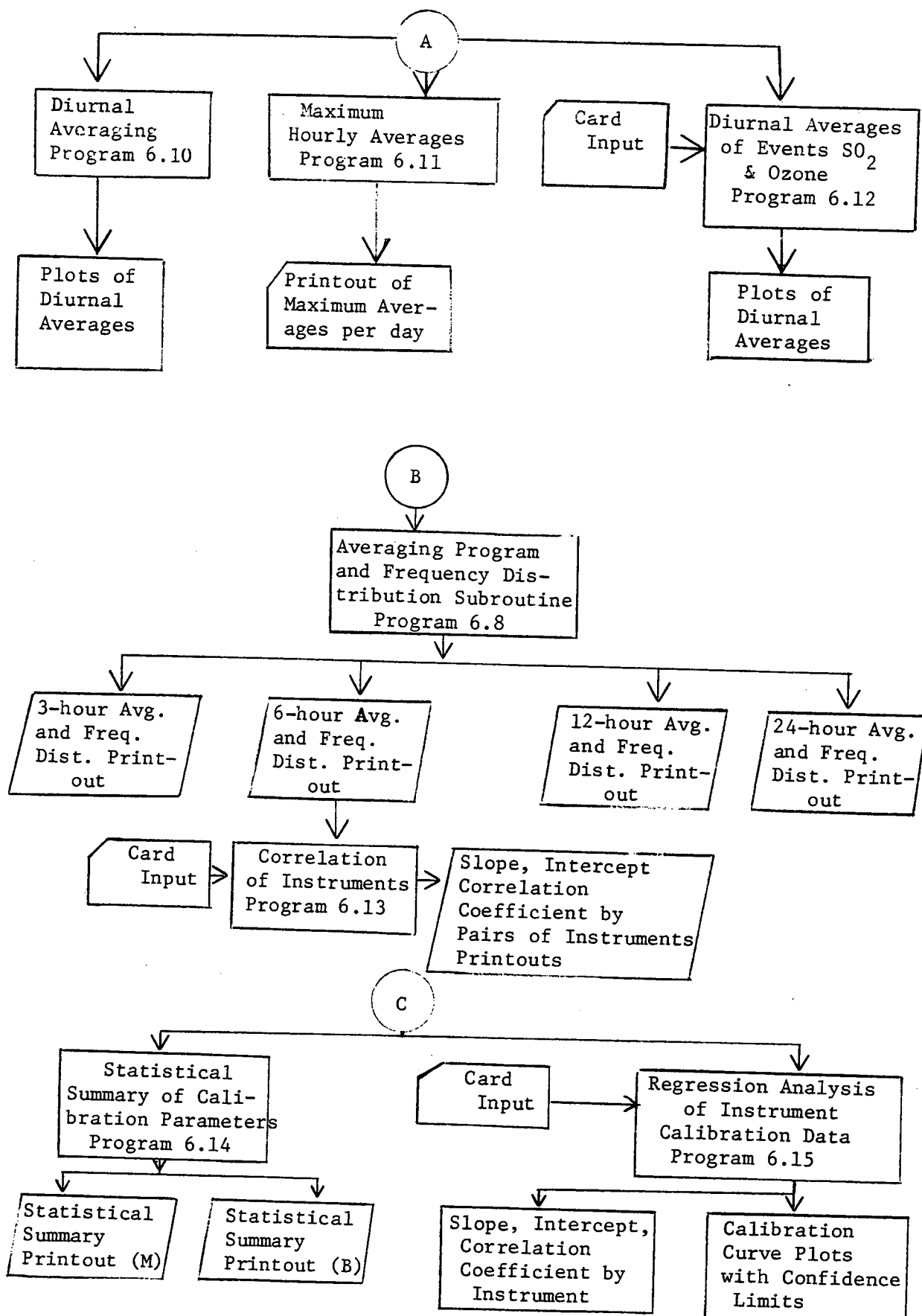


FIGURE 6.1 (b). Data Processing Flow Chart

Correlation of instruments measuring the same pollutants were performed using the output of Program 6.8 for all hours in which sensor pairs had valid data. In addition to the ambient air data analysis and regression analysis, a statistical summary of all instrument calibration data was performed. The mean, standard deviations, average drift per day, standard deviation of drift, and confidence limits were calculated using the output from Program 6.4.

7.0 INSTRUMENT EVALUATION

7.1 Performance Characteristics

A general set of performance criteria was established in the earlier report of the Los Angeles Study [1]. These criteria were based on instrument characteristics that are independent of the type of instrument being evaluated or the application in which it was to be used. Following this philosophy the evaluation program used performance data of one or more instruments operating under realistic field conditions to assess the level of performance in each of the important performance areas.

Instrument performance characteristics fall into four major groups. These are physical characteristics, measured responses to standard test procedures, field data quality, and functional capacity. Physical characteristics are usually obvious and worthy of only minimum analysis. Response times of the instruments measured using standard test procedures pose no significant problems in determination of values for comparison with suggested performance specifications [19]. However, lengthy response times require substantial time to obtain good multi-point calibrations. Field data quality was concerned with calibration requirements, stability, accuracy, and limits of detection. Performance in the area of functional capability was concerned primarily with instrument failure. The most obvious negative functional characteristics are instrument downtime and maintenance costs.

7.2 Calibration Stability

A summary of calibration data for a few selected performance factors is shown in Table 7.1. The selected data are typical for each

instrument during its best 90 day period of performance during the evaluation study. The minimum detectable concentration is estimated from the standard deviations of the intercept values of the calibration curve (transfer function). The standard deviation about the higher concentrations is equal to the minimum detectable change at the point of measurement on a long-term basis (approximately 65% confidence). On a short-term basis the variability would be expected to be much less and therefore a smaller minimum detectable change for an equivalent confidence level. This broadening effect with time is typical of stability estimates. Factors that are used to assess the minimum detectable change can thus be seen to depend upon the testing conditions.

Calibration data for the selected period were used to determine a single linear regression estimate of the transfer function and correlation coefficient for each instrument in Table 7.1. A higher correlation coefficient is indicative of greater long term stability of the analyzer. Many performance factors such as response time, interferences, maintenance time and physical parameters were described in earlier reports [1,2,3] and are worthy of analysis in choosing the proper instrument.

7.3 Operational Summary

Operational data are summarized in Table 7.2 for each analyzer evaluated during this program. The operational time is divided into the following categories: (1) ambient monitoring time, (2) calibration time, and (3) downtime. The ambient monitoring time category includes the percent of time that the instrument was available for monitoring. The calibration period includes only the percentage of time required for

calibrating the analyzer. The downtime data include repair, routine maintenance, awaiting maintenance, and awaiting repair.

The ozone/oxidant and sulfur dioxide analyzers group includes 8 instruments that were operational better than 93% of the evaluation period. Approximately one-half of the analyzers were operational 85% of the total time tested.

TABLE 7.1 Summary of Long Term Calibration Data

Instrument	Pollutant	Number of Calibration Points	Minimum Detectable Concentration (ppm)	Average Zero Drift (ppm/day)	Average Span Drift (%/day)	Correlation Coefficient
Bendix Env. Sci.	O ₃	23	0.0066	0.0001	0.072	0.882
Bendix Process	O ₃	105	0.0003	-0.0000	-0.128	0.998
RTI (Solid Phase)	O ₃	52	0.0004	0.0000	-0.074	0.992
Dasibi	O ₃	21	0.0011	-0.0001	-1.749	0.967
Beckman	O _x	67	0.0122	-0.0001	0.592	0.963
Mast	O _x	103	0.0003	0.0000	-0.129	0.993
Technicon	O _x	74	0.0118	-0.0004	-0.552	0.947
Beckman	NO ₂	74	0.0131	0.0000	0.518	0.978
Technicon	NO ₂	6	0.0192	----	---	0.993
Thermo Electron	NO ₂	49	0.0101	0.0000	0.505	0.995
Aerochem	NO	83	0.0042	-0.0001	0.083	0.998
Beckman	NO	38	0.1303	-0.0015	-0.066	0.824
Thermo Electron	NO	73	0.0075	0.0000	0.565	0.990
Beckman	SO ₂	65	0.0108	0.0003	0.128	0.990
Leeds & Northrup	SO ₂	60	0.0114	-0.0002	0.269	0.957
Melpar	SO ₂	20	0.0047	-0.0006	0.398	0.969
Philips	SO ₂	46	0.0039	-0.0000	-0.050	0.994
Pollution Monitor	SO ₂	14	0.0244	0.0009	-0.781	0.988
Technicon	SO ₂	23	0.0084	-0.0001	-1.620	0.983
Tracor	SO ₂	26	0.0097	0.0003	0.003	0.805
Technicon	H ₂ S	11	0.0047	0.0003	-2.320	---
Tracor	H ₂ S	16	0.0033	0.0007	0.000	0.958
Beckman	THC	35	0.1357	0.0067	-0.006	0.999
Power Design	THC	15	0.1318	-0.0000	-0.043	0.999
Beckman	CO	36	0.1275	0.0098	-0.045	0.999
Mine Safety Appliances	CO	26	0.786	-0.0124	3.033	0.852
Beckman	CH ₄	35	0.0077	0.0004	0.126	0.998

TABLE 7.2 Operational Summary

	Number of Days Tested	Ambient Monitoring Time (%)	Calibration Time (%)	Downtime (%)
Bendix Env. Sci. O ₃	94	94.7	2.9	2.4
Bendix Process O ₃	74	94.3	2.4	3.3
RTI (Solid Phase) O ₃	185	94.1	2.7	3.2
Dasibi O ₃	32	98.5	1.4	0.1
Mast O _x	256	94.2	3.3	2.5
Technicon O ₃	256	87.5	4.5	8.0
Beckman O ₃	65	90.0	5.5	4.5
Beckman NO ₂	154	81.1	5.9	13.0
Technicon NO ₂	90	78.4	3.6	18.0
Thermo Electron NO ₂	65	82.1	6.4	12.5
Aerochem NO	146	82.8	2.9	14.3
Beckman NO	84	41.5	33.9	24.6
Thermo Electron NO	65	83.6	6.9	9.5
Beckman SO ₂	95	94.9	3.6	1.5
Leeds & Northrup SO ₂	184	93.5	2.6	3.9
Melpar SO ₂	260	93.5	3.0	3.5
Philips SO ₂	260	86.0	2.4	11.6
Pollution Monitor SO ₂	124	57.3	2.8	39.9
Technicon SO ₂	90	74.4	4.0	21.6
Tracor SO ₂	205	67.0	2.7	30.3
Technicon H ₂ S	90	47.3	1.9	49.2
Tracor H ₂ S	199	67.0	2.7	30.3
Beckman THC	148	72.0	2.1	25.9
Power Design THC	139	85.0	1.0	14.0
Beckman CO	148	72.0	2.1	25.9
Mine Safety Appliances CO	124	82.5	3.7	13.8
Beckman CH ₄	148	72.0	2.1	25.9

7.4 Comparison of NO₂ Measurements by Chemiluminescent, Coulometric, Saltzman, and Jacobs-Hochheiser Methods

During the latter part of Phase II of the St. Louis Study, a study was conducted to compare the classical colorimetric procedures to measure NO₂ with chemiluminescent and coulometric NO₂ instruments. Included in this study was Beckman's coulometric NO₂ analyzer, Technicon's colorimetric analyzer, Thermo Electron's chemiluminescent NO₂ analyzer (NO_x-NO), and the Jacobs-Hochheiser 24-hour integrated method. This study is the first to compare the chemiluminescent and coulometric methods with the Jacobs-Hochheiser reference method.

Eighteen 24-hr Jacobs-Hochheiser samples were collected at 3-day intervals during the period October 14, 1971 to December 17, 1971. Table 7.11 includes the 24-hr average data for the instruments on the days when the reference method (Jacobs-Hochheiser) was run. Table 7.12 shows the correlation coefficients between the instruments and the Jacobs-Hochheiser reference method. The average of the absolute values for each instrument is also shown.

The average concentration of NO₂ as measured by the Jacobs-Hochheiser procedure for eight days when Jacobs-Hochheiser, chemiluminescent, coulometric, and colorimetric data were available, was 0.051 ppm. Average values obtained with the chemiluminescent, coulometric, and colorimetric (Saltzman) monitors were 0.046, 0.033, and 0.047 ppm, respectively. An agreement of better than 90% of absolute concentration of NO₂ was obtained among the Jacobs-Hochheiser, Saltzman, and chemiluminescent methods at this sampling site, when the mean concentration of NO₂ for a 24-hr period was below 0.1 ppm.

TABLE 7.11. Nitrogen Dioxide Method Comparison Study

DATE	BECKMAN NO ₂ (PPM)	THERMO-ELECTRON NO _x -NO (PPM)	J-H* METHOD (PPM)	TECHNICON SALTZMAN** (PPM)
10-14-71 ^A	0.056	---	0.060	0.036
10-18-71 ^A	0.021	---	0.038	0.023 ^B
10-21-71 ^A	0.035	---	0.055	0.061 ^B
10-25-71 ^A	0.041	---	0.052	---
10-28-71 ^A	0.055	---	---	0.047
11-1-71 ^A	0.021	0.023	0.036	0.046
11-4-71 ^A	0.031 ^B	0.052 ^B	0.055	0.040
11-9-71	0.023	0.052	0.042	0.038
11-12-71	0.066	0.085	0.082	0.068
11-16-71	0.059	0.090	0.079	0.069
11-19-71	0.012	0.006	0.031	0.034
11-23-71	---	0.040	0.064	0.048
11-26-71	---	0.027	0.054	0.038
11-30-71	0.018	0.020	0.034	---
12-3-71	0.026 ^B	0.032 ^B	0.050	---
12-7-71	0.023	---	0.044	---
12-10-71	0.021	0.032	0.030	---
12-14-71	0.027	0.039	0.058	0.047
12-17-71	0.021	0.022	0.023	0.031

* Jacobs-Hochheiser Method

** Technicon Saltzman from St. Louis County Hunter Road Station

^A 24-hour period from 0900 hours on date given to 0900 hours next day and all other data 0000-2400 hours on given date.

^B Sensor data available for more than 12 hours, but less than 24 hours.

TABLE 7.12. Correlation Coefficients and Average NO₂ Values

	<u>Correlation Coefficients</u>	<u>Average NO₂ (PPM)</u>	<u>Case Count</u>
Thermo Electron (NO _x -NO) (CHEM 2)		0.041	
Beckman NO ₂ (COUL)	0.945	0.038	9
Beckman NO ₂ (COUL)		0.032	
J-H* Method (COLOR)	0.911	0.047	14
Thermo Electron (NO _x -NO) (CHEM 2)		0.043	
Saltzman (COLOR)	0.894	0.047	9
Thermo Electron (NO _x -NO) (CHEM 2)		0.040	
J-H* Method (COLOR)	0.849	0.049	11
J-H* Method (COLOR)		0.053	
Saltzman (COLOR)	0.823	0.045	11
Beckman NO ₂ (COUL)		0.038	
Saltzman (COLOR)	0.699	0.046	9

* J-H is Jacobs-Hochheiser Method

7.5 Comparison of SO₂ Measurements by Coulometry, Flame Photometry, and Modified West-Gaeke Procedure

Twenty-four hour integrated bubblers were run at 3-day intervals and analyzed using the Modified West-Gaeke reference procedure during the period October 14, 1971 to December 17, 1971. These measurements were compared with measurements obtained with the Philips coulometric and Melpar flame photometric analyzers. Table 7.13 is a tabulation of the correlation coefficients of the SO₂ monitors with the 24-hour West-Gaeke method. The average value of the 24-hour measurements for each analyzer is also included. The coulometric analyzer had the best correlation with the West Gaeke procedure with a value of 0.933. The average concentration of SO₂ as measured by the West-Gaeke procedure was 0.026 ppm, while values obtained with the coulometric and flame photometric analyzers were 0.016 and 0.006 ppm, respectively.

TABLE 7.13. Correlation Coefficients and Average Values for SO₂ Principles Tested

<u>Instrument</u>	<u>Correlation Coefficient</u>	<u>Average SO₂ (PPM)</u>
Melpar SO ₂ (FPD)	0.830	0.006
Philips SO ₂ (Coul)		0.016
Melpar SO ₂ (FPD)	0.874	0.007
W-G* (Color)		0.026
Philips SO ₂ (Coul)	0.933	0.016
W-G* (Color)		0.026
W-G* (Color) #1	0.978	0.029
W-G* (Color) #2		0.029

*West-Gaeke Procedure

8.0 AIR POLLUTION SUMMARY

8.1 Los Angeles Study [September 4 to December 1, 1970]

The ambient air monitoring that was performed at the Los Angeles site in the course of evaluating each instrument's performance indicated several characteristics of this environment. Diurnal averages, frequency distributions, and other pertinent data for each parameter are presented in the Interim Report for the Los Angeles Study [1].

A. Ozone

The ozone concentration was relatively high during the daylight hours averaging 0.033 ppm from 0600 to 1800 with maximum hourly averages above 0.1 ppm between 1200 and 1500 hours. Occasionally, nighttime ozone was observed. The ozone standard of 0.08 ppm maximum hourly average was exceeded 151 times during the 90 day evaluation period.

B. Oxidant

The primary oxidant was ozone. On many occasions ozone concentrations were actually higher than indicated oxidant values, due to SO₂ interference with oxidant readings.

C. Nitrogen Dioxide

Sustained levels of NO₂ were observed with hourly averages above 0.1 ppm about 33% of the time. The twenty-four hour average for NO₂ exceeded 0.05 ppm fifty days during the 90 day evaluation period.

D. Sulfur Dioxide

Sulfur dioxide levels were relatively low with a daylight average of 0.011 ppm. Hourly averages frequently rose above 0.030 ppm and on four occasions, real time peaks were between 0.1 and 0.15 ppm. Other sulfur compounds such as H₂S and mercaptans were generally below the minimum detectable level of the instrument.

8.2 St. Louis Study: Phase I (May 13 to August 17, 1971)

The availability of more than one instrument measuring the same environment provides the option of selectively screening the data in a manner that is designed to improve the estimate of air quality. Data on air quality determined during the period of time May 13 to August 17, 1971 are summarized here. Diurnal averages, frequency distributions, plots of air pollution events, and other pertinent information are included in the Interim Report for the St. Louis Study: Phase I [2].

A. Ozone

Ozone concentrations are normally about 0.01 ppm at night and rise to approximately 0.06 ppm in the early afternoon. The average daily ozone concentration was approximately 0.030 ppm. During the daylight hours the ozone standard of 0.08 ppm maximum hourly average was exceeded approximately 15 percent of the time.

B. Oxidant/Nitrogen Dioxide

The primary oxidant in the St. Louis atmosphere was ozone, although atmospheric gases such as oxides of nitrogen contribute to the response of the oxidant instruments. The average daily concentration of NO was 0.010 ppm with NO₂ being 0.018 ppm.

C. Sulfur Dioxide

The average SO₂ level for the evaluation period was 0.010 ppm with peak hourly average concentration frequently in excess of 0.05 ppm. An inverse relationship between SO₂ and O₃ was observed.

D. Carbon Monoxide

Data on CO were considered to be less reliable than those for SO₂ and O₃. The average daily concentration was approximately 1 ppm.

E. Hydrocarbons

Total hydrocarbon concentration averaged 2 ppm during this period of time with the average methane concentration being 1.7. Non-methane concentration averaged approximately 0.3 ppm.

8.3 St. Louis Study: Phase II (October 7 to December 20, 1971)

Data regarding the air quality at the evaluation site during this period of time are summarized. Diurnal averages, frequency distributions, plots of air pollution events, and other pertinent information are included in the Interim Report for the St. Louis Study: Phase II [3].

A. Ozone/Oxidant

Typical ozone levels observed at the evaluation site during the afternoon were 0.04, 0.03, and 0.01 ppm for the months of October, November, and December, respectively. The nighttime ozone average for this period was 0.005 ppm. Overall average was approximately 0.01 ppm and constituted approximately 50% of total oxidant. The remaining 50% of total oxidant can not be attributed to oxides of nitrogen interference, since oxidant data were corrected for these interferences.

B. Nitric Oxide

Hourly averages of NO above 0.25 ppm occur almost every day and values of 0.50 ppm are frequent. The average for this period was 0.05 ppm.

C. Nitrogen Dioxide

Hourly averages of NO₂ above 0.05 ppm occur almost every day and concentrations of 0.08 ppm are frequent. The average for this period was 0.032 ppm.

D. Sulfur Dioxide

Typical SO₂ levels observed at the evaluation site at mid-day were 0.02, 0.03, and 0.042 ppm for the months of October, November,

and December, respectively. Overall average for the period was approximately 0.01 ppm. No measureable concentration of H_2S was observed during this period.

E. Carbon Monoxide

Hourly averages of CO above 4 ppm occur almost every day and values of 5-6 ppm are frequent. The average for this period was 1 ppm.

F. Hydrocarbons

Total hydrocarbons and methane averages for this period were 2.2 and 1.7 ppm. The daily average concentration was approximately 0.45 ppm. The average non-methane hydrocarbon concentration between 0600-0900 hours was 0.80 ppm.

9.0 SUMMARY OF FINDINGS

This field evaluation program has provided valuable information on instrument evaluation procedures, instrument performance, the effects of interferences, and the characteristics of the local environment. It has shown that the use of an environmentally controlled mobile laboratory, with automatic data acquisition and mode switch inputs that describe the operational status of each instrument and magnetic tape storage of data calibration information in computer compatible format, is a rapid and economical approach to a large scale instrument evaluation program. Noteworthy observations from each of the three studies are presented in the following paragraphs:

A) Los Angeles Study

1. Coulometric and conductimetric SO_2 measurements were generally higher than values obtained with the colorimetric West-Gaeke, flame photometric, and gas chromatographic-flame photometric analyzers.
2. In the oxidant category, the gas and solid phase chemiluminescent and the coulometric instruments exhibited excellent long term stability with a standard deviation near zero of about 0.001 ppm and a standard deviation about a single average calibration curve of less than 8 percent.
3. The following instruments were operational better than 96% of the time: gas phase O_3 , solid phase O_3 , flame photometric SO_2 , and gas chromatographic-flame photometric SO_2 .

B) St. Louis: Phase I

1. The Philips and Beckman Coulometric SO₂ instruments exhibited excellent long term zero and span stability with a standard deviation near zero of about 0.010 ppm and had a standard deviation about a single calibration curve of less than 5%.
2. Electronic and flow problems experienced during this study seriously impaired the Melpar flame photometric and Tracor gas chromatographic-flame photometric instruments.
3. The following ozone-oxidant instruments exhibited excellent long term zero and span stability with a standard deviation near zero of less than 0.010 ppm and a standard deviation about a single average calibration curve of less than 8 percent; Bendix gas phase O₃, RTI solid phase O₃, and Mast coulometric O_x.
4. Specific ozone measurements techniques are more reliable than adjusted ozone values obtained from non-specific total oxidants measurements that have been corrected for oxide of nitrogen and other interferences.
5. The Aerochem chemiluminescent instrument exhibited excellent long term zero and span stability with a standard deviation near zero of 0.011 ppm and a standard deviation about a single average calibration curve of 5 percent. The chemiluminescent technique is a major improvement in the measurement of nitric oxide.

6. The Beckman gas chromatographic-flame ionization analyzer required several field modifications before an acceptable level of performance was attained near the end of the study.
7. The following instruments were operational 99.5 percent of the time: Aerochem (NO), RTI (O₃), Melpar (SO₂), and Mast (O_x). Calibration during this study accounted for approximately 4 percent of this time.

C) St. Louis: Phase II

1. The coulometric SO₂ instrument exhibited excellent long term zero and span stability with a standard deviation of zero level of less than 0.005 ppm and a standard deviation about a single average calibration curve of less than 3 percent.
2. For this study SO₂ measurements obtained with a coulometric, a flame photometric, and a gas chromatographic-flame photometric analyzer were compared with measurements made with the reference method (modified West-Gaeke procedure). In general these analyzers displayed similar diurnal patterns; however, only the coulometric analyzer has a correlation coefficient with the West-Gaeke procedure of better than 0.933.
3. The following ozone-oxidant instruments exhibited good long term stability during the 75-day period with a standard deviation of zero level of less than 0.002 ppm

and a standard deviation of less than 7 percent about a single average calibration curve: (1) chemiluminescent O_3 and (2) coulometric O_x .

4. The chemiluminescent method is a major improvement in measuring nitric oxide. Good long term zero and span stability and excellent correlation were observed for NO measurements with both chemiluminescent analyzers.
5. Good correlation was obtained between the chemiluminescent and coulometric NO_2 measurements. The coulometric analyzer, however, recorded concentrations of NO_2 approximately 30 percent lower than the chemiluminescent analyzer.
6. This study was the first to compare chemiluminescent, colorimetric, and coulometric NO_2 analyzers with the reference method for measuring NO_2 (Jacobs-Hochheiser Method). The average concentration of NO_2 for eight sets of data as measured by the Jacobs-Hochheiser procedure was 0.051 ppm, while values obtained with the chemiluminescent, coulometric and colorimetric (Saltzman) monitors were 0.046, 0.033, and 0.047 ppm, respectively. An agreement of better than 90% of absolute concentration of NO_2 was obtained among the Jacobs-Hochheiser, Saltzman colorimetric, and chemiluminescent methods, at this monitoring site.
7. The average non-methane hydrocarbon concentration between 0600-0900 hours was 0.8 ppm. The standard for non-methane hydrocarbons is 0.24 ppm and was exceeded 75% of the time.

8. Acceptable measurements for carbon monoxide, methane, and total hydrocarbons can be obtained with the gas chromatographic-flame ionization analyzer, provided the proper purity of combustion and calibration gases can be maintained.
9. The following instruments were operational 98 percent of the time: (1) chemiluminescent O_3 , (2) coulometric O_x , and (3) coulometric SO_2 .

10.0 RECOMMENDATIONS

During the three phases of the evaluation program covering almost two years in time and about nine months of actual field testing, instrumentation based on new concepts in air pollution monitoring became commercially available and their performance was evaluated under field conditions. Most noteworthy of the new instruments were the chemiluminescent analyzers for measuring O_3 , NO, NO_2 , and NO_x . In addition, the GC-FID technique for measuring THC, CH_4 , and CO and the gas chromatographic-flame photometric technique for measuring H_2S and SO_2 appear to be satisfactory; however, improvements are needed to decrease maintenance requirements.

Recommendations for future instrument evaluation programs are as follows:

1. Standardized test protocol should be developed for determining performance characteristics, such as drift, accuracy, interference equivalent, etc.
2. Evaluation studies should include more than one model of any instrument for a more accurate assessment of its performance.
3. The duration of the evaluation period should be of sufficient length to identify weaknesses in the monitoring principle or design and to make appropriate adjustment.
4. On-line data processing would facilitate early identification of degradation in instrument performance.

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