

MONITORING FROM AIRBORNE PLATFORMS FOR AIR QUALITY ASSESSMENT

(SELECTED PAPERS)

MARCH 26-27, 1975

HELD AT THE

NATIONAL ENVIRONMENTAL RESEARCH CENTER

U. S. ENVIRONMENTAL PROTECTION AGENCY

LAS VEGAS, NEVADA

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FOREWORD

The Monitoring Applications Laboratory of the National Environmental Research Center in Las Vegas is very pleased to have sponsored this meeting on Monitoring from Airborne Platforms for Air Quality Assessment. In the past few years there has been a rapid increase in both the number and the objectives of aerial sampling missions. Concern over generalized environmental degradation and the potential impact of the accelerated energy resource development activities has contributed to the growth of aerial monitoring programs. With this in mind, the primary focus of the meeting was in exchanging information among the scientists and groups involved in performing and/or evaluating aerial platform measurements for environmental quality assessment. These proceedings should serve to promote uniformity in the application of technology that has been developed over these past few years. The technical papers are arranged in the order that they appear in the Meeting Program Agenda. The program and agenda were prepared by a Program Committee with Roy B. Evans as Chairman.

David N. McNelis

General Chairman
May 8, 1975



MONITORING FROM AIRBORNE PLATFORMS FOR ENVIRONMENTAL QUALITY ASSESSMENT
NATIONAL ENVIRONMENTAL RESEARCH CENTER-LAS VEGAS
Wednesday and Thursday, March 26 and 27, 1975

AGENDA

D. N. McNelis, General Chairman
NERC-Las Vegas

March 26

Welcome

J. R. McBride
Acting Director
NERC-Las Vegas

- - - - -

SESSION I
APPLICATIONS OF AIRBORNE PLATFORM MONITORING: KNOWN AND POTENTIAL

R. Neligan, MDAD, EPA
Session Chairman

Utilization of an Airborne Platform
in an Eastern, High-Ozone Concentra-
tion Study

J. J. B. Worth
Research Triangle
Institute

Measurement and Characterization of
the St. Louis Urban Plume

R. Husar
Washington University

Airborne Remote Monitoring in Air
Enforcement and Regulatory Programs

C. Ludwig
SAI

The Los Angeles Reactive Pollutant
Program

W. A. Perkins
Metronics

Assessment of Three-Dimensional
Pollutant Variability With Airborne
Platforms

D. L. Blumenthal
MRI

Measurements of Power Plant Plumes
With Light Aircraft

Dr. Paul Harrison
MRI

Assessment of the Impact of Halo-
carbons on Stratospheric Ozone

F. S. Rowland
University of
California-Irvine

SESSION II
EXPERIMENTAL DESIGN
R. B. Evans, NERC-LV
Session Chairman

Sample Size Requirements for
Statistical Validity

D. Mage
NERC-LV

Meteorological Considerations
for Statistical Validity

J. McElroy
NERC-LV

SESSION III
MEASUREMENT TECHNIQUES
R. Stevens, NERC-RTP
Session Chairman

March 27

Determination of Particulate
Chemical Composition

Ron Draftz
IITRI (Chicago)

Analysis of Size Fractionated
Aerosols

T. Dzubay
NERC-RTP

Particulate Size Measurement
Methods
Minnesota

K. Whitby
University of

Methods of Analysis of Halocarbons
Air Pollutants

N. Hester
NERC-LV

Instrumentation to Measure Gaseous
and Particulate Pollutants From
Airborne Platforms

R. Stevens
NERC-RTP

DATA VALIDITY AND DATA HANDLING

J. J. B. Worth, RTI
Session Chairman

Development of Standard Reference
Materials for Air Quality Measurement

E. Hughes
NBS

SESSION IV (Cont'd)

Measurement of Ozone and Oxides
of Nitrogen in the Lower Atmo-
sphere From an Airborne Platform

J. B. Tommerdahl
RTI

Instrument Time Response and Its
Implications

D. Mage
NERC-LV

Data Processing Related to Field
Data Acquisition Systems

R. Browning
NERC-RTP

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AIRBORNE REMOTE MONITORING
IN AIR ENFORCEMENT AND
REGULATORY PROGRAMS

Claus B. Ludwig
Michael Griggs
Science Applications, Inc.
La Jolla, CA 92038

The work upon which this presentation is based
was performed pursuant to Contract No. 68-02-2137
with the Environmental Protection Agency.

OVERVIEW

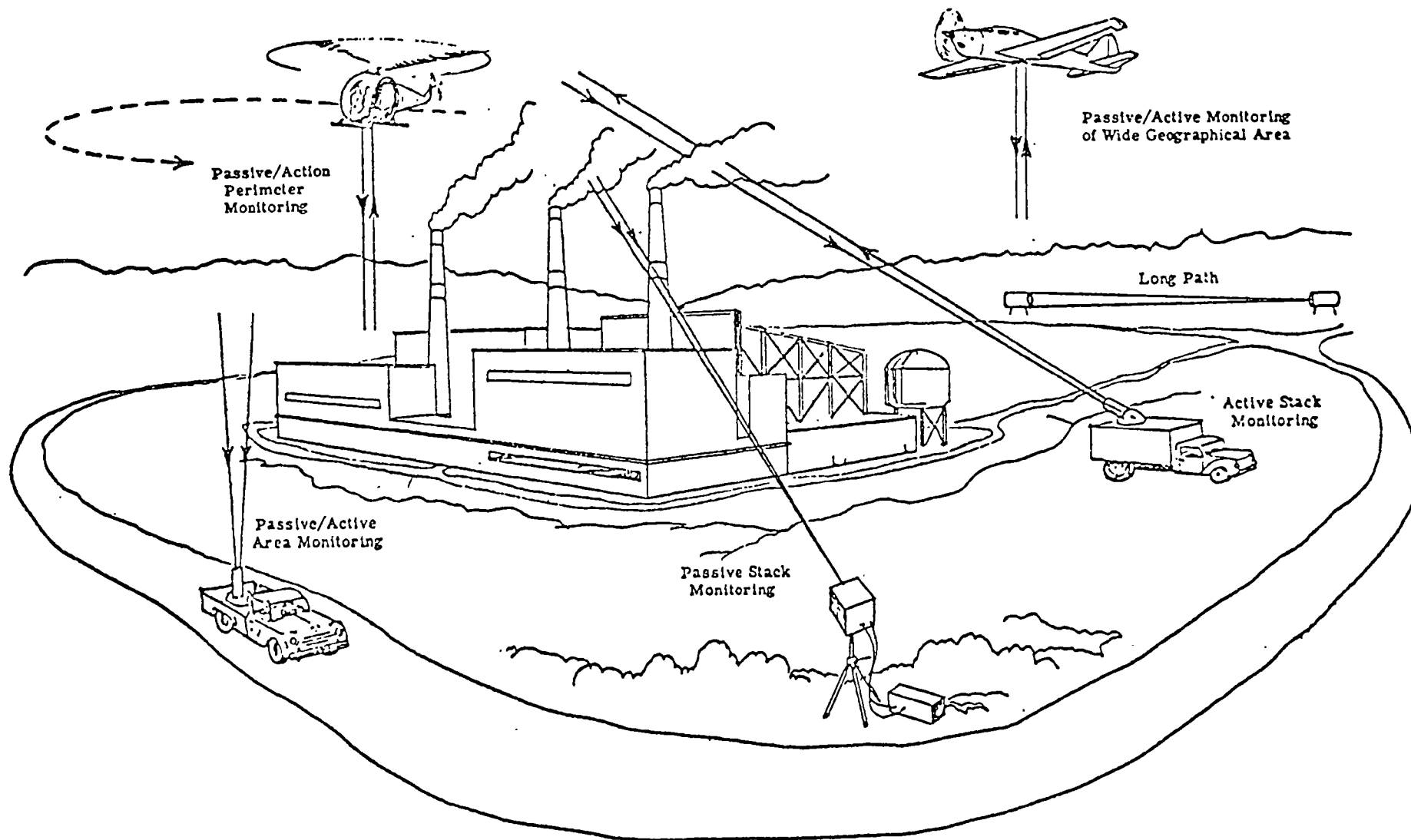
REMOTE SENSING TECHNIQUES CAN BE USED IN:

STACK EMISSION MONITORING

PERIMETER MONITORING

AMBIENT AIR QUALITY MONITORING

OVERVIEW OF REMOTE MONITORING USES



APPLICATIONS

- ENFORCEMENT
 - COMPLIANCE MONITORING (Evidence Presented to Plant Owner)
 - EVIDENTIARY MONITORING (Evidence Presented to Court of Law)
- ASSIST IN DEVELOPMENT OF REGULATIONS FOR
 - STANDARDS OF PERFORMANCE OF SOURCES
 - PERFORMANCE SPECIFICATIONS OF MONITORING EQUIPMENT
- SURVEILLANCE
 - ASSIST IN ENFORCEMENTS
 - WIDE AREA COVERAGE

ADVANTAGES

- COST EFFECTIVE
- INSTRUMENTS MORE OBJECTIVE IN OPACITY MEASUREMENTS
- MONITORING CLANDESTINE VIOLATORS
- NON-INTERFERING
- THE ONLY PRACTICAL WAY TO MONITOR WIDE GEOGRAPHICAL AREAS
- RAPID RESPONSE MONITORING

DISADVANTAGES

- POSSIBLE HIGH INITIAL CAPITAL COST
- LIMITED APPLICATIONS IN CERTAIN ATMOSPHERIC CONDITIONS
- CALIBRATION PROCEDURES AND EQUIVALENCY MORE COMPLICATED
- POSSIBLE SAFETY HAZARD FOR SOME LASER SYSTEMS

ENFORCEMENT MONITORING ---

• COMPLIANCE

- Presenting evidence to plant owner

• EVIDENTIARY

Court acceptance depends upon:

- Is the scientific principle underlying the instrument's operation valid?
- Does the instrument successfully embody and apply this underlying principle?
- Was the instrument in proper working order at the time of the test?
- Was the person conducting the test qualified to do so?
- Did the person conducting the test use the proper procedures?
- If different from the person conducting the test, is the person interpreting the test's results qualified to do so?

RECOMMENDED ACTION PLAN FOR
REMOTE TECHNIQUES

- make candidate technique available to field personnel;
- field personnel satisfied that technique produces reliable data;
- data introduced into court and test cases established;
- EPA develops and proposes performance specs (guidelines) for different source industries;
- performance specs promulgated;
- EPA develops and proposes performance criteria (equivalency) for different source industries;
- performance criteria promulgated.

NEW LEGAL ISSUES

RECENT RULINGS BY THE APPELLATE COURT IN WASHINGTON:

- There are no requirements for the use of a method of testing to observe possible violations of a standard (surveillance). (Portland Cement Association)
- However, if a method of testing is used as a standard, and if violations can result in enforcement actions, this method must be consistent with the statute and congressional intent (Clean Air Act), i. e., well-conducted and documented tests, response to public comments and specific citations in literature. (Portland Cement Association)
- The techniques used in arriving at the standards and in determining compliance with the standard should not differ significantly. (AMOCO Oil)
- There is no fixed requirement to promulgate standards and test methods at the same time. (AMOCO Oil)
- Statistical error must be smaller than the deviation from the standard. (AMOCO Oil)

WESTERN ENERGY DEVELOPMENTS

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STATEMENT BY RICHARD J. DENNIS, JR. (GENERAL COUNSEL, EPA)

"Courts are looking much more closely at test methods and technical support for standards than they once did. Therefore logical quantitative relationships between standards and tests used for compliance must be developed and clearly articulated in support of all EPA test methods. Mere reliance on agency "expertise" will no longer be adequate to withstand legal attacks on EPA standards and test methods."

NEW ADDITIONAL REQUIREMENTS

- Establish "Equivalency" between Reference and Remote Method
- Establish Stack Emission and/or Clean Air Standards by Remote Techniques

PERFORMANCE SPECIFICATIONS OF REMOTE MONITORS

Existing for Continuous Monitors	Additional Requirements
• Span (lower detectable limit to upper level which must be greater than the emission standard by a given factor) • Noise (usually 0.5 of the lower detectable limits) • Accuracy (percentage difference between values measured by the [remote] sensor and the applicable reference method) • Calibration error (absolute mean value plus 95 percent confidence interval) • Zero and calibration drift (absolute mean value plus 95 percent confidence interval) • Response time (rise and fall time to 95 percent) • Interference equivalent (influence on pollutant signal by interfering gases in plume)	• Range (minimum and maximum distance between source and observer, in which the instrument must give data with the specified accuracy) • Field-of-view (should be small enough for the source plume to fill the fov) • Interference equivalent (influence on pollutant signal by the intervening atmosphere as well as sky radiation beyond the plume) • Sampling time (involves integration time which will depend upon the plume turbulence) • Supporting plume data (velocity, temperature, etc.)

REMOTE vs. ON-SITE

- Supreme Court Decision in Western Alfalfa Case
 - Remote monitoring does not violate the 4th Amendment
- Possible New Argument
 - Since enforcement action can involve heavy penalties, on-site inspection without search warrant conflicts with the right of privacy guaranteed by the 4th Amendment (even though the Clean Air Act provides the right to enter). The use of remote sensing could provide the tool to prove probable cause for obtaining search warrant (J. B. Zimpritch)

**Assessment of Three-Dimensional Pollutant Variability
with Airborne Platforms**

by

D. L. Blumenthal

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Altadena, California 91001**

For presentation to Conference on Monitoring from Airborne Platforms for
Environmental Quality Assessment, National Environmental
Research Center - Las Vegas, March 26 and 27, 1975.

Introduction

The formation, distribution, and transport of air pollutants are three-dimensional phenomena. To properly understand them, measurements must be made throughout and above the surface mixing layer as well as at the surface. Instrumented light aircraft are effective, versatile, and relatively inexpensive sampling platforms for making these measurements.

This paper presents excerpts of data obtained and analyses performed during a two-year airborne sampling program in the Los Angeles basin, sponsored by the California Air Resources Board. The results presented here are intended to demonstrate the versatility of the airborne sampling technique and to show the types of analyses which can be performed using three-dimensional data. More extensive discussions of the data are contained in reports by Blumenthal et al., 1974.^{1, 2}

Sampling Program

The sampling program utilized two light aircraft, each of which made morning, midday, and afternoon flights over a preselected route on each sampling day. For reference, the three sampling routes normally used and a map of the L. A. basin are presented in Fig. 1. Only two of the three routes were flown on any one day. A typical flight consisted of a sawtooth pattern with about 8 to 10 vertical traverses (spirals). The aircraft would depart from an airport, climb to the top of the mixing layer over the next traverse point, and then spiral down (see Fig. 2). When the traverse point was at an airport, the aircraft would descend to within 10 feet of the ground; elsewhere, it descended to within 500 feet of the ground.

Both aircraft were equipped to measure continuously; O_3 , CO , NO_x , scattering coefficient, condensation nuclei count, temperature, turbulence, relative humidity, altitude, and position. All data were recorded in digital form on magnetic tape. The standard data format produced from the traverses was a series of graphs of pollutant concentration versus altitude (vertical profiles).

In addition to the aircraft data, extensive surface pollutant and meteorological data, as well as upper air wind data, were obtained for each sampling day. Analysis of the data yielded a great deal of information about both the chemistry and the transport processes at work in the L. A. basin. In addition, the combination of meteorological and pollutant parameters measured by the aircraft contributed to a better understanding of the meteorology of the basin than could be obtained by meteorological measurements alone.

Mixing Layer Structure

A key element in forecasting and understanding air pollution phenomena is an understanding of the mixing layer structure. Figure 3 is a vertical profile which clearly shows how pollutants are trapped beneath a slight temperature inversion. Above the inversion, the pollutant concentrations, as well as the turbulence indicative of the mixing, drop off. In the particular profile shown in Fig. 3, the temperature inversion clearly defines the top of the mixing layer; in other cases, however, temperature alone cannot be used to define the mixing depth, yet the pollutant parameters themselves still indicate a confined layer.

From the combination of all the vertical profiles from a flight, a mixing layer isopleth map can be constructed. These maps are useful in explaining the distribution of pollutant concentrations at the surface. Figure 4 is a mixing layer map showing the structure in

the L. A. basin during a mild "Santa Ana" condition. The region of low mixing layers is influenced by the sea breeze and contains the highest pollutant concentrations. The marine air is trapped under warmer air aloft. The regions of high mixing height indicate the influence of the hot desert winds from the north and east. In these regions, the sea breeze and desert winds converge, pollutants are mixed through a deeper layer, and surface concentrations are lower.

Pollutant Budgets

Surface data alone can give an indication of health effects and of human exposure, but to develop control strategies, the sources, total pollutant budgets, and transport patterns should be understood. In a location such as the L. A. basin, the mixing depth can change rapidly and three-dimensional data are required to estimate pollutant budgets.

A useful technique for studying the total pollutant budget within an air mass is to integrate the pollutant concentration through the depth of the mixing layer, thus obtaining the total pollutant burden over a point on the ground. This technique lets one follow the growth of the pollutant burden in the air mass as the air moves along a trajectory and yet takes into account changes in depth of the mixing layer along the way. This method was used to analyze the data within the envelope of possible trajectories of air arriving at Redlands at 1800 PDT on July 25, 1973 (Fig. 5). The envelope shown in Fig. 5 was constructed from both surface and upper air winds. Pollutants arriving at Redlands at 1800 originated somewhere within the envelope. When aircraft data were available for a given point within the envelope, an actual integration was performed. In some locations, however, ground data were used to supplement the aircraft data. In these cases, the ground concentration was assumed constant throughout the mixing height and was merely multiplied by the prevailing height in the area. Mixing layer heights were determined from the aircraft soundings and interpolated between soundings.

Figure 6 shows how integrated contaminant loadings within the surface mixed layer changed along the trajectory to Redlands (RED). The aircraft data showed that pollutants were well mixed within the mixing layer and that the top of the surface mixing layer was always well defined.

Although there is considerable scatter in the data, the trends are quite clear. There are large increases in the loadings of CO, O₃, and visibility-reducing particulates between the coast and the boundary between the western and eastern portions of the basin (near Brackett [BRA]) across an area which includes most of the emission sources in the Los Angeles basin. East of Brackett (BRA), loadings of CO actually declined, as local emissions in the eastern basin were apparently not sufficient to offset the effects of dilution or reaction. The emissions in the western basin were sufficient to account for the CO seen along the trajectory in the eastern basin. Ozone loadings east of Brackett remained relatively constant, possibly due to continued formation of ozone by previously emitted precursors and to the lack of fresh emissions to scavenge it.

Nearly all the CO in the Los Angeles atmosphere comes from the exhaust of motor vehicles. Motor vehicles are also the source of about 75 percent of the NO_x and 87 percent of the reactive hydrocarbons. Using CO as a tracer for ozone precursors which were not measured directly, we deduced that a large fraction of the ozone precursors introduced into the air mass sampled at Redlands was emitted in the western basin.

Another type of analysis which can be performed using 3-D data, but which is impractical with surface data alone, is the estimation of pollutant fluxes from one area to another. Both the budget and the flux type analyses are useful for developing control strategies. Figure 7

presents the result of a flux calculation performed for about 1700 PDT, July 25, 1973. The ozone flux from the western to the eastern portion of the L. A. basin was calculated using vertical profiles and wind data from pilot balloon soundings. The figure shows that enough ozone was being transported across the boundary between the two sections of the basin to cause the federal ambient air oxidant standard to be exceeded in the eastern basin, even with no local emissions.

Figure 8 is still another example of the use of 3-D data in determining pollutant budgets. Isopleths of scattering coefficient integrated through the mixing layer are shown for midday, September 20, 1972. Basically, the plot is an indication of the mass of light scattering aerosol ($0.1 < \text{aerosol diameter} < 1 \mu\text{m}$) within the mixing layer. This large concentration of aerosol was later shown to be transported eastward into the convergence zone shown earlier in Fig. 4. The transport was masked in the surface data, however, because the deepening mixing layer to the east caused a decrease in surface concentration, but not in total budget.

Layers Aloft

Pollutants which are trapped in layers aloft and are isolated from fresh surface emissions may have important effects on surface concentrations. For example, these upper layers can impinge on elevated terrain, or be transported long distances and then be reentrained within the surface layer when the mixing depth deepens enough to include them. Slow chemical reactions such as the conversion of SO_2 to sulfate or the reactions of nitrogen oxides and ozone to form nitrates can take place aloft without interference by fresh emissions or scavenging of reactants by the surface. The chemical and transport processes occurring within these layers can be most easily studied by an airborne sampling system. Some examples of layering phenomena follow.

One major type of mechanism for the creation of layers aloft is buoyancy. Warm point source plumes can penetrate into a stable layer and become trapped aloft. Likewise, solar heating of mountain slopes can warm nearby air and drive it aloft to an equilibrium elevation. Figure 9 is a vertical profile which shows a layer formed by upslope flow. Air from the surface layer which was normally confined by the slight inversion based at around 2500 feet was carried up the mountain slopes north of Rialto (RIA in Fig. 1) and then carried back over the basin. The heated air reached an equilibrium in the stable isothermal layer aloft. A layer of clean air can be seen between the two polluted layers.

Another mechanism for the creation of upper layers is shown in Fig. 10. This figure contains vertical cross-sections of scattering coefficient from the coast at Torrance (TOA) inland to Redlands (RED). Higher numbers indicate poorer visibilities or higher concentrations of particulates. This figure shows the effect of convergence between the sea breeze (westerly) and a mild Santa Ana wind (easterly). The high aerosol concentrations seen near Fullerton (FUL) in the midday cross-section were transported east by afternoon and then carried aloft in the convergence. Between 4000 and 5000 ft msl, some of the aerosol was actually carried back toward the coast by the upper winds.

A common type of mechanism in the Los Angeles basin for the formation of layers aloft is the undercutting of a portion of a previously well mixed layer either by an intrusion of cleaner and cooler sea air or by the formation of a nighttime radiation inversion. Figures 11 and 12 show the effect of undercutting by the sea breeze. Figure 11 is a vertical profile obtained at El Monte (EMT) after the passage of the sea breeze "front". Sea air containing relatively fresh emissions is seen up to about 1400 ft msl. The air between 1500 feet and 2500

feet was previously part of the surface mixing layer, but was isolated from the surface by the onset of the cooler marine air below. The pollutant ratios in the upper layer are indicative of an air mass in which the pollutants are relatively well aged compared to the surface layer. Figure 12 is a vertical b_{scat} cross-section from the coast at Santa Monica (SMO) to Redlands (RED) similar to the one in Fig. 10. The undercut layer from Fig. 11 can be seen to extend from the coast across the basin to the Pomona area (BRA), a distance of about 40 miles. This layer aloft was not detected by surface monitors, and the ozone concentration within the layer exceeded 0.5 ppm even near the coast.

An example of a plume trapped aloft is shown in Figs. 13 and 14. Figure 13 is another b_{scat} vertical cross-section for the northern portion of eastern L. A. basin. A relatively dense layer of aerosol was spread out over much of the eastern basin at about 1800 ft msl. This layer resulted from the plume from a power generation and steel mill complex near Rialto (RIA). The plume was buoyant enough to penetrate the surface based inversion and stable layer, but was trapped within the upper subsidence inversion. From Fig. 14, one can see that the plume and the surfaced based radiation inversion layer contained large amounts of primary pollutants which were photochemically "young". These data were obtained at night and the ozone was virtually completely scavenged within the plume and the surface layer. Other layers aloft above the plume, left over from the day before, still contained relatively high ozone concentrations and were well aged. These upper layers as well as the plume were reentrained as surface heating deepened the surface mixing layer.

A combination of many of the phenomena mentioned so far is shown in the vertical profile in Fig. 15. In this figure, the temperature profile by itself reveals little, if anything, about the structuring

of the pollutant layers, but the combination of parameters taken as a whole is quite revealing of both the chemistry and the meteorology. Using the pollutant parameters, a surface mixing layer can be clearly defined into which fresh pollutants were being emitted and in which some photochemical ozone production was starting to occur. Above that layer, a large buoyant plume of fresh pollutants can be distinguished. The high NO, condensation nuclei, and CO and the deficit of ozone identify this layer as containing relatively fresh emissions. Above the plume, a third layer can be seen which contained very well aged pollutants. The ozone and b_{scat} concentrations were well correlated and the primary pollutant concentrations were very low. This layer was still separated from fresh surface emissions and contained pollutants left over from the day before.

A look at Fig. 16 shows what happened later in the day. Surface heating raised the mixing layer, and all the layers up to 3000 ft msl were entrained. Above 3000 ft msl, a remnant of the layer left over from the previous day can still be seen. Without understanding the three-dimensional morning layered structure, the afternoon surface concentrations would be difficult to interpret and understand.

Special Effects

During the sampling program in the L. A. basin, several special experiments were performed to look at specific phenomena. During one of these, a series of north-south horizontal traverses was made at varying altitudes over Upland (CAB). Upon examination of the data, we saw that several bulges had occurred in the mixing layer and that in specific areas, pollutants were penetrating through the inversion for several hundred feet. A vertical cross-section of ozone concentration along one north-south route is shown in Fig. 17. The wind at the time was east-west and the bulges were shown to

coincide with the major roadways in the area. We believe that solar heating of the roads rather than auto exhaust is primarily responsible for generating the buoyancy necessary to distort the top of the mixing layer. The bulge near San Antonio Dam on Fig. 17 is probably due to surface heating of the mountain slopes adjacent to the dam.

Conclusions

From the data presented, one can see that the 3-D distribution of pollutant concentrations and the meteorological structure of the atmosphere can be very complex. In order to understand the evolution of surface concentrations and to devise effective control strategies, three-dimensional effects must be taken into account. Airborne monitoring systems have proven to be versatile and cost effective tools to obtain an understanding of the 3-D distribution and transport of pollutants.

REFERENCES

1. Blumenthal, D. L., et al., "Three-dimensional pollutant gradient study - 1972-1973 program," MRI 74 FR-1262 report to the California Air Resources Board, prepared under Agreement Nos. ARB-631 and ARB 2-1245 (1974).
2. Blumenthal, D. L., et al., "Determination of the feasibility of the long-range transport of ozone or ozone precursors," EPA-450/3-74-061, report to the Environmental Protection Agency under Contract No. 68-02-1462 (1974).

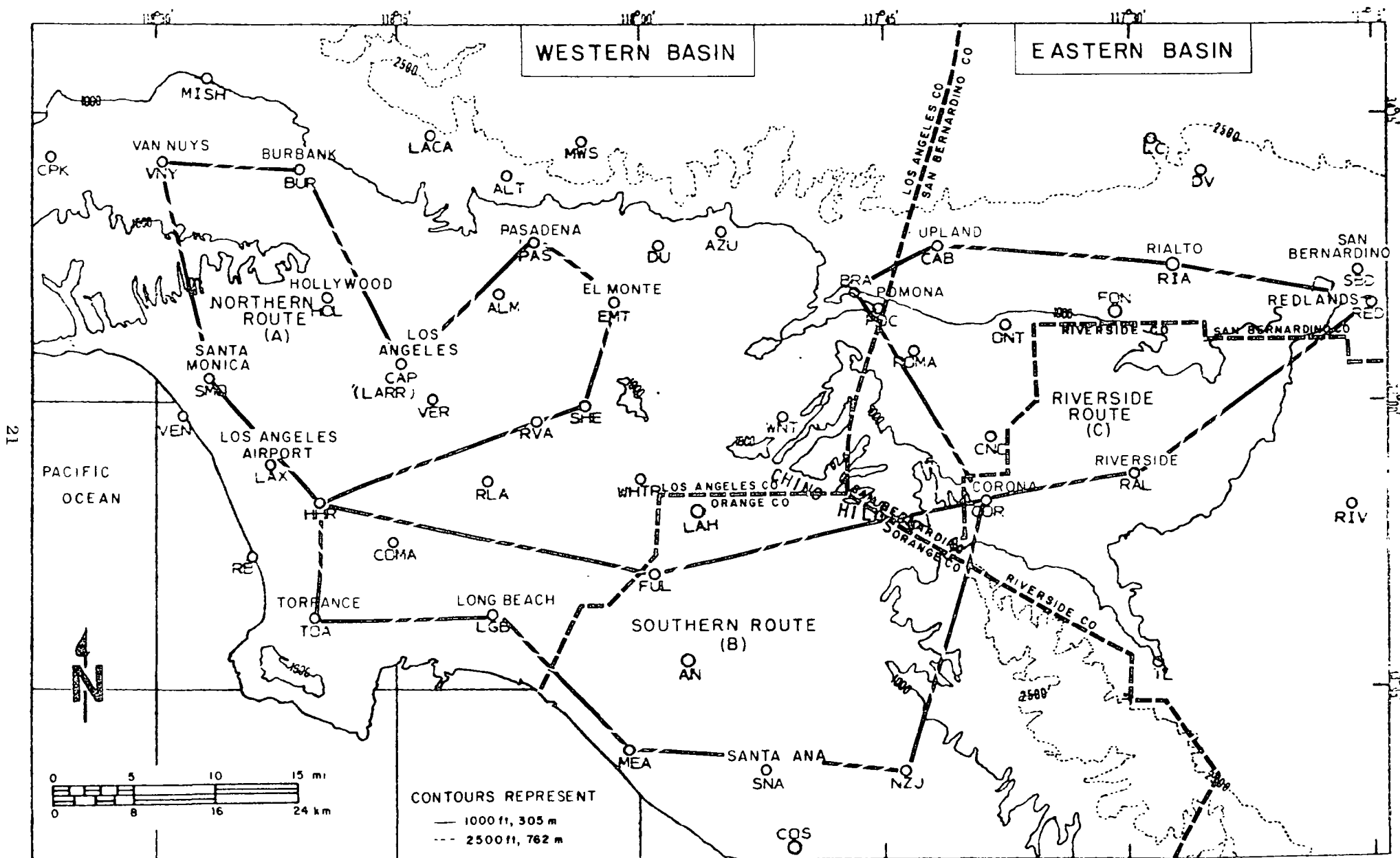


Fig. 1. SAMPLING ROUTES IN THE LOS ANGELES BASIN

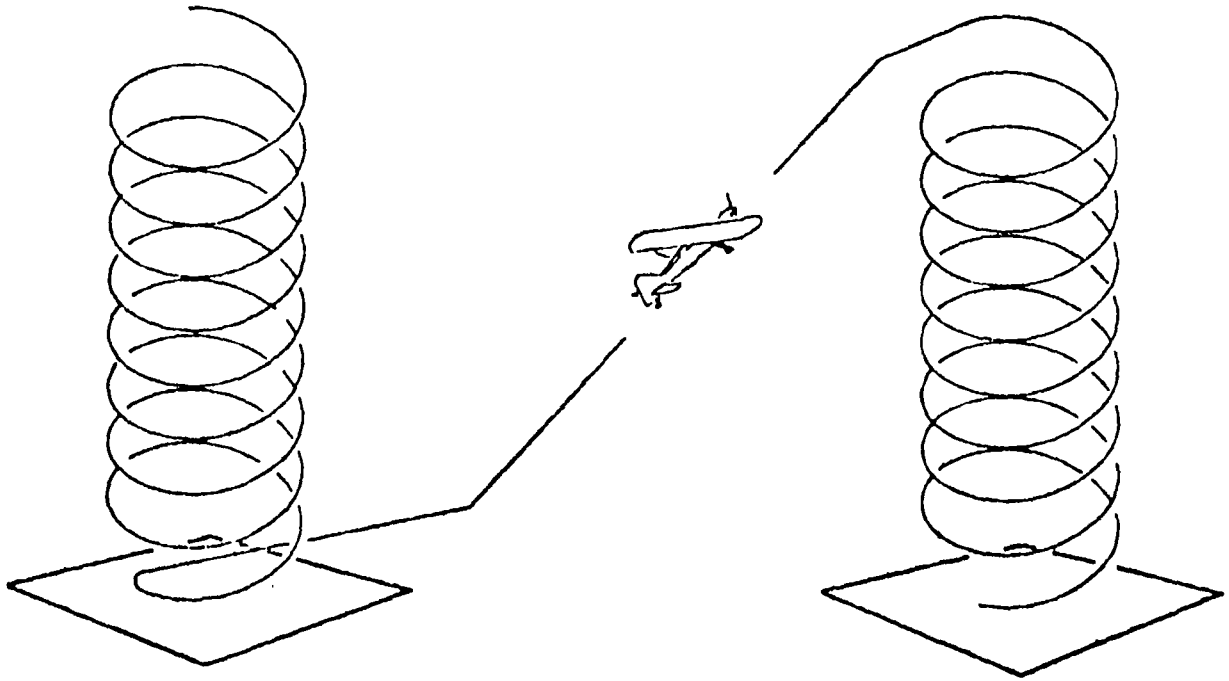


Fig. 2. VERTICAL PROFILE FLIGHT PATH

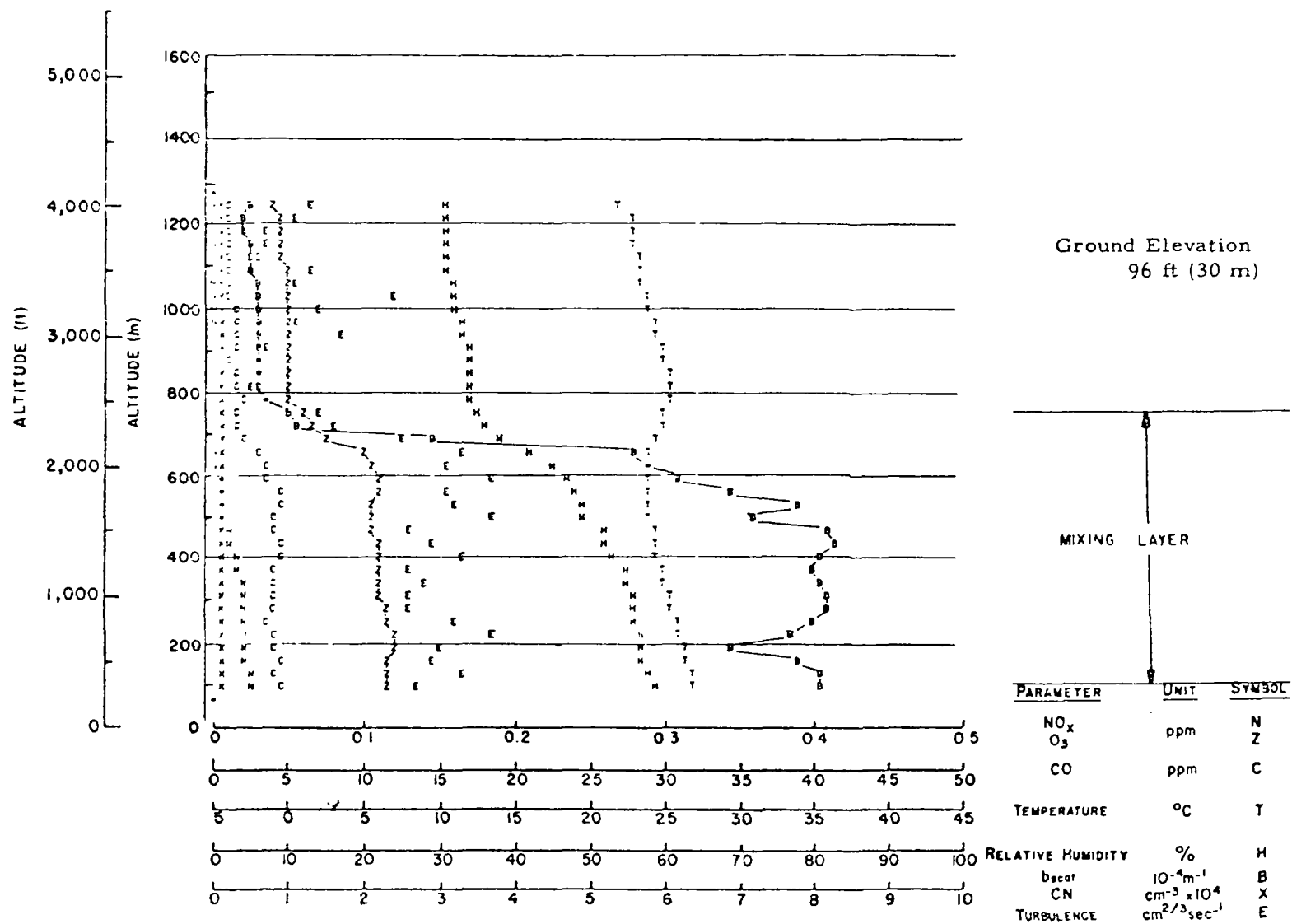


Fig. 3. VERTICAL PROFILE OVER FULLERTON (FUL)
SEPTEMBER 20, 1972, 1240 PDT

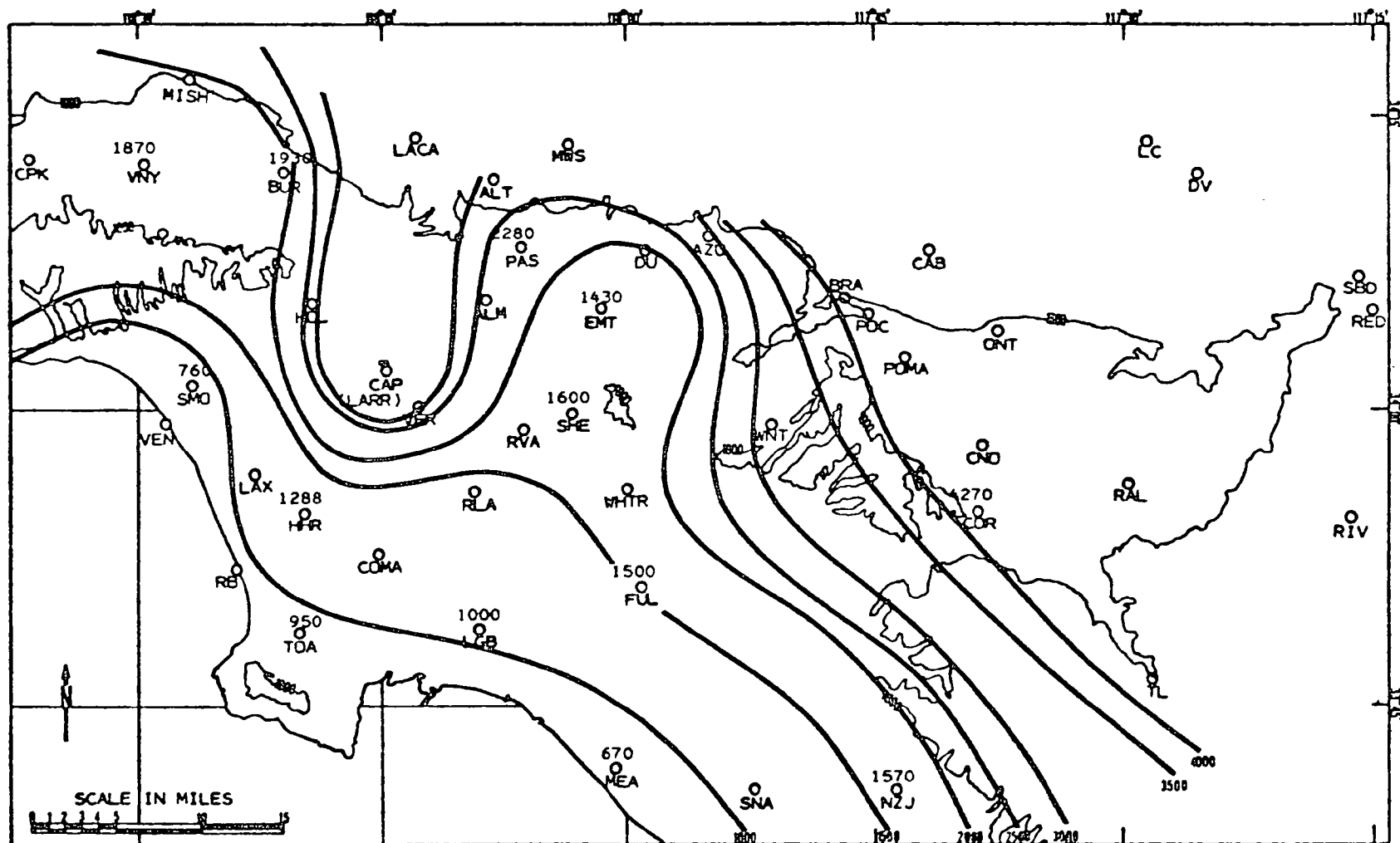


Fig. 4. MIXING LAYER HEIGHTS (ft) - AFTERNOON
September 20, 1972

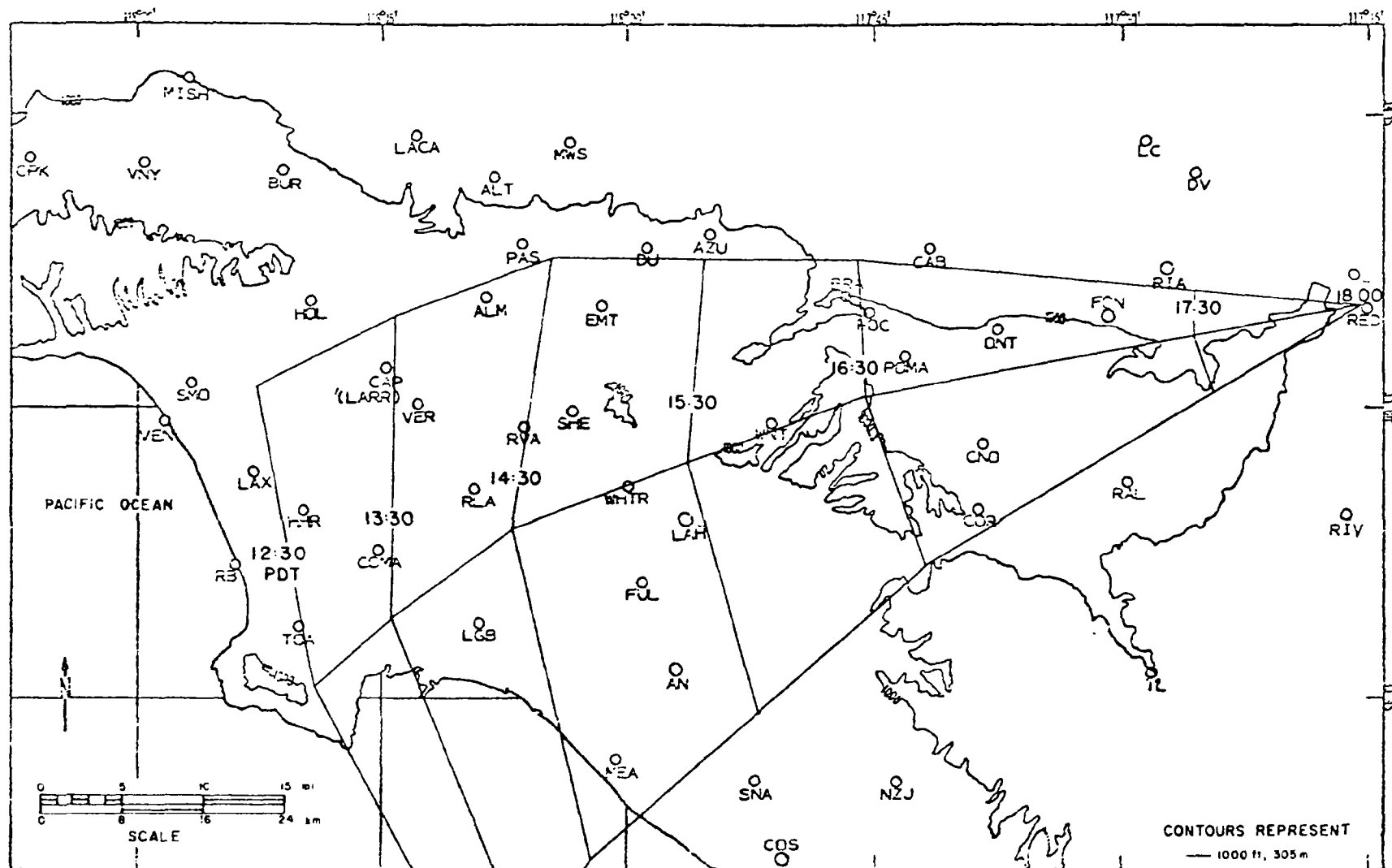


Fig. 5. TRAJECTORY ENVELOPE FOR AIR ARRIVING OVER REDLANDS AT 1800 PDT, JULY 25, 1973

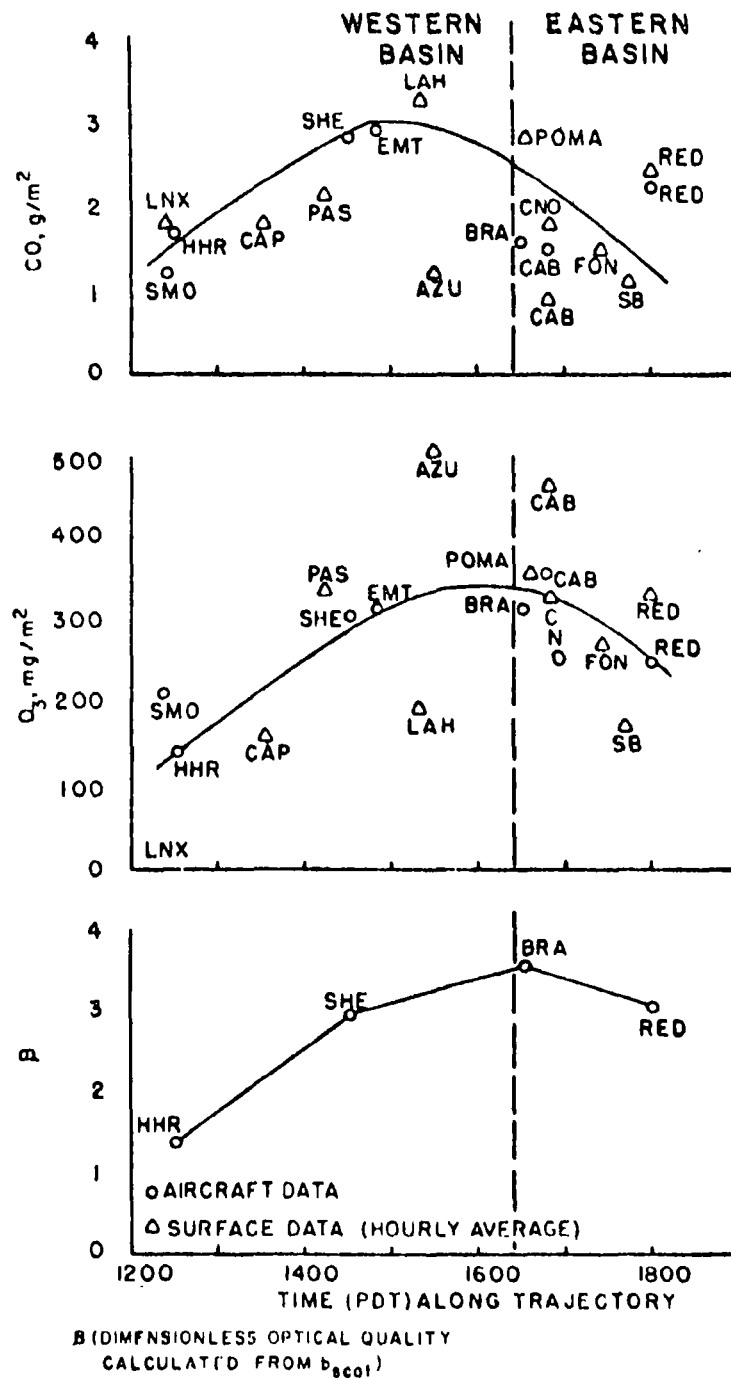


Fig. 6. POLLUTANT LOADINGS IN SURFACE MIXED LAYER ALONG TRAJECTORY ARRIVING AT REDLANDS IN AFTERNOON OF JULY 25, 1973. (Aircraft measurements plus estimates made from ground data and mixing height.)

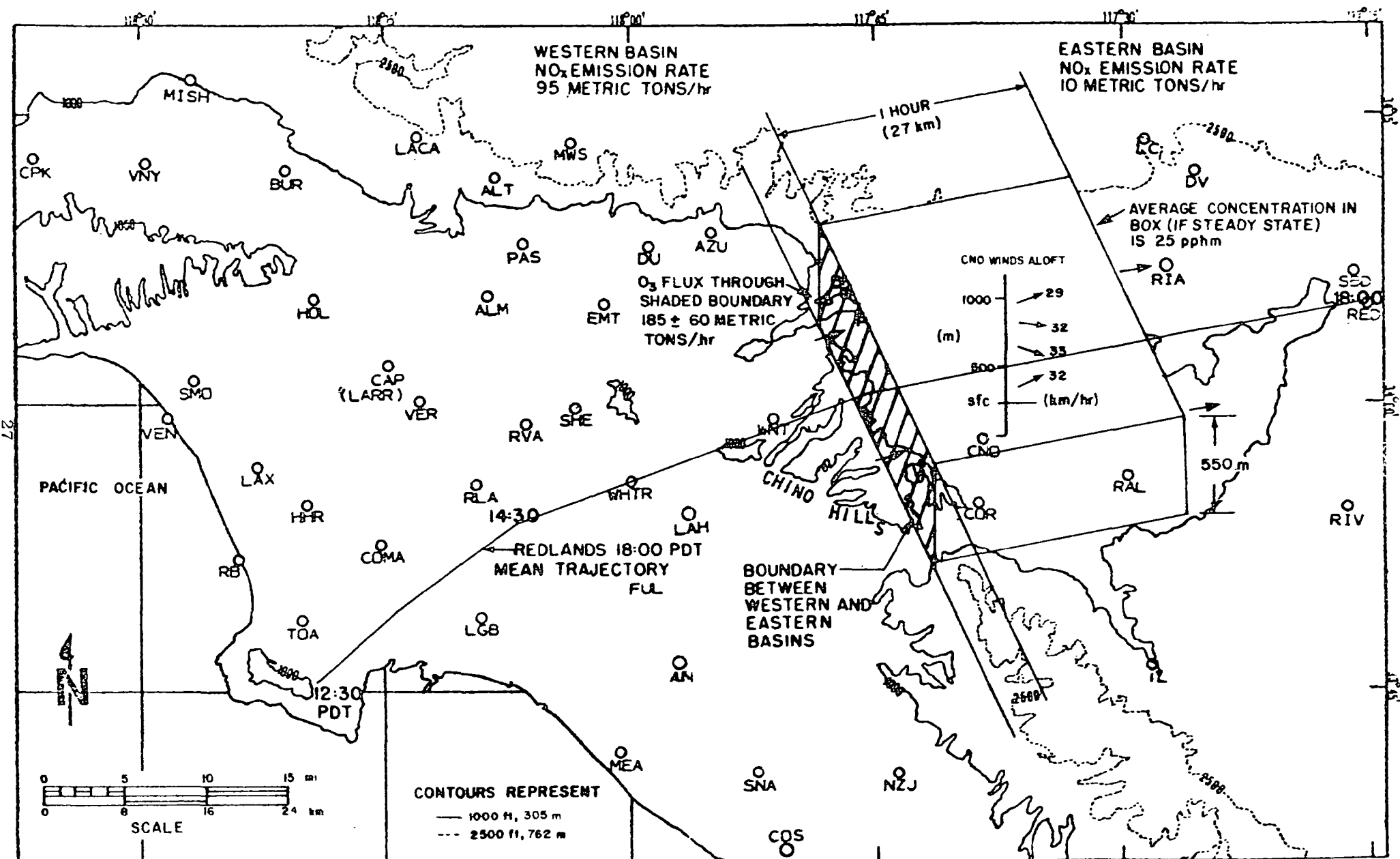


Fig. 7. ESTIMATED OZONE FLUX FROM WESTERN TO EASTERN BASIN, JULY 25, 1973, 1700 PDT

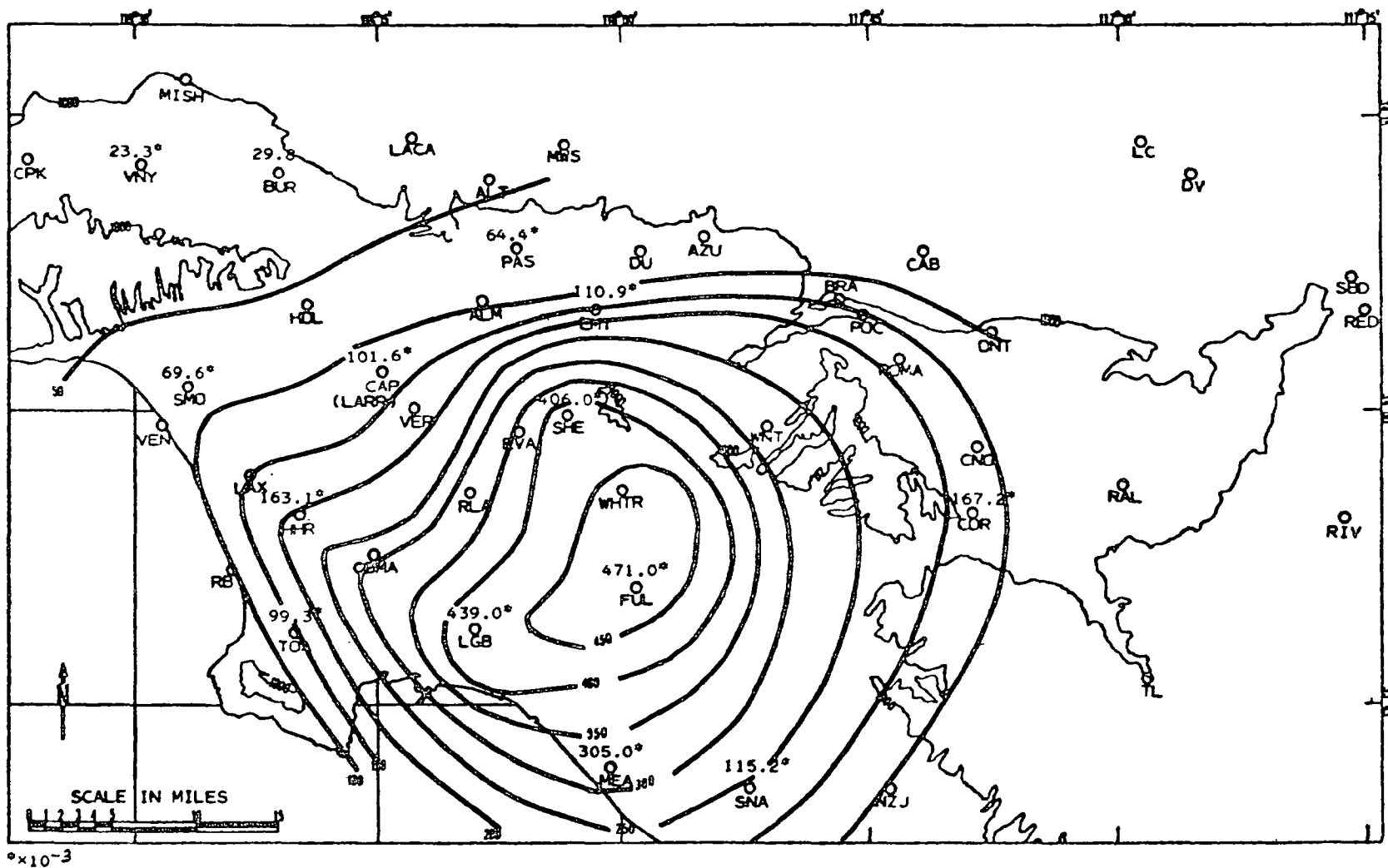


Fig. 8. b_{scat} INTEGRATION - MIDDAY

September 20, 1972

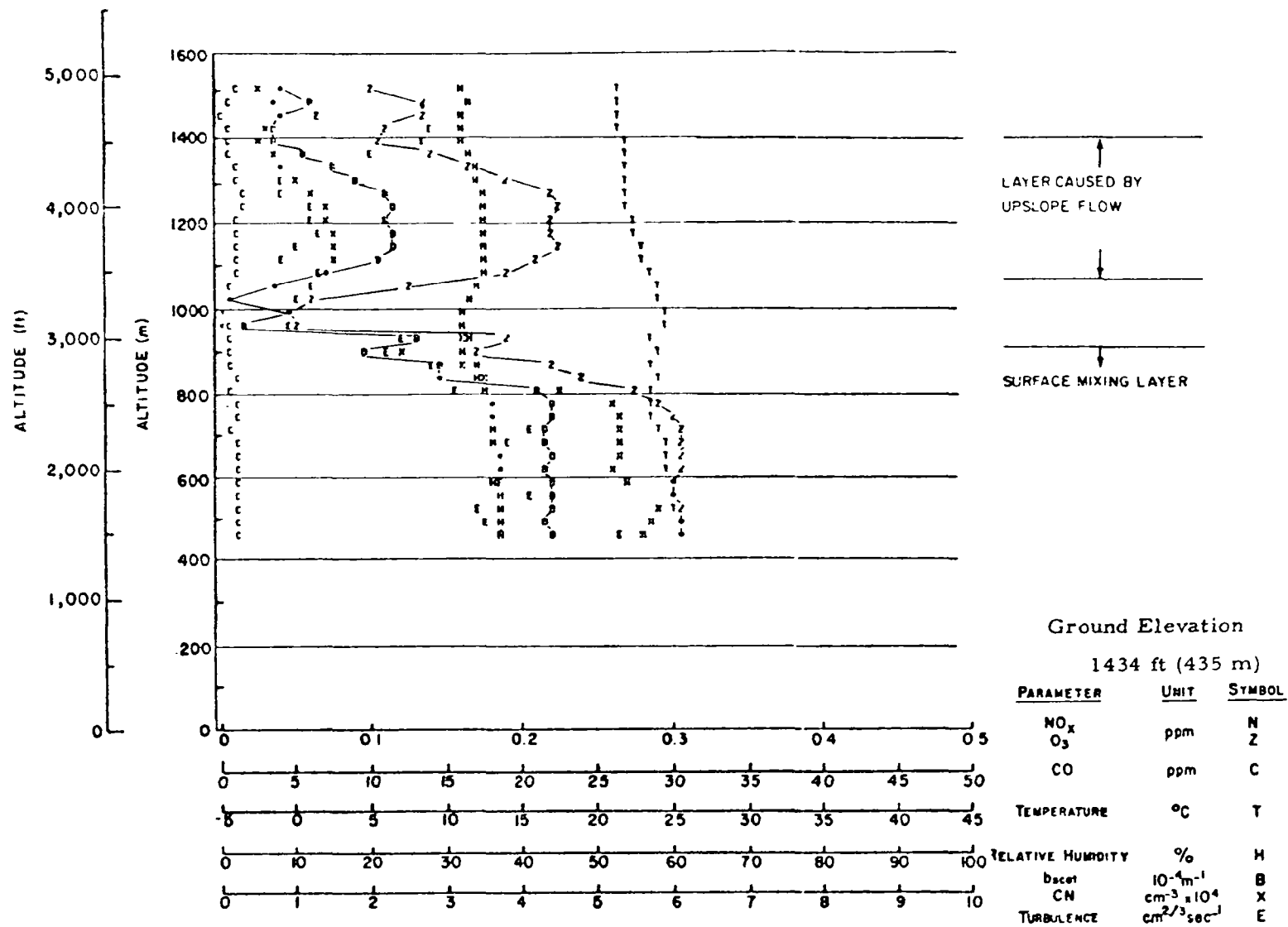


Fig. 9. VERTICAL PROFILE AT RIALTO (RIA) JULY 19, 1973, 1738 PDT, SHOWING LAYER CAUSED BY UPSLOPE FLOW

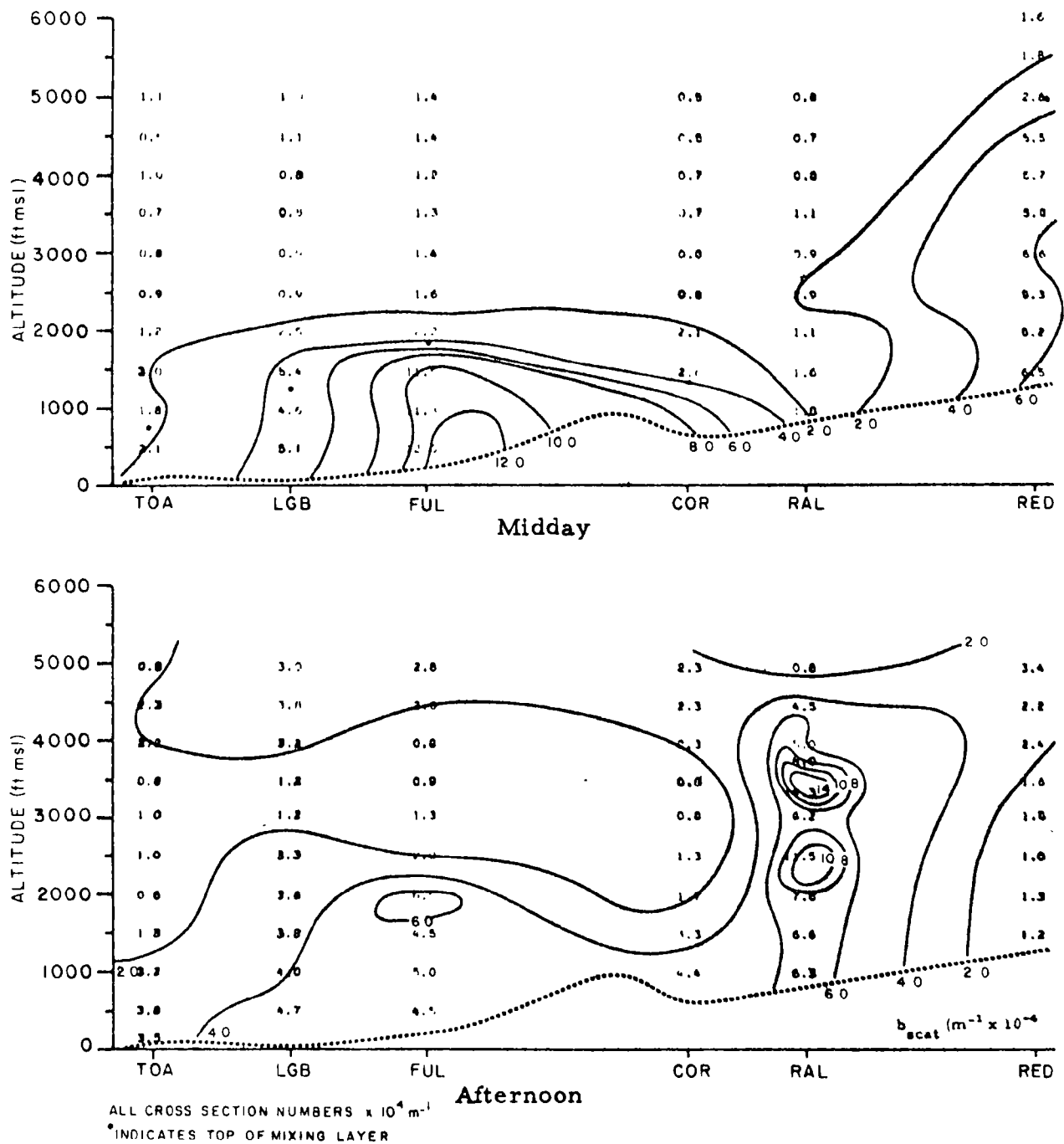


Fig. 10. VERTICAL CROSS-SECTION OF b_{scat} MIDDAY AND AFTERNOON, OCTOBER 24, 1972

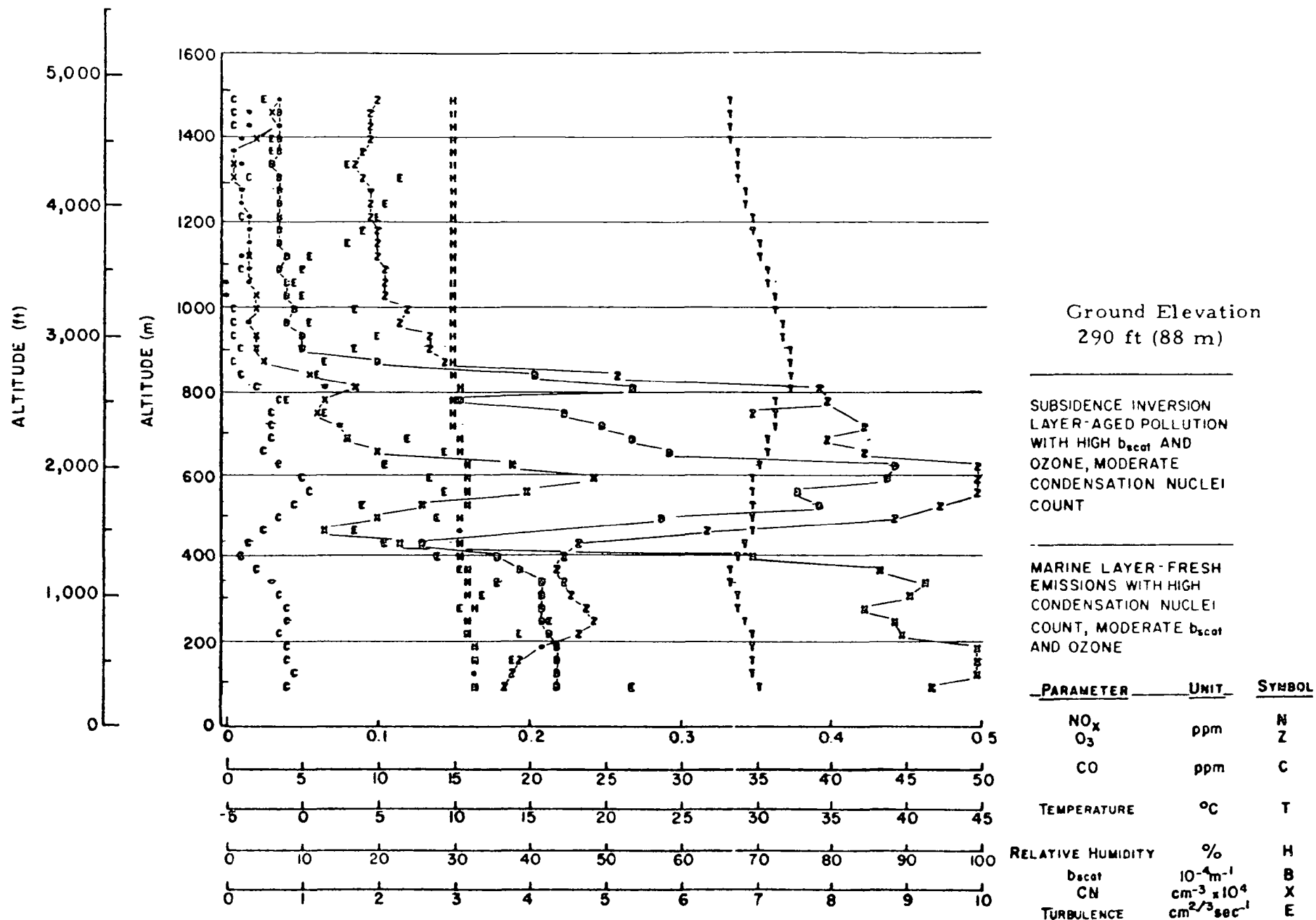


Fig. 11. VERTICAL PROFILE OVER EL MONTE (EMT) JULY 25, 1973, 1655 PDT, AFTER PASSAGE OF SEA BREEZE FRONT

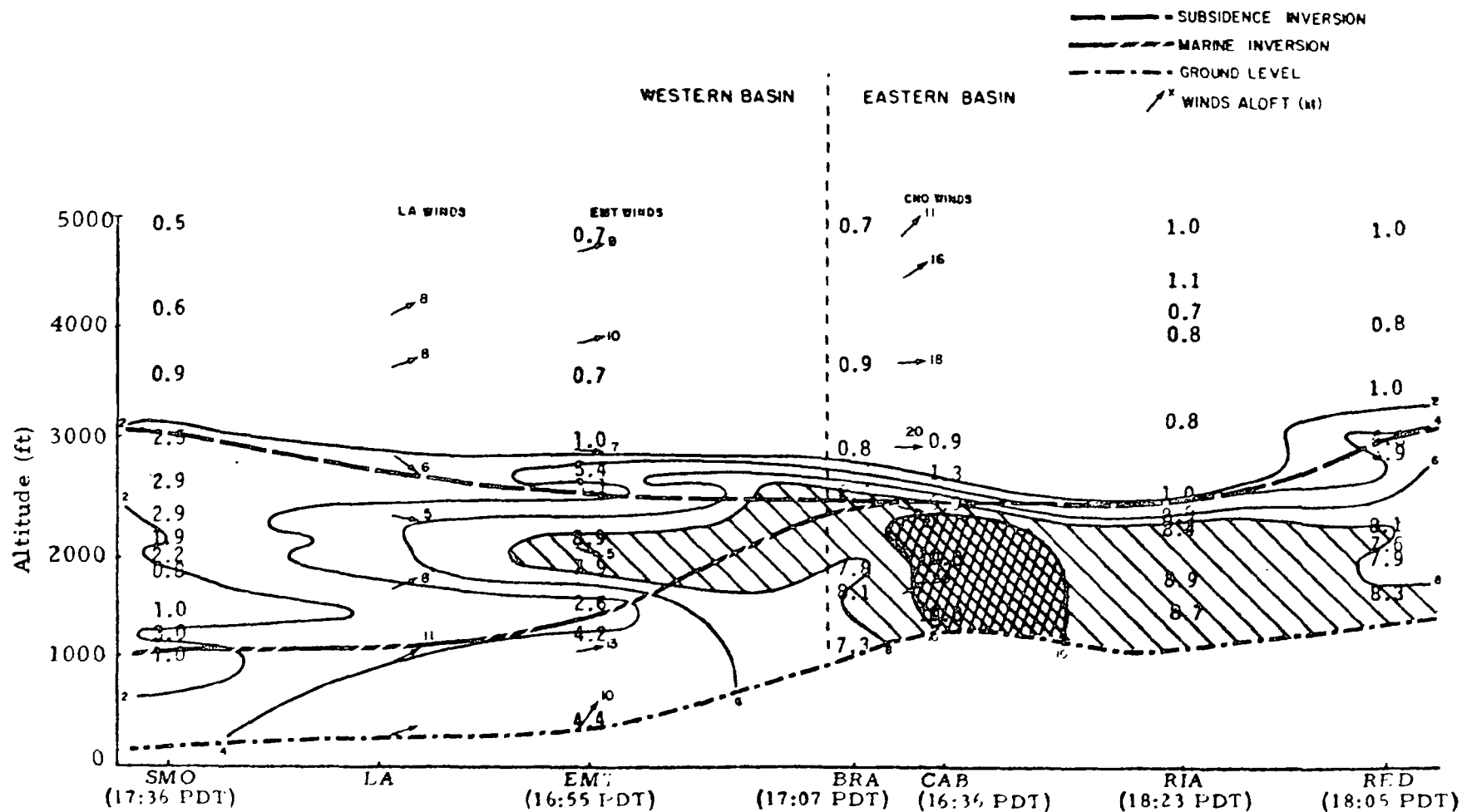


Fig. 12. VERTICAL CROSS-SECTION OF b_{scat} FOR AFTERNOON OF JULY 25, 1973
(Units are 10^{-4} m^{-1} .)

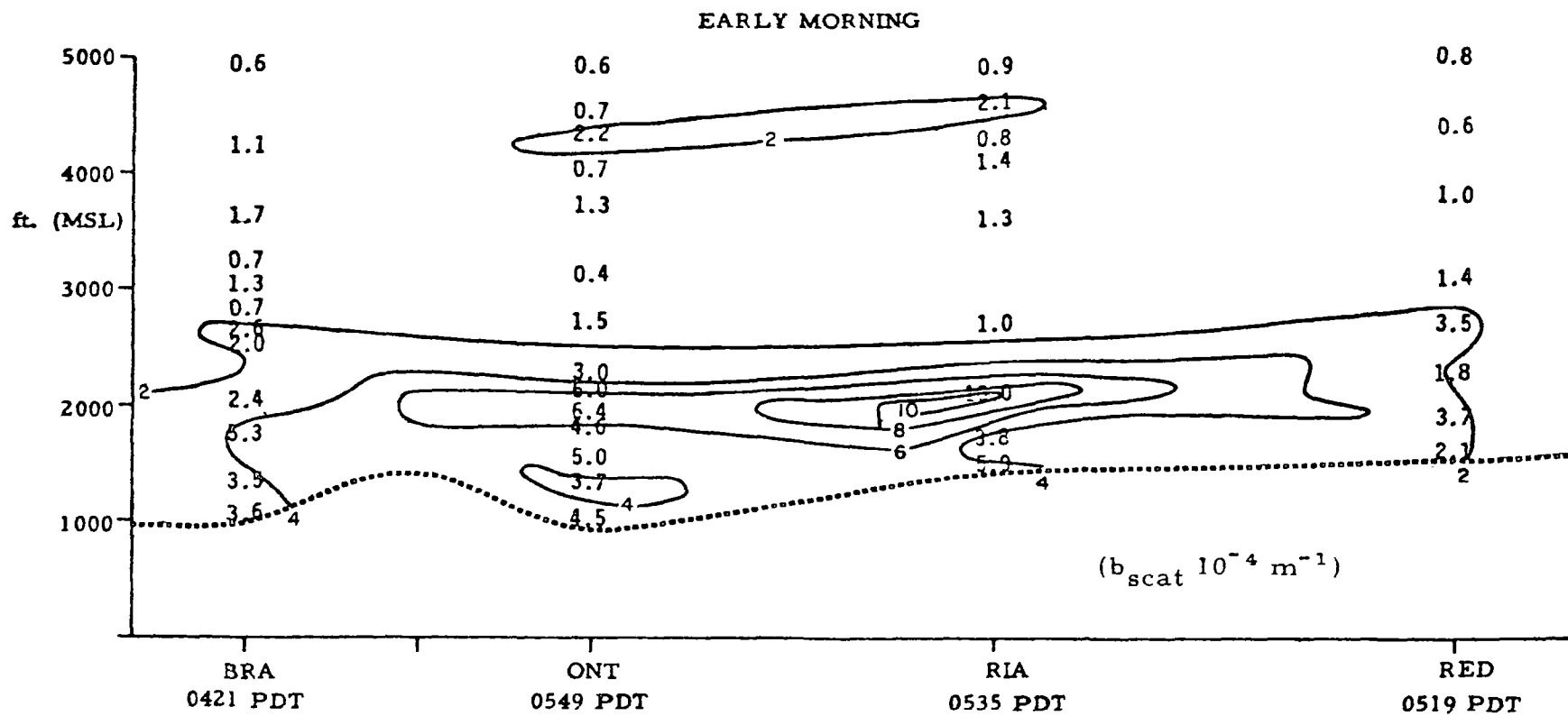


Fig. 13. VERTICAL CROSS-SECTION OF b_{scat}
26-27 July 1973

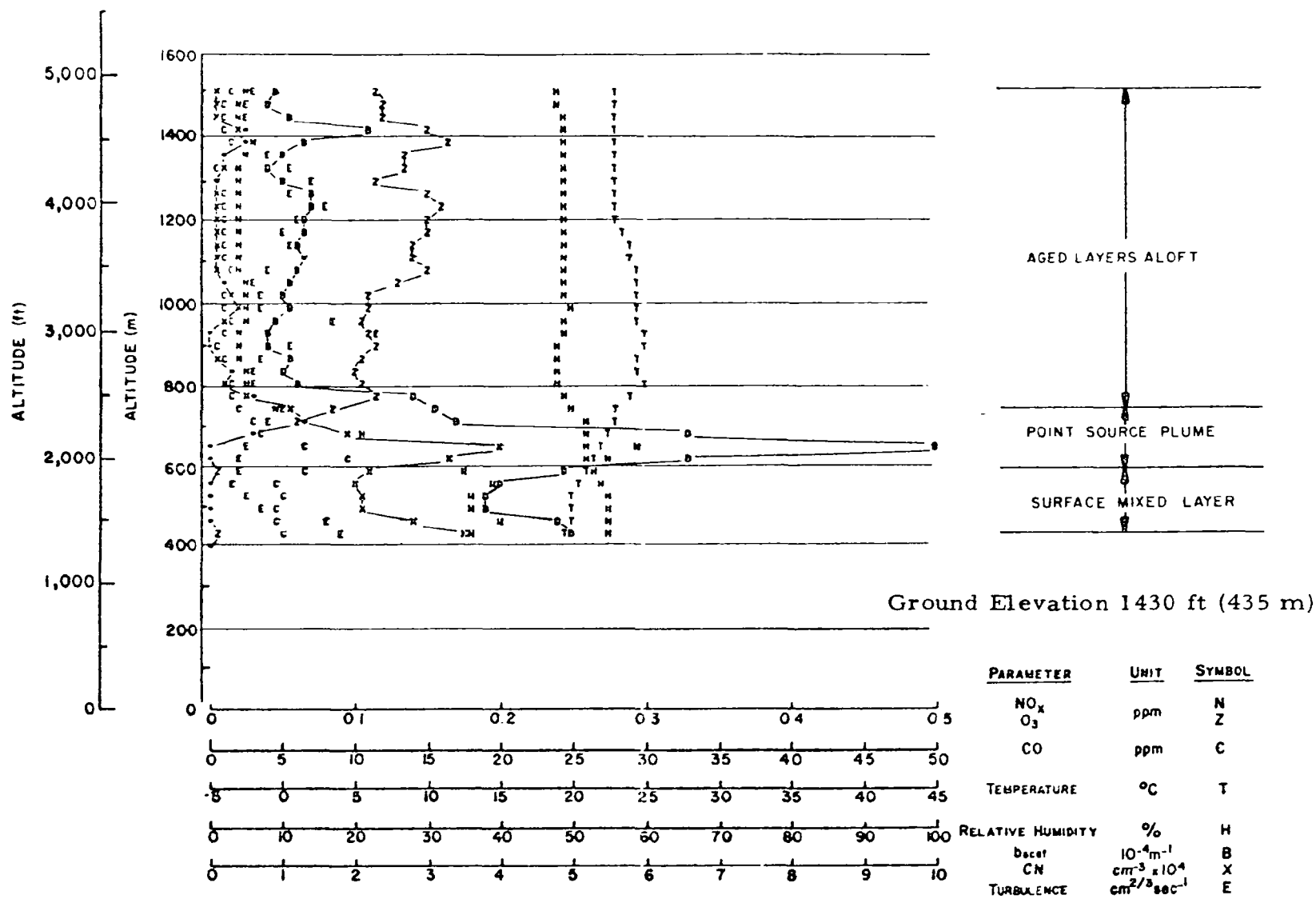


Fig. 14. VERTICAL PROFILE OVER RIALTO (RIA) 0535 PDT JULY 27, 1973

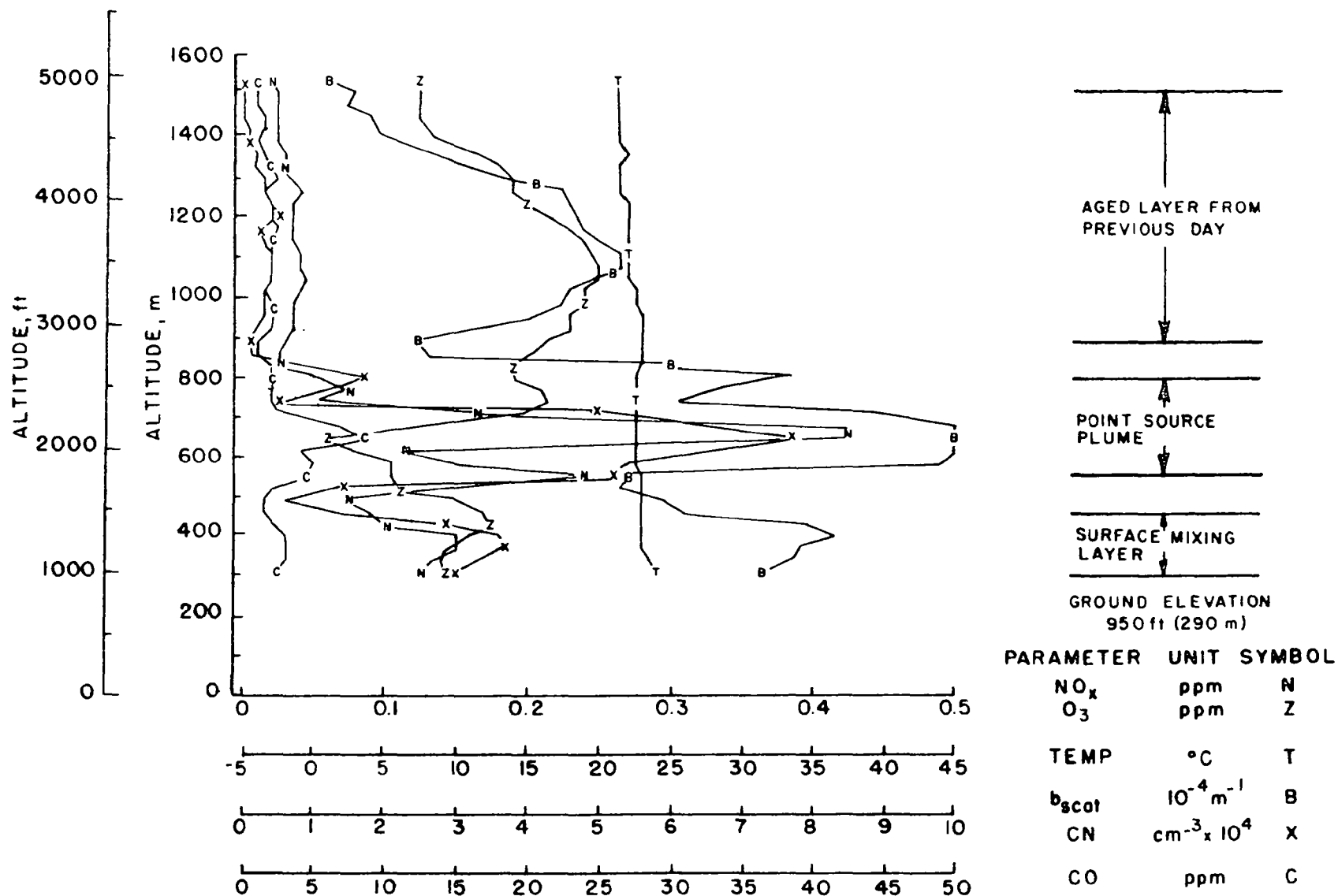


Fig. 15. VERTICAL PROFILE OVER ONTARIO (ONT) 0953 PDT JULY, 26, 1973

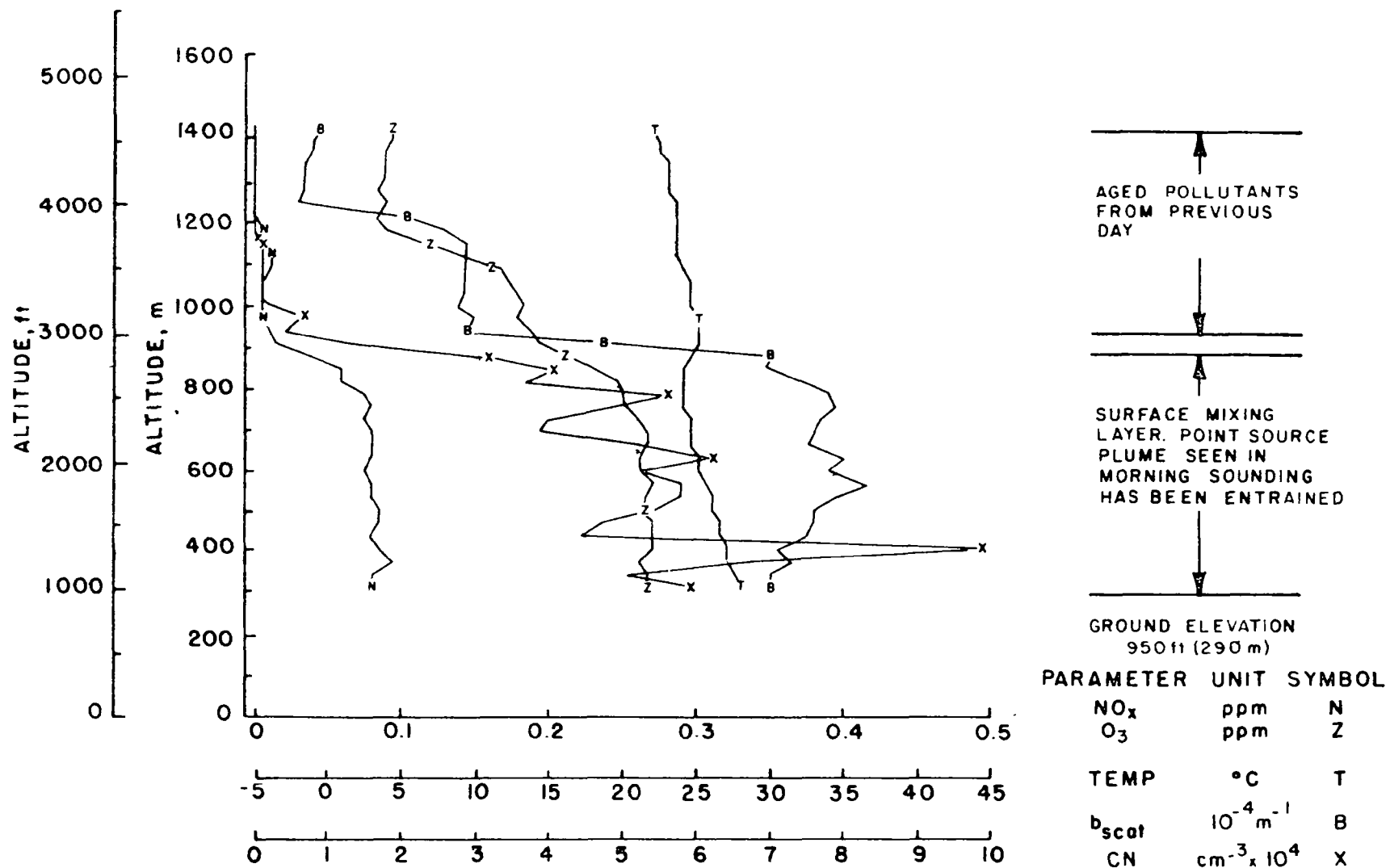


Fig. 16. VERTICAL PROFILE OVER ONTARIO (ONT) 1318 PDT JULY 26, 1973

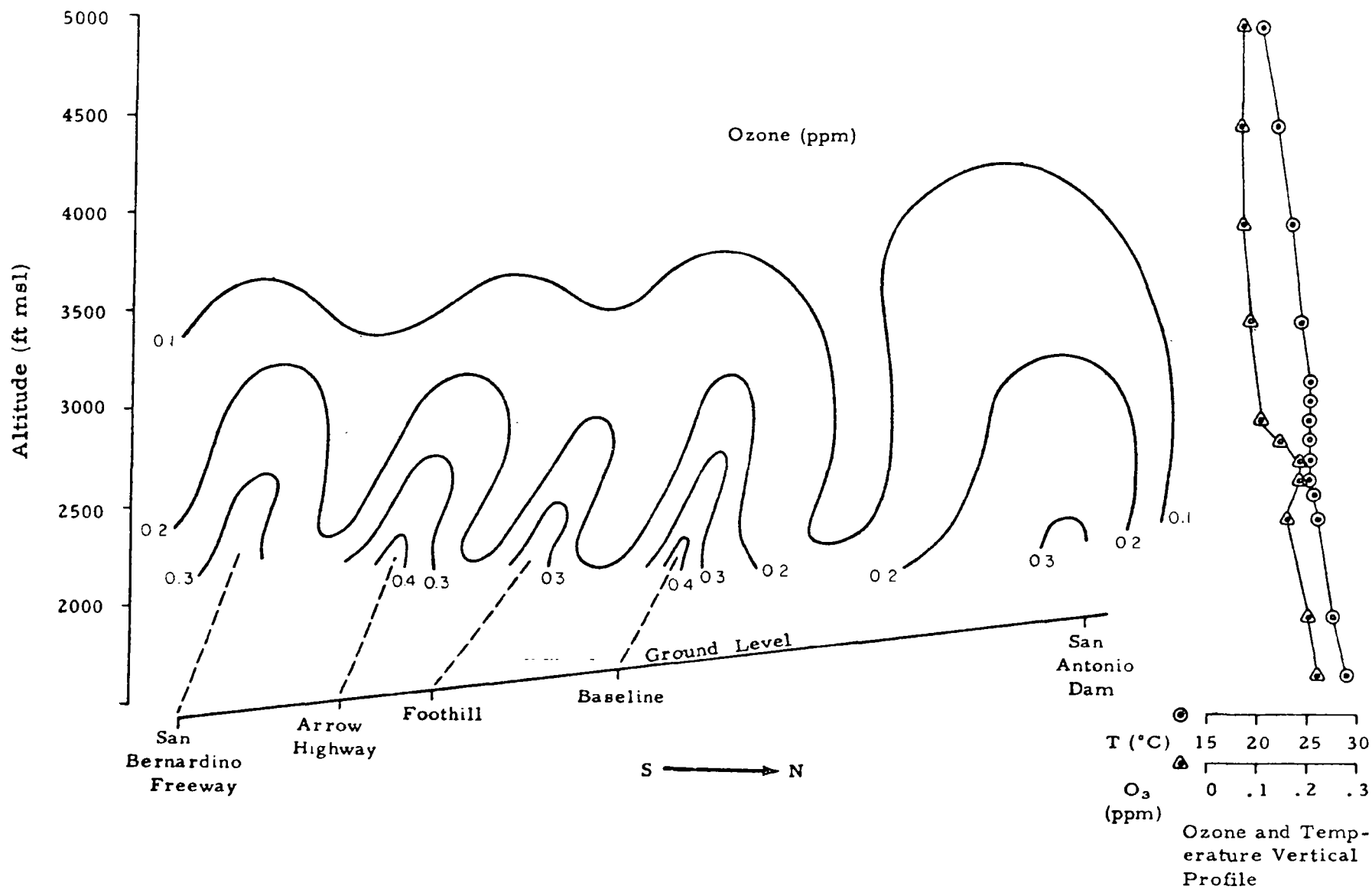


Fig. 17.

VERTICAL CROSS-SECTION OF OZONE CONCENTRATIONS ALONG
EUCLID AVE., UPLAND, OCTOBER 4, 1973, AFTERNOON

SAMPLE SIZE REQUIREMENTS FOR STATISTICAL VALIDITY

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I. INTRODUCTION

Aircraft sampling produces almost instantaneous measurements of air pollution at points in space connected by the flight path. These data can be used to estimate the time average concentration at these points in space or in given surrounding volumes. However, air quality standards and diffusion models usually relate to time averages on the order of one hour. The instant measurement (i.e. once every five seconds) represents a sample of size 1 from the population of 720 samples which compose the full hour. The accuracy with which the single sample represents the entire distribution depends primarily on the variance of the population being sampled. We can express this accuracy by use of a confidence level that the measurement is within a given value of the true mean of the distribution. To achieve a greater confidence level or to minimize the uncertainty a larger sample size is necessary. Based upon the desired accuracy and confidence level of the measurements to be made, and an estimate of the variance of the population to be sampled one can design the sampling process. Because these data are highly correlated, a one-minute flight producing 12 consecutive samples every five seconds, will not be the same statistically as 12 separate flights during the hour each producing one data point, with the spacing between flights chosen randomly. Standard statistical techniques may be misleading if independence is assumed. This paper discusses the problem from the point of view of the experimental design and presents the areas which must be considered in the process.

II. STATEMENT OF THE PROBLEM

At the inception of the project, a goal should be clearly stated for the measurement in terms of

1. how accurately it is to be made, and
2. the desired level of confidence for the measurement.

As an example, the estimation of the hourly average of a pollutant $\bar{C}$ might be the objective of the experimental measurements, where:

$$\bar{C} = \frac{\iiint C dx dy dz dt}{\iiint dx dy dz dt}$$

The specification may be that this measurement is to be within 2 ppm of the true value with a confidence level of 90%.

Inherent Limitations

Measurements from airborne platforms are subject to greater uncertainties than the identical measurement made on a bench in an air conditioned-temperature controlled laboratory. For a given instrument the errors to be considered are:

a. Instrumental

The instrument itself has a fundamental accuracy due to variability of manufactured components, nonlinearities, sensitivity to contaminants, minimum detectable levels, hysteresis, etc. These uncertainties are usually stated by the manufacturer, for example, as a concentration or per cent uncertainty; i.e. ± 1 ppm or $\pm 1\%$ of full scale, whichever is greater.

b. Calibration gas

The impurities in a zero gas, and the accuracy of a span gas analysis and its subsequent change with time in the cylinder add additional uncertainty to the measurement.

c. Environment

In non-pressurized aircraft, variations of altitude (pressure)

can produce an effect as well as variations in temperature. Vibration may also cause problems unanticipated in equipment designed for laboratory use.

d. Response Time

In an aircraft moving at high speed, the finite response time of an instrument will spread the measurements out in space and time, damping out maxima and raising minima. The details of this type of error are discussed in a paper to be presented by the author later in this meeting. Each of these four categories of uncertainty introduce an error into the measurement. Assuming these errors are independent and normally distributed one can describe the uncertainty as a standard deviation in terms of the four standard deviations as

$$\sigma_t = \sqrt{\sigma_a^2 + \sigma_b^2 + \sigma_c^2 + \sigma_d^2}$$

If σ_t is 1 pphm then there is a 68% chance of being within ± 1 pphm of $\bar{C}$ and a 95% chance of being within ± 2 pphm of $\bar{C}$ even if the aircraft samples the entire volume continuously for one hour. The limiting accuracy should be compared with the goal, and the flight plan could be designed to give the minimum sample size necessary to meet it.

Theory

Before discussing the results for correlated consecutive samples, it is useful to consider implications of the central limit theorem for consecutive data sampled as if it were independent. The theorem states that "the distribution of the mean of n independent observations from any distribution, or even from up to n different distributions, with finite mean and variance, approaches a normal distribution as the number of observations in the sample becomes large--that is, as n approaches infinity." This theorem applies without regard to the distribution of values comprising the initial population.

The only conditions it requires is that samples be statistically independent. There is ample evidence that consecutive samples are correlated and are not statistically independent. With random sampling, however, the samples are no longer consecutive, and the time between samples varies in a random fashion. If the samples are statistically independent, the central limit theorem should apply, leading to a normal distribution.

The normal distribution (Figure 1) has a probability density function given by equation (1):

$$f_X(x; \mu, \sigma) = \frac{1}{\sigma\sqrt{2\pi}} \exp \left[-\frac{(x-\mu)^2}{2\sigma^2} \right] \quad (1)$$

The two parameters μ and σ are the location and scale parameters, respectively, of the distribution. Although the function cannot be integrated directly, tables are widely available to calculate the probability associated with particular ranges of x . The shaded area under the curve in Figure 1 represents 5 percent of the total area and corresponds, approximately, to the probability of occurrence of values of x outside the interval $x \pm 2\sigma$ (actually $x \pm 1.96\sigma$).

According to the central limit theorem, the means of individual sample groups, each comprised of n random samples, must have the same distribution as in Figure 1. Furthermore, the average of the sample group means must approach the actual population mean μ_p , while the dispersion of these means, as determined by σ , is related to n and σ_p , the standard deviation of the original population:

$$\sigma = \frac{\sigma_p}{\sqrt{n}} \quad (2)$$

Thus, as n becomes large, the dispersion of the means of sample groups approaches 0, which is what would be expected; as n becomes large, the sample group more closely resembles the original population. If the standard

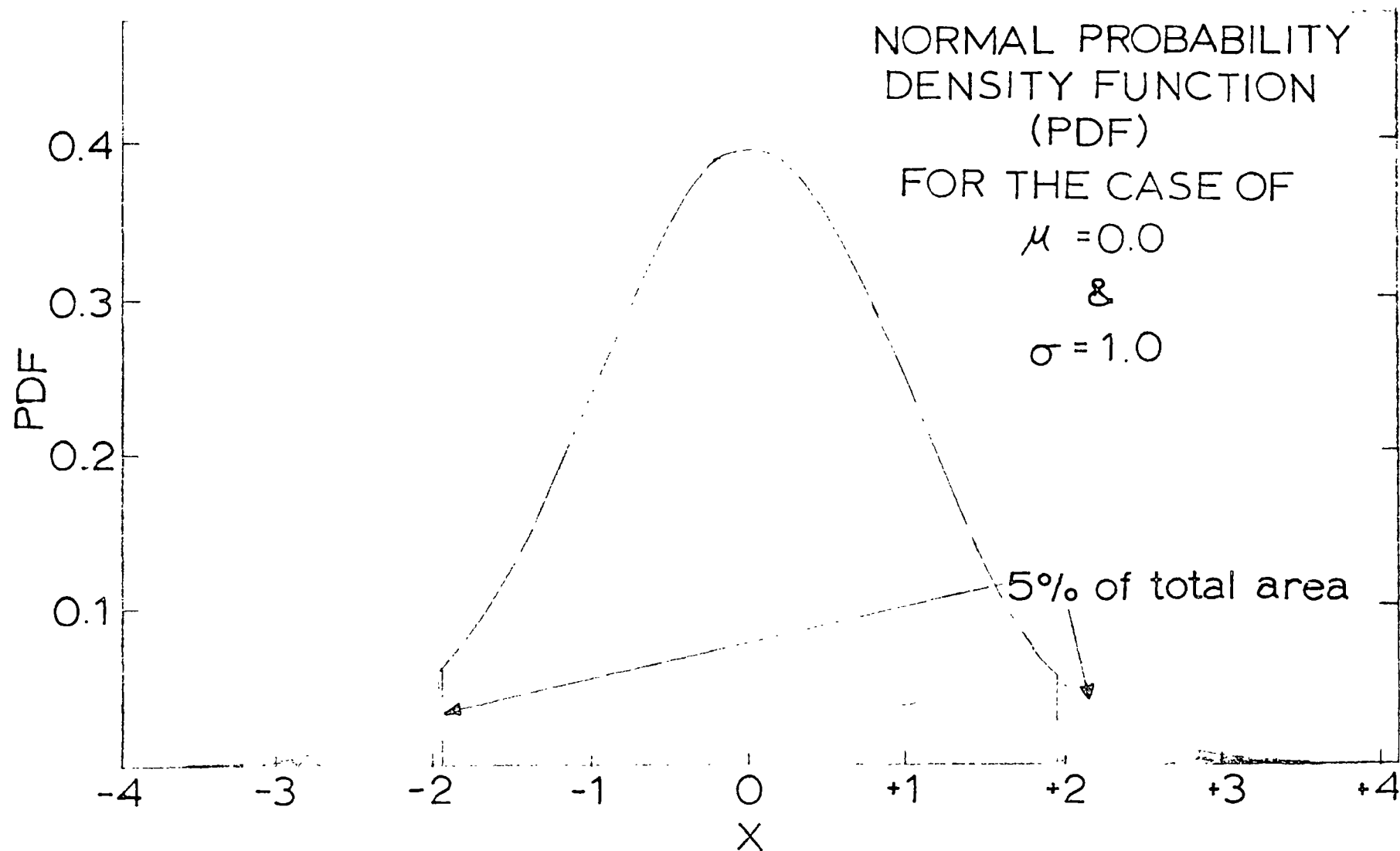


FIGURE 1

deviation σ_p is known confidence levels can be determined prior to the experiment.

A more valid approach from a statistical standpoint is to calculate the sample variance s_i^2 for the group of n samples obtained from each location i and then use this variance to determine the confidence interval. The sample variance s_i^2 is only a rough estimate of the true variance σ_i^2 at location i , and we must, therefore, introduce the Student's t -distribution to calculate the confidence interval. Tables are available giving the value of the factor $t_{CL,n-1}$ for any confidence level CL , and the mean is said to lie within the following confidence interval:

$$\bar{x}_i \pm (t_{CL,n-1}) \frac{s_i}{\sqrt{n}} \quad (3)$$

Suppose, for example, that the calculated mean for a group of 2 samples from a particular location is 4.0 ppm with a calculated standard deviation of 0.5 ppm. By referring to the t -distribution tables for $CL = 0.90$ and $n = 2$, we find that $t_{90,1} = 6.3$. (This value also can be read from Figure 2.) The mean and its confidence interval is:

$$4 \pm (6.3) \frac{0.5}{\sqrt{2}} = 4.0 \pm 2.2 \text{ ppm}$$

In general, if n is large, the factor $t_{CL,n-1}$ approaches values that would be obtained from a normal probability density function. If n is small, the factor $t_{CL,n-1}$ rapidly increases. This can be seen in Figure 2, where the factor is plotted as a function of $n-1$. It is evident that sample groups of size 5 or less have very large confidence intervals, even when the samples are random and independent.

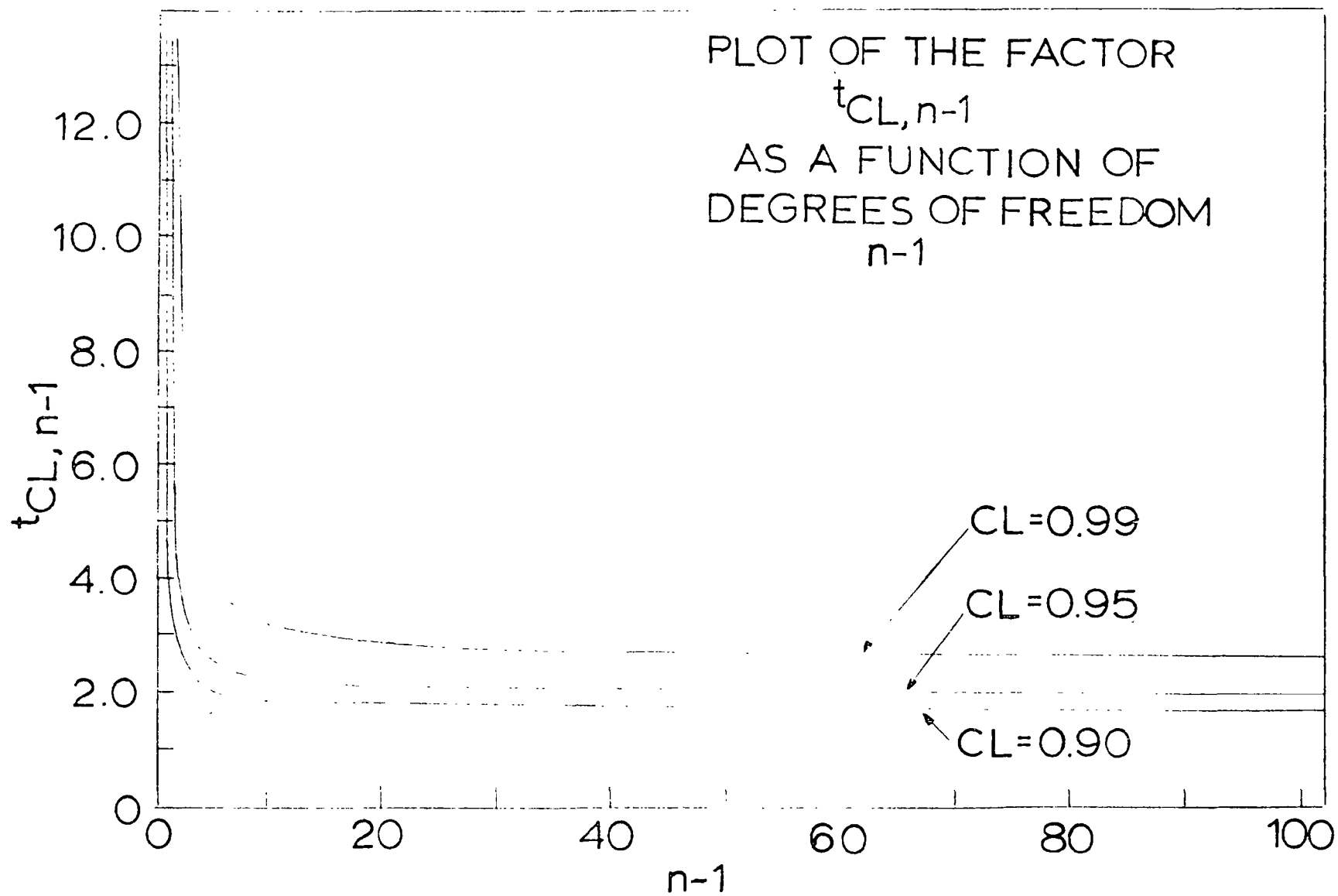


FIGURE 2

Sampling Statistics - With Correlation

To discuss non-independent sampling statistics we can look at different pollutant distributions each with a mean ($\bar{C}$) of 0.5 during a 1-hour period, where $\bar{C} = \int C f(C) dC$, shown in Figure 3.

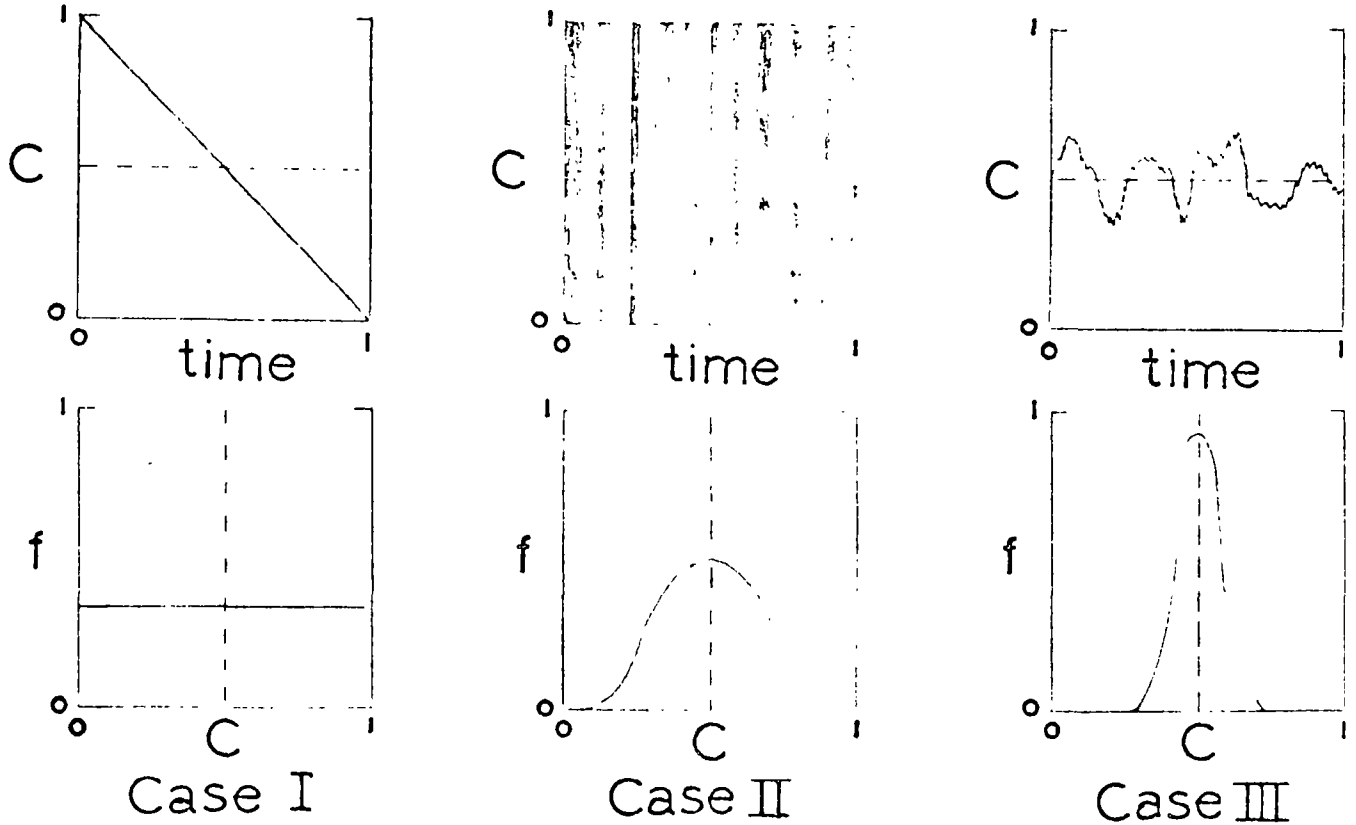


Figure 3. Different Types of Distributions

The bottom diagrams correspond to the frequency distribution of the means of consecutive samples over time Δt taken from the distributions at random, where Δt is large compared to the frequency of data fluctuations. The first distribution is one which is not stationary, i.e. the mean is decreasing with time. The second distribution is composed of random fluctuations between 0 and 1, corresponding to flips of a coin. The distribution has a stationary mean of 0.5 but a rather high standard deviation. The third distribution is the nicest to sample from, i.e. the mean is stationary at 0.5 and the random fluctuations about it are of small amplitude. The frequency distribution

of samples will have a small standard deviation and a small sample will have a high probability of success. It is quite obvious that one sample of size Δt is not equivalent to n samples of size $(\Delta t/n)$ chosen randomly throughout the hour. Indeed the last two cases shown, where consecutive values fluctuate about the mean, corresponding to the flip of a coin, are the only cases shown where the central limit theorem as previously discussed would apply directly to an increase in Δt . We may therefore look at the previous case of independent consecutive observations as the best possible situation and an upper limit on the confidence for the sample.

Examples of Variability

Figures 4 and 5, represent two spirals taken as part of a plume study on February 19 by a RAPS helicopter 10 miles downwind of the Labadie Power Plant, west of St. Louis. These spirals down from 3000 msl to 1000 msl took 5 minutes each. An additional three minutes were necessary to climb from 1000 to 3000 ft. so one could treat them both as samples separated by an eight minute interval. Neglecting the correction for response time, it is readily seen that there are significant differences as seen on Figure 4. The first spiral measured a maxima of 1.05 ppm SO_2 at 1200 ft. and 0.4 ppm SO_2 at 2400 ft. The second spiral measured 0.40 ppm SO_2 at 1200 ft. and a maxima of 0.7 ppm SO_2 at 2400 ft. Figure 5 shows the NO_x data measured simultaneously in the same spirals. At 1200 ft. the first spiral had a maxima of 0.24 ppm NO_x compared to 0.10 ppm NO_x at 1200 ft. found in the second spiral. The difference between the two spirals is probably due to the fact that the wind may have shifted slightly in the eight minute interval between the samples. A shift of 5.7° would be sufficient to move the plume center line by 1 mile at a distance of 10 miles from the source. It is of interest to note that Turner in his Workbook of Atmospheric Dispersion Estimates only

FIGURE 4
RAPS 2 FEB 19, 1975
PLUME 1 - (SO_2)

Duplicate Spirals
at Ten Miles
from Stacks

Altitude, ft. MSL

2500

2000

1500

1000

0

0.2

0.4

0.6

0.8

1.0

(SO_2), ppm

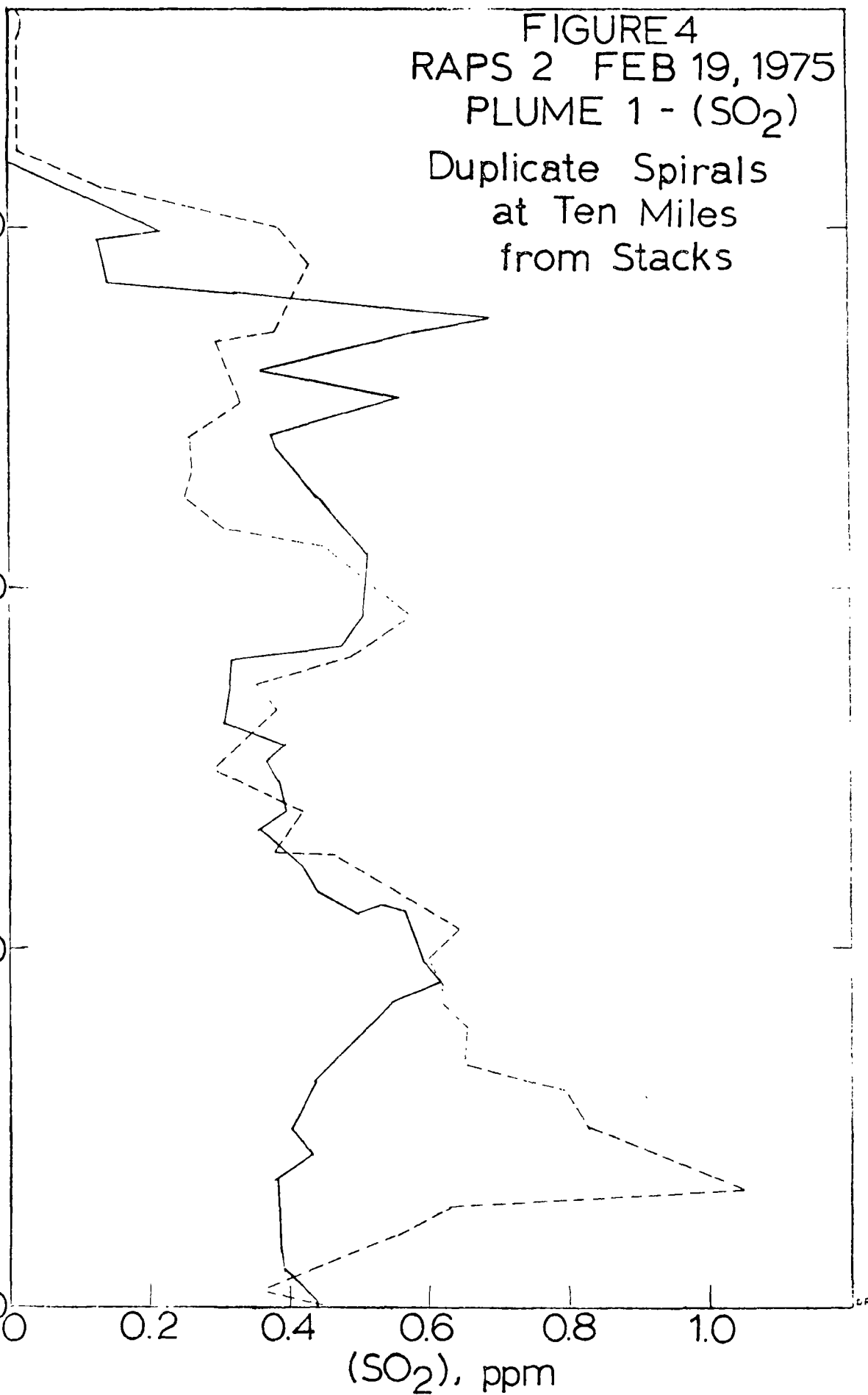


FIGURE 5
RAPS 2 FEB 19, 1975
PLUME 1 - (NO_x)

Duplicate Spirals
at Ten Miles
from Stacks

Altitude, ft. MSL

2500

2000

1500

1000

0

0.05

0.10

0.15

0.20

0.25

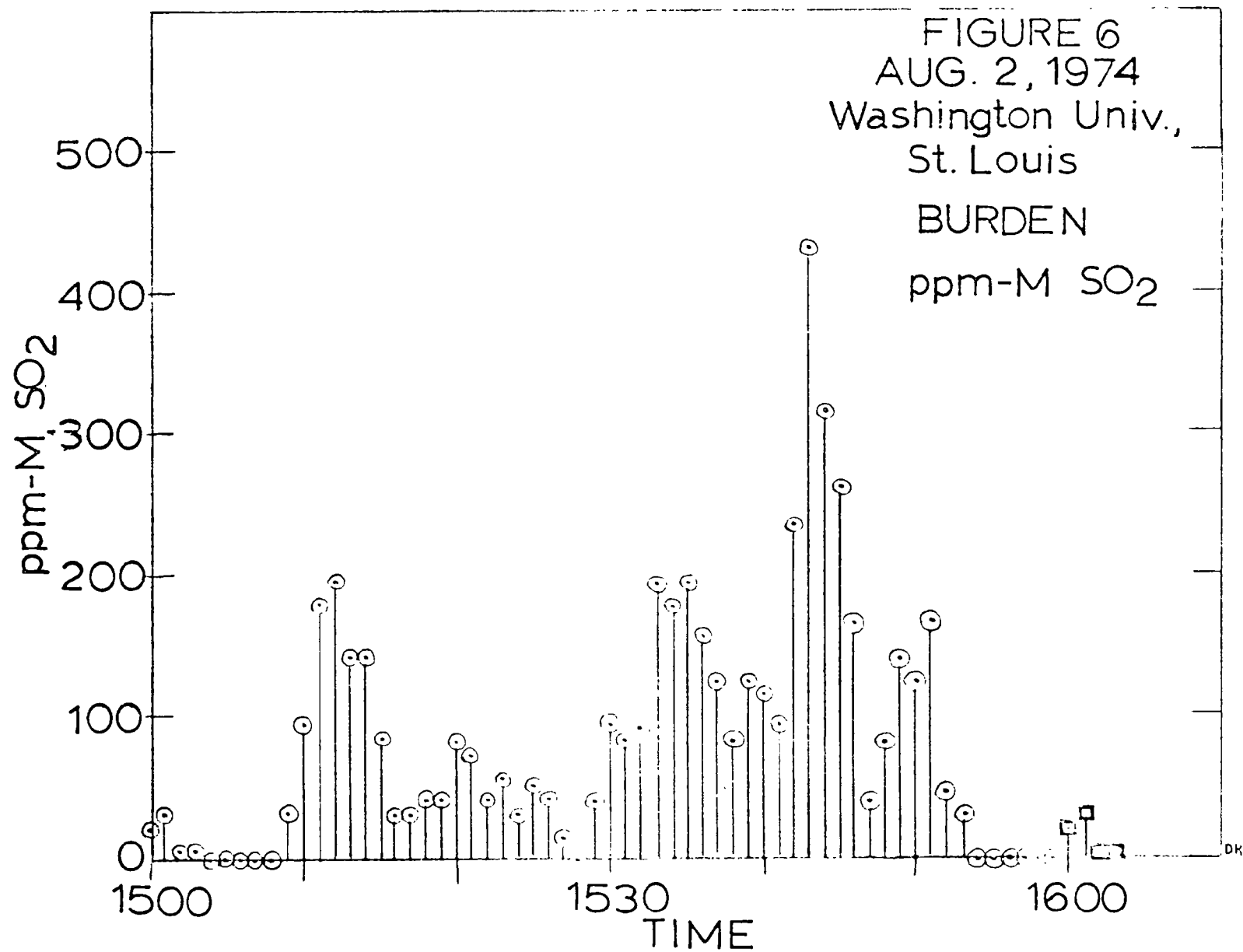
(NO_x), ppm

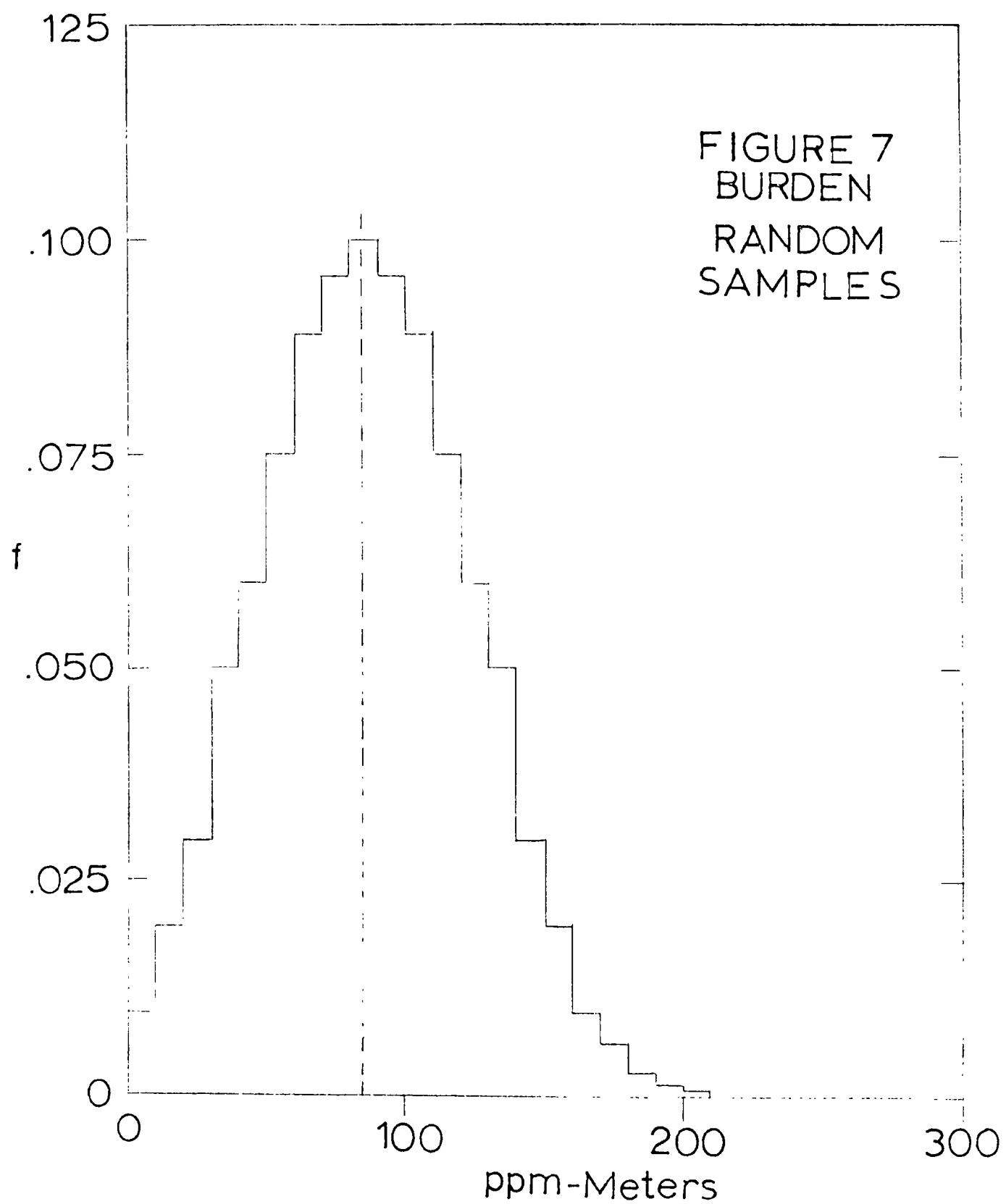
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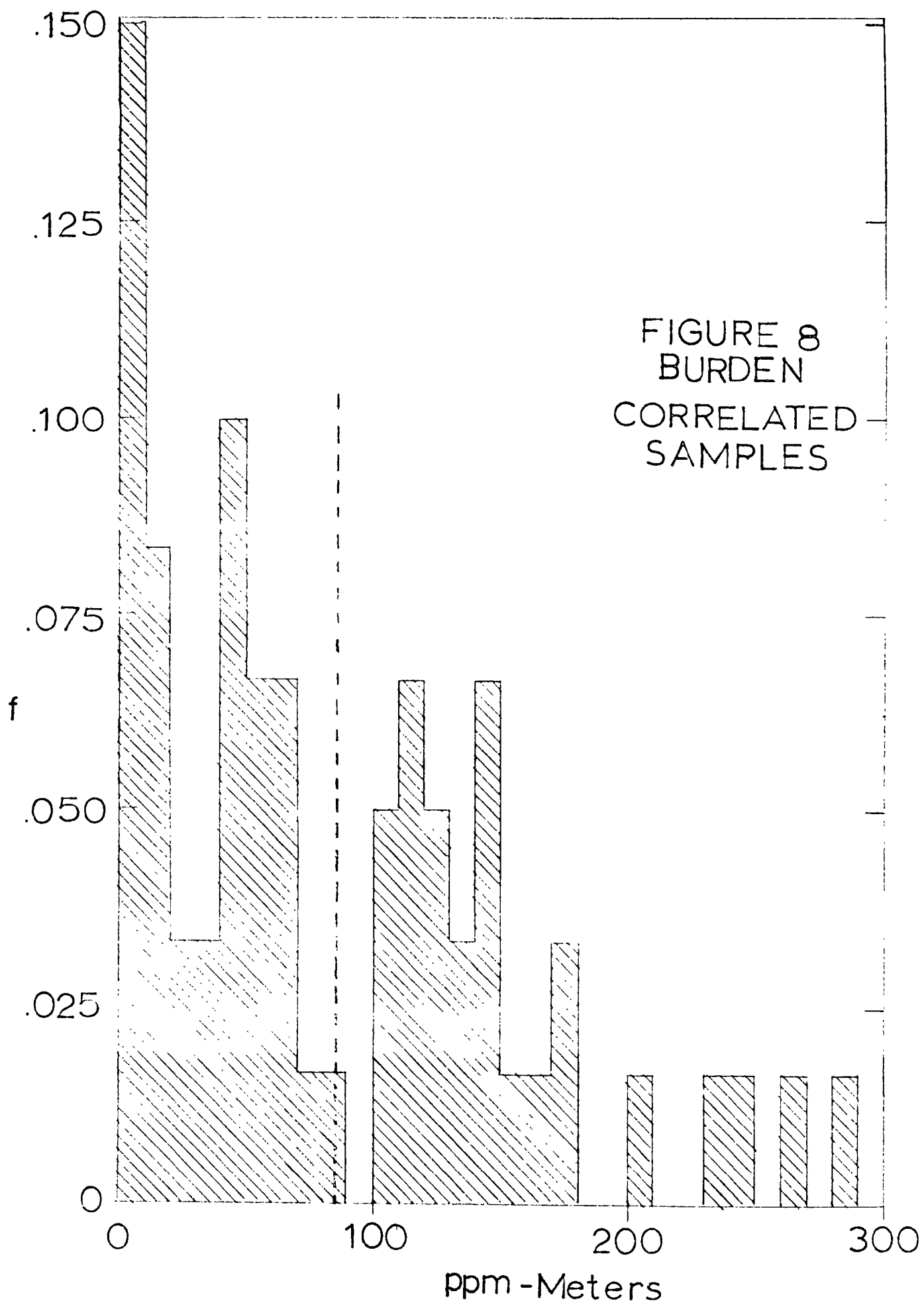
gives atmospheric dispersion coefficients which "represent time periods of about 10 minutes". Thus these spirals, under the influence of an elevated source, may be only valid estimates of the mean of an eight minute period, where consecutive eight minute mean values are changing with time and their sequence is non stationary. To put it more bluntly, if we assume the NO_x samples at 1200 ft. are random and independent the sequence 0.24, 0.10 would probably fluctuate about 0.17 if the spirals were continued. If the data are correlated the next sample would be expected to be below 0.10 and the mean of the series would be closer to 0.10 than 0.17. Even if we have 2 samples we are in a quandary. When we only have one small sample the uncertainties may be so great that an estimate of an hourly average may only be made within a very large confidence interval.

Figure 6 shows the burden of SO_2 in ppm-Meters at Washington University, St. Louis, Missouri measured by a correlation spectrometer on 2 August 1974 reported by EMI at the January 1975 RAPS conference at St. Louis. Assuming SO_2 does not penetrate the inversion capping the mixing layer, and the mixing layer is 1000 meters deep, a burden of 100 ppm-M corresponds to an average concentration of 0.10 ppm SO_2 in the 1000 meter layer. The average concentration measured by the helicopter in a spiral would approximate this value.

It is evident that these burden data are highly correlated since high values cluster together and low values cluster together. For the 40 one-minute values between 1500 and 1559 the average $\bar{C} = 85.4$ ppm-Meters and the standard deviation $s = 88.1$ ppm-Meters. By the central limit theorem, if this hour were sampled by 5 independent, or randomly chosen samples, an infinite number of times, the averages of these 5 minute samples would form a normal distribution with a mean $\bar{C} = 85.4$ and a standard deviation $\sigma =$







$\frac{88.1}{\sqrt{5}} = 39.4$ ppm. This distribution is shown in figure 7 as a histogram of the fraction of the population occurring in each interval of 10 ppm-M. The helicopter spirals could start at any time during this hour, and for the purpose of this paper, let us allow 60 possible starting points each separated by one minute. These 60 flights would produce 60 5-minute averages of consecutive data which are not independent, but on the contrary, highly correlated. These data were averaged consecutively 5 at a time. The resulting distribution of these data is shown as figure 8. The mean is still 85.4 ppm-Meters but the standard deviation is 72 ppm-Meters, still relatively high, and almost double the standard deviation which would occur if the 5 one-minute samples were independent. Faced with these observations how can one give a confidence level to an arbitrary 5-minute sample taken by an aircraft in a region where elevated plumes may or may not be present. The following section describes a technique by which confidence levels for non-independent samples may be obtained.

Development of Estimates of Confidence Levels for Non-Independent Samples

1. Obtain several data sets, such as figure 6, for an entire 1-hour period, for various stability classes and wind directions, from the ground or from the air by continuous spiraling.

2. Prepare an autocorrelation diagram showing the autocorrelation coefficient as a function of time lag $\tau = n \Delta t$ for the cases of interest.

3. Develop an autoregressive (Markov) process $C_{t + \Delta t} = a_t C_t + b_t$ where a_t and b_t are random variables uncorrelated with C_t . Choose the distributions of a and b such that the series $C_t, C_{t + \Delta t}, C_{t + 2 \Delta t}, C_{t + 3 \Delta t}, C_{t + 4 \Delta t}, \dots, C_{t + n \Delta t}, \dots$

has a similar autocorrelation diagram to the data. Develop the computer

model for this analysis.

4. Run the computer model to generate a time series of 60 values from C_t through $C_t + 59\Delta t$, and randomly choose a value for a starting point and compute the average of the 5 consecutive values at that point $\bar{C}_5$, comparing this to the mean of the distribution $\bar{C}_{60}$. Repeat this procedure a large number of times.

5. From these realizations of the process of generation and sampling develop a histogram of frequency of $\frac{\bar{C}_5}{\bar{C}_{60}}$ and from this diagram obtain the

confidence intervals for the 5-minute sample.

Summary and Conclusion

Each airborne measurement should be treated as a random sample from a distribution of non-independent data. Standard sampling theory for independent observations can lead to quite erroneous results if used for these data. Proper experiment design requires knowledge of confidence levels for various sample sizes and sampling schemes. A procedure is outlined by which confidence levels may be obtained for non-independent samples. Without a careful analysis, sample sizes may be too small to give any reasonable confidence to the results of comparisons between the measurement and models which predict the measured parameters for a significant larger averaging time.

ANALYSIS OF SIZE FRACTIONATED AEROSOLS*

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* Presented at conference on "Applications of Airborne Platform Monitoring," NERC-Las Vegas, March 27, 1975

INTRODUCTION

The measurement of aerosols must be given a high priority in studies to characterize the urban plume. Aerosols can not only contain toxic substances, but because of the ability of particles to discolor a blue sky and to degrade visibility, aerosols cause one of the most obvious and objectionable aspects of air pollution.

In a modern aerial platform study a variety of chemical and physical parameters need to be measured. Measurement of only the total mass concentration would be insufficient because the size distribution of an aerosol has a large effect on its ability to affect visibility or to be inhaled into a human respiratory system.

Previous measurements by Whitby et al have demonstrated the existence of a bimodal distribution of particle volume (and hence mass) in the atmosphere (1). In a recent experiment, particles in the two modes were separately collected in a dichotomous sampler and analyzed by x-ray fluorescence spectroscopy (2). This measurement confirmed that the fine and coarse particles differed completely in chemical composition. The fine particles contained elements which were characteristic of combustion products; the coarse fraction contained elements which are commonly found in the earth's crust. A comprehensive program to monitor the composition of size fractionated aerosol could provide a valuable indication of the atmospheric burden of particles due to various energy and transportation sources. A set of measuring methods for such a program is briefly described in the text that follows.

AEROSOL SAMPLING

Cascade Impactors: The cascade impactor has come into widespread use for collecting suspended particles according to aerodynamic size. Subsequent chemical and gravimetric analysis can be performed on the particles which are collected in each size range.

For quantitative sampling of aerosols using a cascade impactor, it is necessary that the impaction surface have an adhesive coating. If the adhesive coating is not used, particles can bounce off of their intended impaction surfaces and be collected on subsequent stages or on the backup filter. This leads to severe distortion of the apparent size distribution. An example of this distortion is shown in Figure 1, which compares size distributions made using two identical cascade impactors which were coated with dry and with grease-coated impaction surfaces (3). In a series of measurements, it was found that the apparent mass median diameter of the size distribution, which one deduces, is erroneously decreased by factors ranging from 2 to 5 when the grease-coated impaction surface is replaced by a dry aluminum surface. Although the use of an adhesive coating is desirable for quantitative sampling, that coating often interferes with chemical procedures for analyzing the deposits.

DICHOTOMOUS, VIRTUAL IMPACTORS: A virtual impactor can be used as a means of eliminating the particle bounce problem. In a virtual impactor, particles are impacted into a slowly-pumped void and then drawn onto a filter where they are collected. There is no impaction surface for the

particles to bounce off of. A virtual impactor which collects particles in two size ranges is commonly referred to as a dichotomous sampler. For most monitoring applications, the size separation diameter for the dichotomous sampler should be set at about 2 to 3.5 μm . A separation at 2 μm would correspond to the typical location of the minimum in the bimodal distribution (1). A separation at 3.5 μm would correspond to aerosol size separation made by the upper and lower passages of the human respiratory system.

An automated dichotomous sampler which operates on the principle of virtual impaction has been developed by Loo of the Lawrence Berkeley Laboratory (4). The device is illustrated in Figure 2. When operated at a flow rate of 50 liters per minute, the separation between fine and coarse particles occurs at a 50 percent cutpoint diameter of 2.5 μm . The complete size fractionation characteristics and loss curves are shown in Figure 3. The cutpoint could be shifted to 3.5 μm by operating the device at a lower flow rate, which is estimated to be about 42 liters per minute.

Ten of the automated dichotomous samplers have been deployed in St. Louis as a part of the Regional Air Pollution Study. An additional sampler will soon be deployed near a copper smelter in Utah. These devices have the capacity to collect 36 consecutive samples for time intervals adjustable between 1 and 100 hours. A regulator maintains the flow rate at the inlet at 50 liters per minute. In heavily polluted

atmospheres, the maximum sampling duration may have to be limited to 4 to 12 hours in order to prevent excessive loading of the filters.

DETERMINATION OF COMPOSITION

In order to fully characterize an aerosol, it is important to determine the chemical and elemental composition. Carbon compounds, chlorine, bromine and lead are characteristically present in auto exhaust. Sulfuric acid or sulfate compounds are characteristically present in the primary and secondary particles resulting from the burning of fossil fuels to generate electricity. Al, Si, K, Ca and Fe are characteristically present in suspended soil dust. A combination of analytical methods is needed to characterize these species.

Chemical Analysis: A summary of several methods for measuring the chemical composition of aerosols is given in Table I. In the past, there has been a reliance on wet chemical techniques for making chemical measurements. Information on interferences and accuracy for these methods has not generally been available. For the four wet chemical methods for sulfate, given in Table I, a study of interferences, intercomparability and agreement with x-ray fluorescence methods for total sulfur is being conducted (5). Recently, Dr. J. Husar has utilized a flash volatilization technique in which samples are rapidly heated to decompose the sulfate. The resulting SO_3 is detected using a flame photometric detector (FPD). A related technique is being optimized for determining H_2SO_4 which is collected on teflon filters. Sampling times are limited to a few minutes in order to minimize reactions taking place between

particles on the filter. The filters are gently heated in a dry atmosphere containing methanol in order to selectively volatilize SO_3 , which is analyzed using a FPD (6).

Brosset of Sweden has developed a program for determining three species which are associated with the fate of sulfuric acid aerosol. For particles which are collected on Fluoropore filters, sulfate is determined using a wet chemical method, and ammonium ions are analyzed using an ion-selective electrode. Strong acid is determined using a Gran titration procedure, which discriminates against weak acids. With these measurements, the amount of sulfuric acid and ammonium sulfate can be deduced, whenever the concentration of other strong acids (HNO_3 or HCl) is low.

Patterson (7) has developed a combustion technique for determining total carbon in collected aerosol (as well as hydrogen and nitrogen). A technique is presently being developed for determining volatile carbon compounds as well as total carbon (8). For the purpose of determining mass balance in aerosols, these techniques may be somewhat more useful than the methods which only measure benzene-soluble organics.

Elemental Analysis: During the past two years, energy dispersive x-ray fluorescence analysis (XRF) has become widely used for determining the elemental content of aerosol samples. It is nondestructive and requires only a few minutes for analysis. The XRF method is generally applicable to elements which have atomic numbers above 12. In Table II, the detection limits are given for a modern energy dispersive XRF spectrometer, which

uses secondary fluorescers (9). The detection limits in Table II are expressed in units of ng/cm^2 assuming that the particles are collected on a membrane filter which has a mass per unit area of 5 mg/cm^2 . The detection limits are also plotted in Figure 4. Also shown in Figure 4 are typical ranges of concentrations of trace elements which have been measured in urban atmospheres (12).

The detection limits of Table II and Figure 4 can easily be expressed in units of ng/m^3 . This is done by dividing the tabulated values by the volume sampled per unit area of filter (in m^3/cm^2). This manner of expressing detection limits is very convenient because it allows the designer of an experiment to consider a variety of filter media, flow rates and sampling intervals.

Detection limits for trace element analysis by neutron activation analysis (NAA), by atomic absorption (AA) and by emission spectroscopy have been reported by Zoller and Gordon (10) and by Thompson et al (11). The detection limits were reported by those authors for 24-hour samples using specific filter media. The values in Table II are expressed in the more general units of ng/cm^2 . From this table it is clear that XRF compares favorably with the other methods. For certain elements the other methods are definitely more sensitive, but the uniformly good detection limits of XRF give it an advantage for many applications. If only one or a few elements are to be analyzed by AA, then, according to Thompson et al, the procedure can be optimized to obtain much better detection limits (11).

Filter Media: In many applications it is desirable to use very short sampling intervals. In such cases, two criteria must be satisfied. Each element to be analyzed must exceed the blank level in the filter. Also, a sufficiently large sample must be collected so that the detection limits of the analytical method are exceeded. Figure 5 shows a comparison of XRF spectra for glass fiber and Fluoropore (Teflon with polyethylene grid backing) filters. The impurities in the glass fiber filter are far too high for use with XRF or NAA, but the Fluoropore is excellent in this regard. Table III shows typical impurity levels for Millipore AA (mixed esters of cellulose) and Whatman 41 (cellulose) filter media (13).

The ability of a filter to pass air at high flow rates is important when brief sampling intervals are required. A summary of the properties of a wide variety of filter media is given by Lockhart et al (14), and some of these properties are listed in Table IV. Included in Table IV are the flow rates which occur when the pressure drop is 1/3 atm. In a certain sense, these flow rates are the optimum maximum values. Somewhat higher flow rates are possible, but it becomes increasingly difficult to regulate the flow rate as the pressure drop increases above 1/3 atm. Table V shows the volume per unit area which can be sampled through various filter media during a ten-minute sampling interval. The values in Table V can be used to convert the detection limits of Table II or Figure 4 from units of ng/cm^2 to units of ng/m^3 .

The use of IPC 1478 filter media allows one to sample air at extremely high flow rates. This filter medium has been designed for sampling

by aircraft in the upper atmosphere. According to the measurements by Lockhart et al, the collection efficiency is poor at low flow rates (13). The efficiency is expected to improve as the flow rate is increased. However, it is questionable whether the collection efficiency for sub-micron aerosol would be adequate. (The efficiency would be expected to be very good for sampling in the upper atmosphere where the air pressure is very low).

AA Millipore filter has been commonly used for XRF analysis because aerosols are collected close to the filter surface. This minimizes self absorption problems for light elements. However, the ability to analyze 10-minute air samples is limited by the rather low flow rate. Higher flow rates are possible using Whatman 41 filters, but the applicability to elements which have atomic numbers below 20 is questionable due to the greater thickness and greater penetration of aerosol into the filter during sampling.

CONCLUSIONS

The foregoing discussion is a brief outline of some of the capabilities and limitations of presently available instrumentation for chemical and elemental analysis of aerosols. This information could be helpful in the design of an airborne platform system for aerosol analysis. If very short sampling periods are required, then there may be difficulty in collecting enough material for analysis if the most desirable membrane filter were used. If analysis of the light elements is not needed, then Whatman 41 filter material can be used. This problem can be

alleviated as the detection limits on XRF analyzers improve. A new pulsed XRF spectrometer developed at the Lawrence Berkeley Laboratory does achieve significantly improved detection limits. Also, a new XRF analyzer for total sulfur is now under development and should be useful with brief sampling intervals. Finally, a new evaluation of filter media is being conducted, in order to identify a filter which is suitable for XRF analysis and which has flow and efficiency characteristics that are optimum for high speed aerosol sampling(15).

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TABLE 1.

<u>Parameter</u>	<u>Method</u>
Sulfate	NASN colorimetric
	AIHL microchemical
	Brossett colorimetric
	Turbidimetric
	Flash volatilization
Sulfuric Acid	Gran titration
	Volatilization at 100 ⁰ C.
NH ₃	Colorimetric
	Ion selective electrode
Nitrate	Colorimetric
	Ion selective electrode
Carbon	Pyrolysis-Reduction

TABLE II.

DETECTION LIMITS FOR ELEMENTAL ANALYSIS
EXPRESSED IN UNITS OF ng/cm^2

NAA ^a	XRF ^b	ES ^c	AA ^c
Na 1			
Al 1	180		
Si	100		
S	38		
Cl 200	30		
Ca 1000	15		
V 0.5	30	15	50
Mn 1	25	50	5
Fe 1	28	800	50
Cu 20	16	10	5
As	5		100
Se 0.02	5		
Br 2	8		
Cd	50	50	1
Ba 0.1	170		100
Pb	16	50	10

^a These values are calculated from the detection limits given in Reference (10) assuming that 25 m^3 of air is sampled through a 57-mm diameter membrane filter.

^b Present work using Ti, Mo and Sm secondary fluorescers. See also Reference (9).

^c Calculated from the detection limits given in Reference(11) assuming that 2000 m^3 of air are sampled through a 407 cm^2 area of glass fiber filter.

TABLE III.
IMPURITIES IN FILTER MEDIA *

	<u>MILLIPORE AA</u>	<u>W 41</u>
Na	400 - 600 ng/cm ²	150 ng/cm ²
Al	6 - 15	12
Cl	1000 - 1700	100
K	100 - 200	15
Ca	200 - 700	140
Ti	5 - 15	10
Fe	40 - 80	40
Ni	<20	<10
Cu	20 - 90	<4
Zn	10 - 30	<25

* From Reference 13

TABLE IV.

SUMMARY OF PHYSICAL PROPERTIES OF VARIOUS FILTER MEDIA

FILTER TYPE COMPOSITION	AA ESTERS OF CELLULOSE	W41 CELLULOSE	IPC 1478 CELLULOSE	TYPE A GLASS FIBER
Pore Dia., μm	0.8			
Thickness, mm	0.15	0.25	0.56	0.46
Mass/area, mg/cm^2	4.8	8.9	14.8	9.4
Face velocity ^b , m/sec	0.94	3.7	>12 ^c	4.2
Flow rate/area ^b , l/min-cm ²	5.6	22	>72 ^c	25
% efficiency @ 0.3 μm DOP	100	100		100

^a These data are from Reference (14)

^b For these flow rates, the pressure drop is 250 Torr (1/3 atm)

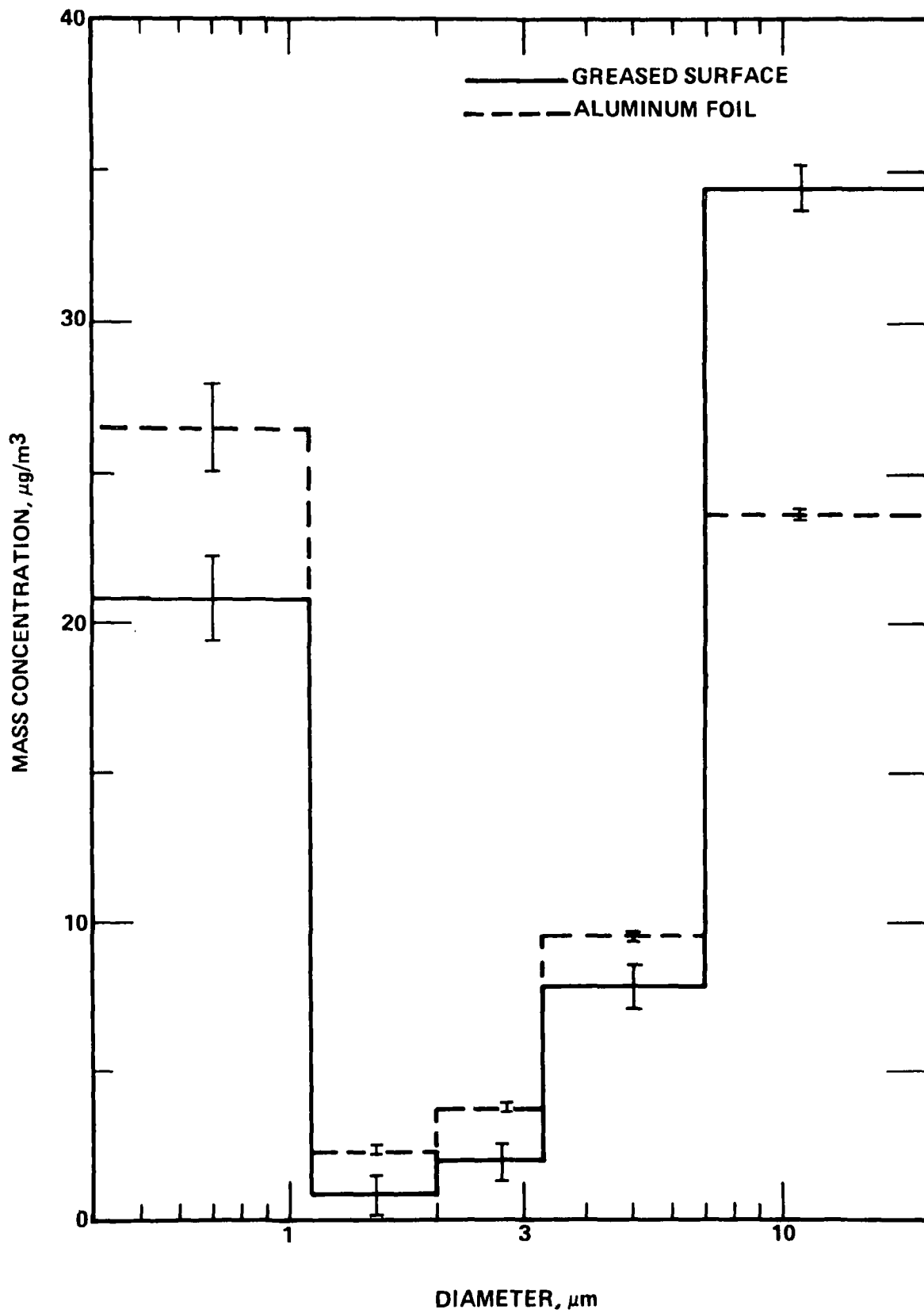
^c Private communication, John Cooper

TABLE V.

VOLUME THROUGHPUT FOR TEN MINUTE SAMPLING INTERVALS

<u>FILTER</u>	<u>VOLUME/AREA (m³/cm²)</u>
AA Millipore/Fluoropore	0.056*
W 41	0.22*
IPC1478	>0.72*
Type A, glass	0.25*
HiVol Sampler	0.038

*Pressure drop = 1/3 atm



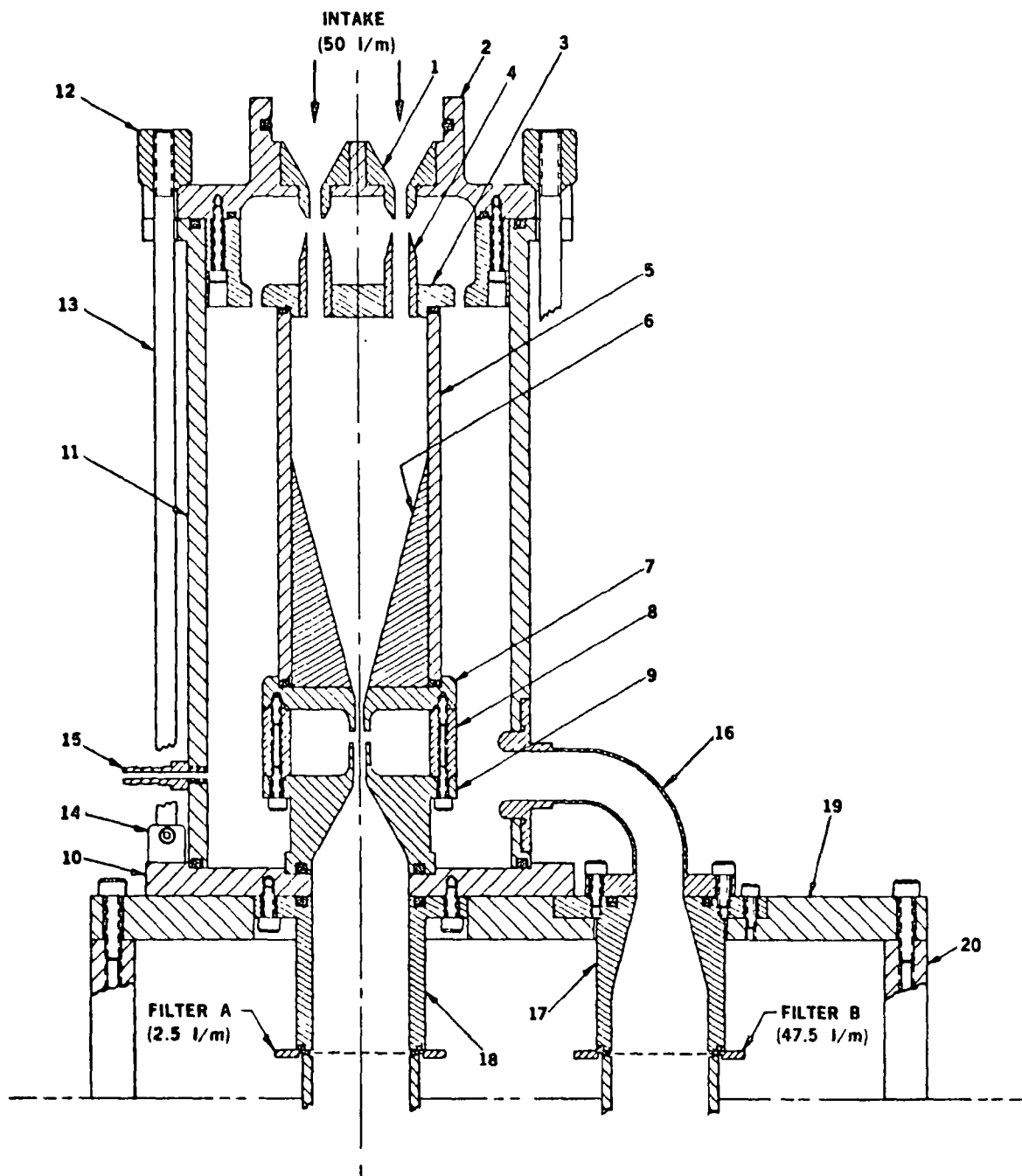


Figure 2: Dichotomous Sampler which uses two substages of virtual impaction. (Ref 4).

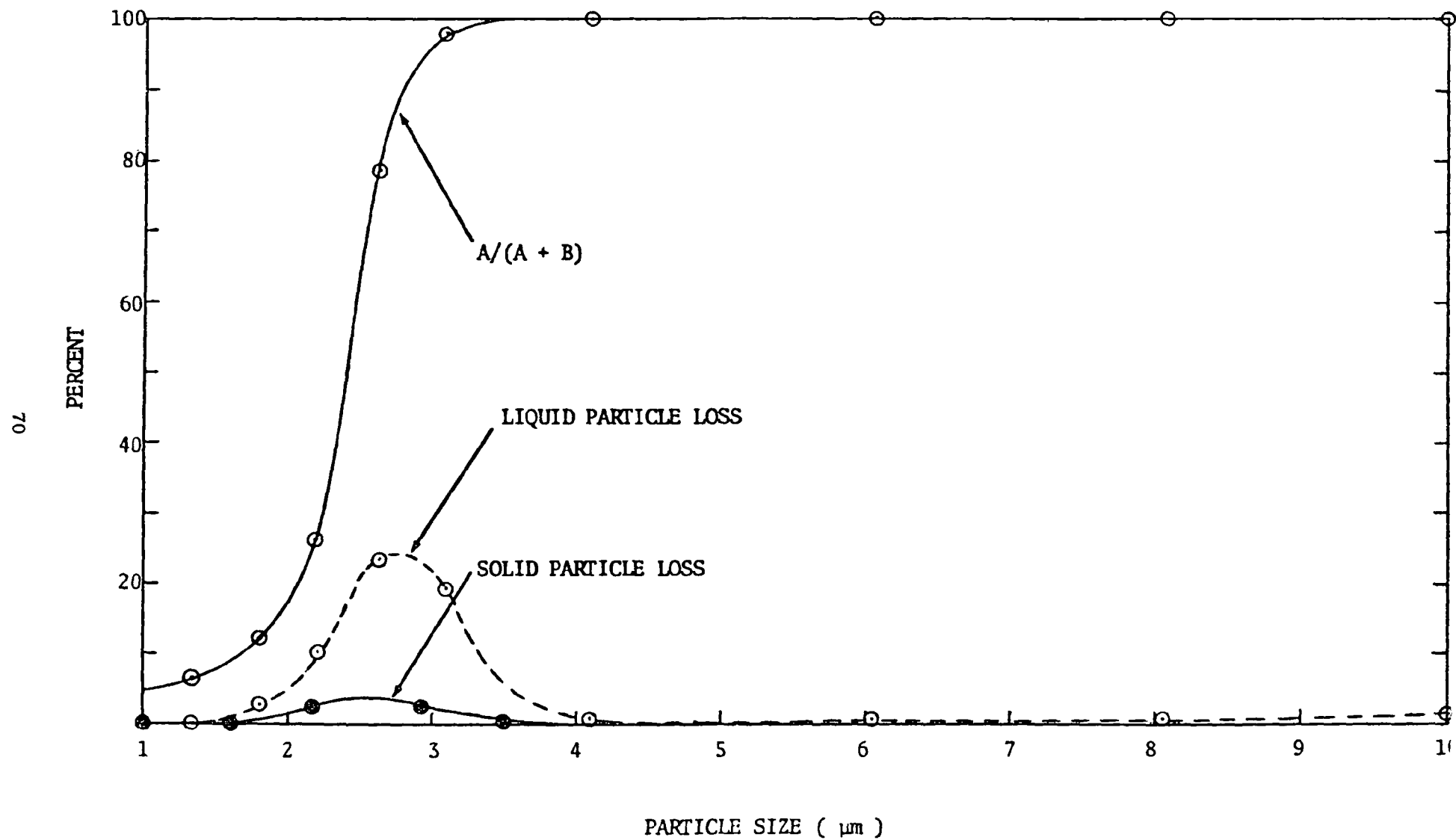


Figure 3: Fractionation characteristics of dichotomous sampler. (Ref 4).

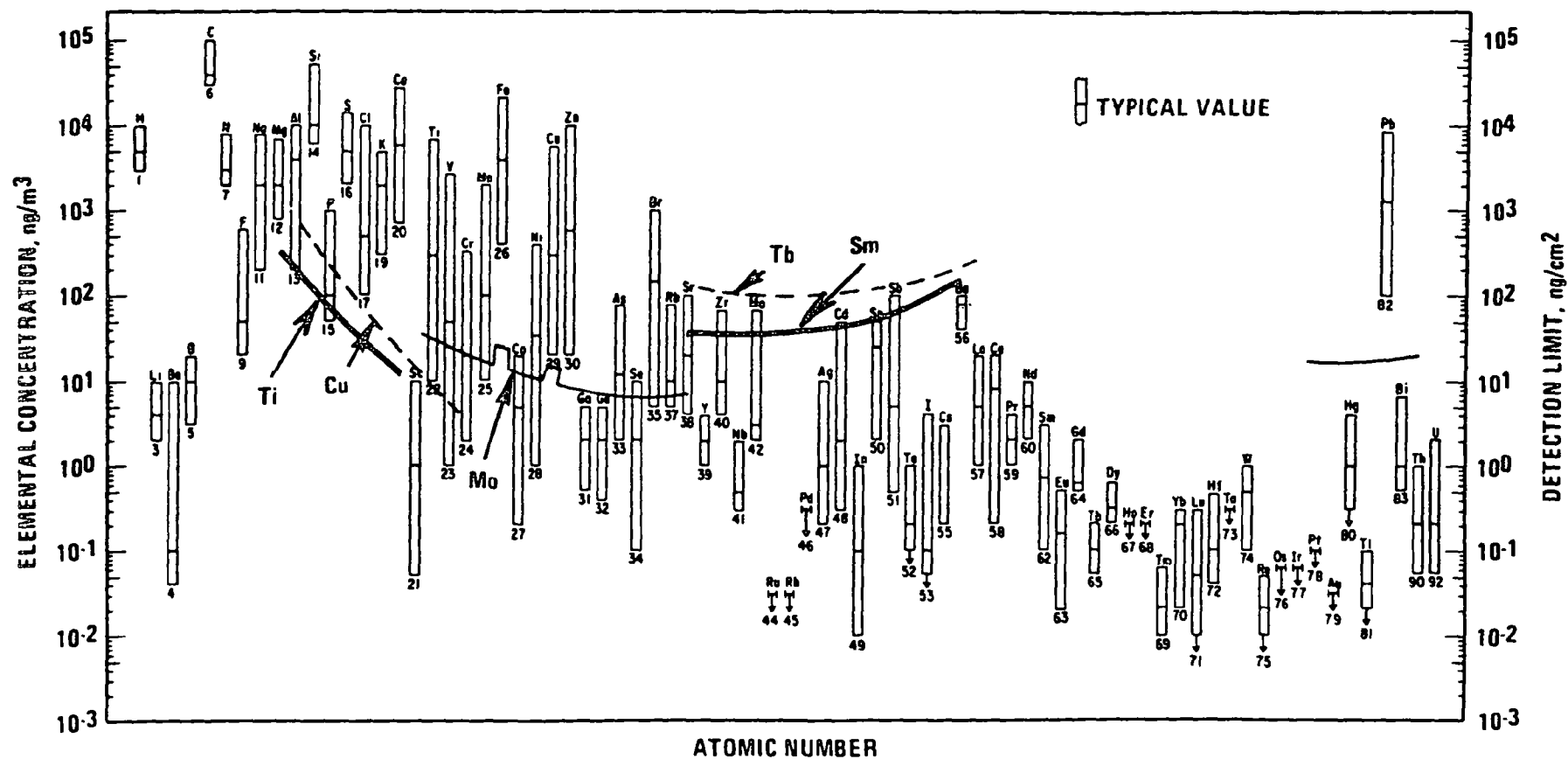


Figure 4: Detection limits for XRF analyzer using a variety of secondary fluorescers. Also shown are typical ranges of trace element concentrations in urban air (Ref. 12).

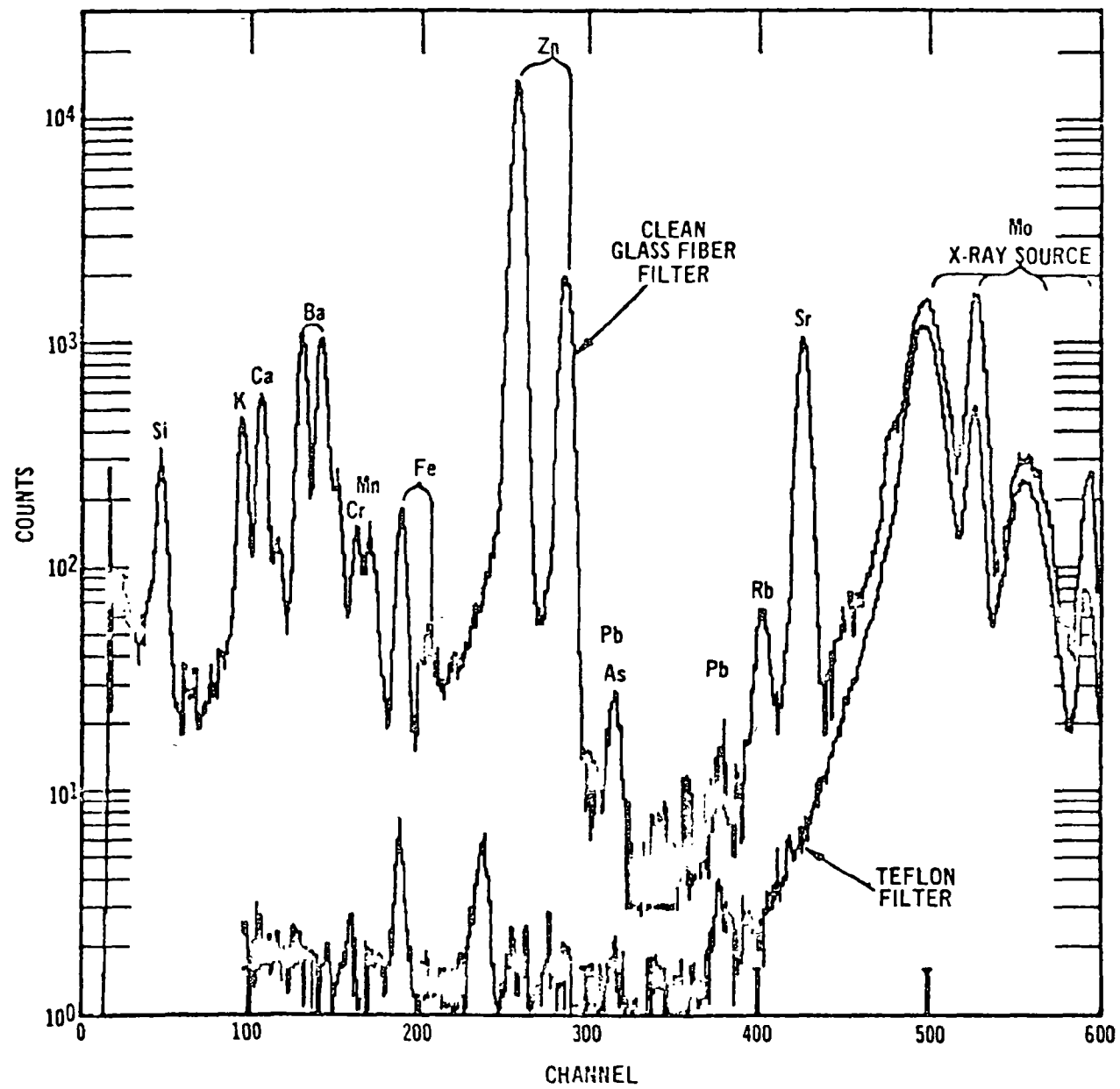


Figure 5

METHODS OF ANALYSIS OF
HALOCARBON AIR POLLUTANTS

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Presently, three major techniques are used to measure the concentrations of fluorocarbon air pollutants. The three methods are:

1. Gas chromatography employing an electron-capture detection system,
2. Gas chromatography followed by a mass spectrometer with a single ion detector,
3. Long-path infra-red spectroscopy.

The advantages and disadvantages of each system are discussed below and a summary is given in Table I.

Gas Chromatography Employing Electron Capture Detection System:

Gas chromatography with an electron capture detector system (GCECD) is by far the most widely used method for analysis of fluorocarbon air pollutants. Most of the published investigations of ambient air concentrations have employed this technique. ¹⁻⁹

GCECD offers several advantages. Such systems are readily available commercially, and they are the least expensive of the instruments used for fluorocarbon measurement (\$4,000 to \$15,000 per unit). The method is very sensitive for detection for fluorocarbons: concentrations as low as 1×10^{-12} v/v* for fluorocarbon 11 and 10×10^{-12} v/v for fluorocarbon 12 can be measured.⁹ These concentrations are at least an order of magnitude below the lowest ambient "background" levels. These systems are portable, and ambient measurements have been taken from aboard ships ^{3,6} and aircraft.⁵ GCECD systems also offer the advantage of being able to analyze for a whole series of halocarbons in each air sample. Fluorocarbons 11 and 12, carbontetrachloride, trichloroethylene, and tetrachloroethylene can all be detected in a single chromatogram.⁸

* v/v = volume of pollutant per volume of air

GCECD systems have some disadvantages also. The electron capture detector's sensitivity is a function of the compound being measured, and the compounds which the instrument can detect are limited to those molecules containing several electronegative atoms. For example, carbontetrachloride (CCl_4) is easily detected, while the compound methyl chloride (CH_3Cl) is several orders of magnitude less detectable. GCECD, as does all forms of gas chromatography, has the limitation that real-time, continuous measurements cannot be made.

Gas Chromatography Followed by a Mass Spectrometer With a Single Ion Detector:

This system of analysis is a relatively new technique for fluorocarbon and halocarbon analysis. It is still in the developmental stage, however, this method seems to be a very promising, versatile technique.¹⁰ The gas chromatography - mass spectroscopy (GCMS) technique is almost as sensitive as the electron capture technique; this method allows the detection of about 5×10^{-12} v/v for both fluorocarbon 11 and fluorocarbon 12. This technique does not show the compound dependence that GCECD does. This means that compounds such as CH_3Cl , CH_2Cl_2 , etc. which cannot be easily detected by electron capture, can now be measured in ambient air in the 10^{-11} - 10^{-12} v/v range.¹⁰ A mass spectrograph of a compound is a "fingerprint" of that compound, and this system can be used to provide a positive identification of each component analyzed.

While the advantages of GCMS include very important features, this system also has several disadvantages. One disadvantage is the cost which may run from \$60,000 to \$150,000 per unit. The present systems used for fluorocarbon analysis are large and cannot be used in a field situation. Being another gas chromatograph system, this instrument cannot make real-time continuous measurements. The biggest disadvantage of the system is that the single ion detection

technique, as it is now used, will allow the researcher to analyze only one compound per sample. This means that the instrument must be "retuned" for each component of an air sample, and that a separate sample of air is required for every pollutant analyzed.

Long-path infra-red spectroscopy (LPIRS): The LPIRS is a versatile technique which can be used to make ambient measurements of a broad spectrum of air pollutants, including fluorocarbons, and other halocarbons.^{11,12}

The main advantage of a long-path infra-red system is that it allows real-time continuous measurements of halocarbons, and depending on the absorption characteristics of the various compounds, several compounds can be monitored at the same time. The ability to measure several compounds at the same time is extremely important when the chemistry of fluorocarbons and other halocarbons is examined, in that, the appearance of reaction products can be followed. Infra-red analysis of a compound, like mass spectrometry provides a "fingerprint" of a compound for positive identification.

Disadvantages associated with LPIRS include the rather high cost (\$20,000 - \$100,000) and the fact that the instruments cannot be used in the field. The sensitivity of the instrument, which varies with the length of the path, is at best two orders of magnitude lower than that of GCECD and GCMS.

Other Techniques: The three methods mentioned comprise the techniques that are presently being used, and which can measure ambient air concentrations without preconcentration (The LPIRS can only be used for samples taken from high concentration areas).

If one preconcentrates a sample, it is possible to measure fluorocarbon concentrations by more common, but less sensitive techniques (e.g. gas chromatography using other detectors, shorter path infra-red systems, mass spectrometers, etc.). For example, cryogenic concentrating techniques have been used to improve the capabilities of LPIRS¹², and to enable one group of workers to use a more common mass spectrometer for fluorocarbon analysis.¹³ Preconcentration techniques followed by analysis with alternate systems undoubtedly have advantages and disadvantages, however, the amount of work in this area that has been reported thus far is insufficient for making an adequate evaluation.

A method has been reported for measuring fluorocarbons in the stratosphere using an infra-red spectrophotometer to measure the solar ir absorption. By examining spectra taken on balloon flights in 1968, Murcray was able to assign certain observed peaks to fluorocarbon absorbances.¹⁴ The volume mixing ratios on the order of 10^{-11} could be detected, however the estimated error in these measurements was $\pm 50\%$. This method of measurement of fluorocarbons holds a great deal of promise. Experiments dedicated to halocarbon measurements should provide a great deal of information on stratospheric concentrations.

Conclusions: Complementary methods of analysis for fluorocarbons and other halocarbons presently exist which will allow the monitoring of these compounds in ambient air samples. The present methods are more than sensitive enough to measure the levels of both fluorocarbons 11 and 12 in tropospheric and lower stratospheric samples, and should be sensitive enough to measure fluorocarbon concentrations in samples taken from the higher stratosphere. This assumes that fluorocarbon concentrations in the stratosphere are greater than 10^{-12} v/v.

The GCECD system, because of its low cost and high sensitivity, is the most widely used method of analysis for fluorocarbons, and will probably continue to remain the method of choice. However, there are gaps in GCECD system capabilities which need to be filled by the other instrumentation discussed.

The GCMS system offers more sensitivity to the whole spectrum of halocarbons than does GCECD, and should find wide use in the analysis of halogenated hydrocarbons which are not easily measured by electron capture.

The LPIRS system offers the capability of real-time, continuous measurements, and will be most useful in the examination of the chemistry of fluorocarbons and other halocarbons.

The solar infra-red system has a great deal of promise for stratospheric measurements.

Other systems require further development and evaluation.

TABLE I

SUMMARY OF ADVANTAGES AND DISADVANTAGES
OF METHODS OF MEASURING FLUOROCARBONS

METHOD	FLUOROCARBON SENSITIVITY		ADVANTAGES	DISADVANTAGES
Electron Capture Gas Chromatography	F11	$1 \times 10^{-12} \text{ v/v}$	low cost, portable, can analyze several components at the same time	sensitivity is a function of the compound, cannot make continuous measurements
	F12	$10 \times 10^{-12} \text{ v/v}$		
Gas Chromatography plus Mass Spectro- meter with Single Ion Detector	F11	$5 \times 10^{-12} \text{ v/v}$	sensitivity not as compound dependent, and can measure compounds not measurable by electron capture, provides positive identification of compounds	high cost, not portable, cannot make continuous measurements, can only analyze one pollutant per sample of air
	F12	$5 \times 10^{-12} \text{ v/v}$		
78 Long Path Infra- Red Spectrometer	F11	$1 \times 10^{-9} \text{ v/v}$	allows continuous monitoring, allows simultaneous monitoring of several components, provides positive identification	high cost, not portable, lower sensitivity
	F12	$1 \times 10^{-9} \text{ v/v}$		

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INSTRUMENTATION TO MEASURE GASEOUS AND PARTICULATE
POLLUTANTS FROM AIRBORNE PLATFORMS - A REVIEW

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INTRODUCTION

Measurements of atmospheric contaminants from airborne platforms have generally been performed with conventional hardware adapted for this task. Problems that result from adapting state-of-the-art instrumentation to airborne studies can be identified in the following areas: (1) space and power requirements; (2) temperature and pressure sensitivity and (3) response time of the sensor. Commercial instrumentation available to monitor SO₂, NO₂, CO, O₃ and hydrocarbons normally weighs from 30-70 pounds, requires on the average of 500 watts power and has response time constant from 20-60 seconds. Recently, some manufacturers have made an effort to reduce the size and power requirements of certain gaseous monitoring equipment.

The text that follows summarizes the adequacy of current ambient air measurement reference methods and areas where research is ongoing to develop more reliable air pollution monitoring instrumentation.

DISCUSSION

Below is a table listing the air quality standards for carbon monoxide, nitrogen dioxide, hydrocarbons, sulfur dioxide, particulate matter and photochemical oxidants. In this table is a list of the analytical techniques cited by EPA in the Federal Register (36(84) 8186 (1971)) as the reference methods for measuring these pollutants.

We have also classified the reference methods as adequate or inadequate with regard to ground level monitoring. The adequacy of each reference method by pollutant will be discussed in detail later in the text.

TABLE I

STATUS OF MONITORING AT GROUND LEVEL CARBON MONOXIDE, NITROGEN DIOXIDE,
HYDROCARBONS, SULFUR DIOXIDE, PARTICULATE MATTER AND PHOTOCHEMICAL OXIDANTS

Substance	Primary Standard		Secondary Standard		Analytical Reference Method	Status
	mg/m ³	ppmv	mg/m ³	ppmv		
Carbon monoxide	10 ^a	9 ^a	40 ^a	35 ^a	Nondispersive IR	Adequate ^k
Nitrogen dioxide	0.10 ^b	0.05 ^b	0.10 ^b	0.05 ^b	Chemiluminescent ^c	Adequate
Hydrocarbons ^d	0.16 ^e	0.24 ^e	0.16 ^e	0.24 ^e	Flame ionization	Inadequate ^l
Sulfur dioxide ^f	0.080 ^b	0.05 ^b	0.365 ^g	0.14 ^g	Colorimetric (pararosaniline)	Adequate ^m
Particulate matter	0.075 ^h		0.26 ^g		High-volume sampler	Adequate ⁿ
Photochemical oxidants ⁱ	0.160 ^j	0.08 ^j	0.160 ^j	0.08 ^j	Chemiluminescent reaction with ozone	Adequate ^o

^a Not to be exceeded more than once a year.

^b Annual arithmetic mean.

^c Proposed reference method.

^d Sum of all hydrocarbons other than methane.

^e Maximum 5-hour concentration(6 to 9 A.M.) not to be exceeded more than once per year.

^f Measured as sulfur dioxide.

^g Maximum 24-hour concentration, not to be exceeded more than once per year.

^h Annual geometric mean.

ⁱ Corrected for interferences due to nitrogen oxides and sulfur dioxide.

^j Maximum 1-hour concentration, not to be exceeded more than once per year.

^k Sensitivity needs improvement.

^l Reliability of method is marginal at air quality standard.

^m Method too complicated.

ⁿ Collection medium needs modification. Method to determine fine particles needs development.

^o Calibration method needs improvement.

The analytical reference methods cited in Table I are not always the methods used for routine monitoring or even the methods used to gather data for preparation of implementation plans.

Because of the variety of methods available to monitor these six air pollutants, EPA has promulgated a document published in the Federal Register which describes tests which compare a proposed method with the reference method. If the proposed method passes the test to the satisfaction of the administrator, EPA then will consider the method equivalent to the reference procedure and the new method can be used by state and local agencies in the preparation of implementation plans.

However, not all of the reference methods are totally adequate for routine monitoring and the following is a status report, by pollutant, on the adequacy of the reference methods:

Carbon monoxide: The non-dispersive IR method is adequate for ambient air monitoring, but more precision is desirable at the level of the air quality standard. New instrumentation for carbon monoxide has been developed and is currently under evaluation. The goal for instrumental performance characteristics includes a factor of ten increase in sensitivity and a simplified procedure to correct for water vapor interference.

Nitrogen dioxide: It has been proposed that the colorimetric method originally cited as the reference method for nitrogen dioxide be replaced by the chemiluminescence procedure.

Hydrocarbons: The reference method for non-methane hydrocarbons is based on chromatographic separation and measurement of methane simultaneously with the measurement of the total hydrocarbons. The measurements are made with a flame ionization detector. This method at present is considered to be unreliable when measuring concentrations at levels below 0.5 ppm. Work is ongoing to delineate those problems and/or to improve the reliability of the analytical method.

Sulfur dioxide: The method is based on the collection of SO_2 for a 24-hour period, followed by colorimetric analysis when the sample is returned to the laboratory. This method is considered adequate but complicated, due to the large number of ultrapure reagents needed in the measurement. For the gaseous pollutants, this is the only non-instrumental reference method. Work is ongoing to develop a low cost, reliable, simple method to serve as an equivalent procedure. In most areas of the United States, flame photometric and coulometric instruments are used to measure SO_2 .

Particulate matter: The HiVolume sampler method of collecting particulates is marginally adequate for routine monitoring. Recent studies

have shown the glass fiber collection surface may convert gaseous SO_2 and NO_2 to sulfates and nitrates respectively, thus adding weight to the filter which could provide an over-estimate of the atmospheric particulate loading. The method provides no means of separating the respirable from the non-respirable particles. Work is in progress to replace the HiVolume collection system in order to develop a sampler which will separate the fine from the coarse particles. In addition efforts are underway to develop a collection surface where artifact formation will be minimized.

Photochemical oxidants : The chemiluminescent ozone-ethylene reaction is the reference method and is considered adequate. Recently, however, EPA has been challenged with regard to the validity of the recommended potassium iodide colorimetric method for calibrating ozone generators (used to calibrate ozone monitors). As a result, EPA is engaged in an intensive in-house, grant and contractual program to investigate the ozone calibration method to determine the adequacy of the procedure.

EPA will continue to maintain a quality assurance program to check on the efficiencies of the current reference and equivalent methods. In addition, EPA will foster development of quality assurance procedures to assure that the data being reported on the condition of the atmosphere will be accurate and reliable.

AIRBORNE INSTRUMENTATION

Table II is a summary of the status of instrumentation for measuring the gaseous pollutants from aircraft. The two major problems with the methods currently employed in airborne monitoring are (1) their slow response times and (2) their sensitivity to changes in altitude. Work is ongoing to develop techniques to correct these operational deficiencies but at present, a totally reliable instrument for airborne gaseous pollutant monitoring studies does not exist.

The techniques employed to circumvent these problems are to calibrate the monitors in flight at the altitude where measurements are to be made and to correct the response time by correlating time and location and knowing the response time of the instrument.

TABLE II

STATUS OF MONITORING HYDROCARBONS, OZONE,
OXIDES OF NITROGEN, CARBON MONOXIDE AND SULFUR DIOXIDE FROM AIRCRAFT

CONCENTRATION REQUIREMENTS PPM	ANALYTICAL METHOD	OPERATIONAL CHARACTERISTICS
HYDROCARBONS		
0.001 - 10.0	Flame Ionization	a. Measures total H.C. b. Requires hydrogen
	FID-G.C.	a. Slow response time b. Marginal sensitivity c. Requires hydrogen d. Altitude sensitive
	Catalytic Combustion FID	a. Requires hydrogen b. Altitude sensitive c. Non-specific d. Marginal sensitivity
OZONE		
0.01 - 1.0	Chemiluminescent	a. Requires ethylene
OXIDES OF NITROGEN		
0.01 - 1.0	Chemiluminescent	a. Marginal sensitivity
CARBON MONOXIDE		
0.05 - 100	NDIR	a. Vibration sensitive
	Conductivity	a. Non-specific b. Slow response time c. Inadequate sensitivity
	Gas Chromatography	a. Slow response time b. Altitude sensitive c. Requires hydrogen
SULFUR DIOXIDE		
0.01 - 10	Conductivity	a. Non-specific b. Lacks sensitivity c. Slow response time
	Flame photometric	a. Sensitivity marginal b. Requires hydrogen c. Altitude sensitive
	Electrochemical	a. Slow response time b. Lacks sensitivity

DEVELOPMENT OF STANDARD REFERENCE MATERIALS FOR AIR QUALITY MEASUREMENT

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ABSTRACT

The National Bureau of Standards is engaged in a continuing program involving gaseous Standard Reference Materials for air pollution measurements. Preparation of such materials requires definition of the stability, homogeneity and accuracy of the samples. This information is obtained by long term studies of the gas systems, by development of absolute methods of analysis and by analysis of large numbers of samples prepared in bulk. The results of studies, extending over several years, of low concentration of carbon monoxide in nitrogen and nitric oxide in nitrogen are reported. Over one thousand samples of these materials have been analyzed and the stability with time and the within-batch homogeneity have been characterized. Accuracy is achieved by use of gravimetric standards and with dynamic dilution systems. Accuracy attainable by either method is described.

The use of permeation tubes of sulfur dioxide and nitrogen dioxide is necessary in some situations because of the reactivity of the gases. Data covering the stability and accuracy of these devices has been collected over a period of several years.

INTRODUCTION

The legal implications of measurements of air pollutants whether at ambient or source levels is such that the accuracy of the measurement must be clearly defined. A substance can be measured accurately in one of two ways. First, an absolute technique of known accuracy may be used in which case the measured value has accuracy equivalent to that of the method. Alternatively, an analytical standard may be employed together with a precise method of comparison. In this case, if the imprecision of the method of comparison is considerably less than the uncertainty of the standard then the accuracy of the measurement is described by the accuracy of the standard.

This paper is concerned with accuracy in the measurement of gaseous pollutants and

it should be recognized that few absolute methods are available to the gas analyst. Those that are available, volumetric adsorption or gravimetric methods for example, are generally useful only at relatively high concentrations. A very few electrochemical methods are applicable at low concentrations. Consequently, accurate measurements of air pollutants will in general require the existence of a standard of known accuracy. The Analytical Chemistry Division of the National Bureau of Standards has been involved in recent years in the preparation of Standard Reference Materials for use in gas analysis and particularly for use in analyses associated with air pollution measurements. There is now available a limited number of gas standards consisting of various concentrations of carbon dioxide in nitrogen, propane in air, methane in air, oxygen in nitrogen and a series of sulfur dioxide permeation tubes. There are standards of nitric oxide in nitrogen and nitrogen dioxide permeation tubes in preparation. Standards for vinyl chloride in air, high concentration of sulfur dioxide in nitrogen and a methane-nonmethane hydrocarbon in air mixture are being investigated as potential Standard Reference Materials.

The preparation of gas mixtures is not particularly difficult and the routine preparation of "standards" is commonplace. However, experience has shown that the accuracy of such standards is often woefully inadequate for the measurements for which the standards are intended. The major reasons for the inadequacy are the uncertainty in assigning an accurate value to the concentration and the uncertainty in the stability of the gas mixture during storage and use. The solution to either of these problems is often very time consuming and expensive and the two uncertainties are the major reason for the small number of Standard Reference Materials available and for their relatively high cost.

It is obvious that accuracy and stability

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are primary requirements for a Standard Reference Material but in addition, availability in sufficient number and size constitute further requirements. Standards should be produced in sufficient quantity and at a range of concentrations to satisfy the needs of diverse laboratories both those engaged in measurement, enforcement and research. This imposes certain problems in that the production of gas mixtures in quantity and with homogeneous compositions at trace levels has not been fully evaluated. Commercial preparation of gas mixtures to rigid specifications appears to be a feasible approach to preparation in quantity and homogeneity is currently assured by individual analysis of each sample. Thus, rapid and precise methods of inter-comparison between the primary standards and the potential Standard Reference Materials must often be developed and used until the homogeneity of a batch can be predicted from experience and from the results of a limited number of measurements.

In some cases it is not possible to prepare mixtures of satisfactory stability in cylinders and alternate standards may be feasible. Permeation tubes offer such an alternate and while permeation tubes cannot be considered primary gas standards in the pure sense, they can be used to generate gas mixtures of predictable concentration. The effort necessary to evaluate the accuracy of such devices as Standard Reference Materials is different from that involved with gas mixtures but it is equally difficult and time consuming.

The total development of any of these Standard Reference Materials is best illustrated by example. A description follows of the general procedure involved in preparation of the carbon monoxide and nitric oxide gaseous Standard Reference Materials and the sulfur dioxide and nitrogen dioxide permeation tubes. These were chosen as typical examples because of the range of problems associated with each.

DEVELOPMENT OF A STANDARD REFERENCE MATERIAL

The development of a gaseous Standard Reference Material involves the preparation of a series of primary standards and a deduction of the accuracy of the standards while simultaneously investigating the stability of the primary standards and of the particular gas mixture in the container in which it will eventually be distributed as a Standard Reference Material.

An accurate gas mixture can be prepared in a similar manner to an accurate solution. A measured amount of an analyzed reagent is mixed with a measured amount of analyzed diluent. The concentration of the reagent species in the resulting mixture can then be calculated with an error dependent only on the accuracy with which the purity of

the reagent and diluent are known and the accuracy of measurement of the quantity of reagent and diluent. Gas mixtures are prepared most often by measurement of the pressure of the reagent added to a cylinder and of the combined pressure of reagent and diluent but the use of gravimetric procedures, in which the weight of each component added to a cylinder is measured, has become quite common in recent years. The latter method could be considered more nearly absolute than the former but in either case it is possible to prepare mixtures with an error of less than one percent.

The analysis of the reagent gases is, in some cases, a greater source of error than the mixing procedure. It is now possible to obtain the more common diluent gases, air and nitrogen, which contain no significant amounts of the reagent gas as an impurity but in all cases it is essential to verify the absence or to determine the concentration of the reagent if it is present. The assay of the pure reagent is an essential and often quite difficult step in the preparation of accurate gas standards. However, the many techniques and the variety of instrumentation involved in this phase of the analysis is too extensive to include in this paper. Suffice it to say that a great deal of effort is expended in defining the composition of the reagent gases and that in general the resulting uncertainties do not contribute significantly to the error assigned to the standard.

Primary standards are prepared by a gravimetric method generally to a concentration of one percent of the starting material. That is, starting with pure reagent and pure diluent a one percent by weight mixture is prepared. The combination of cylinder weight, balance capacity and sensitivity, and the sample weight are such that an uncertainty of ± 0.1 percent could theoretically be attained. In reality, the uncertainty lies between 0.2 and 1 percent for most of the mixtures investigated thus far. The one percent mixture may now be used as starting material for a second mixture with a resulting concentration of 0.01 weight percent (100 ppm). A third mixture may be prepared from the second which will have a concentration of 1 ppm. A series of replicate samples are prepared in this manner having concentration very near the concentration desired for the series of SRM's. It is, of course, essential that the stability of these standards be assured. This cannot be done directly unless an accurate method of analysis is available and unless it is applicable at all concentrations through which the preparative steps are performed. Lacking an absolute analysis it is necessary to deduce the stability by observing the relationship between samples using a relative method of analysis of adequate precision.

Gas mixtures stored at pressure in cylinders

tend to change composition in three ways. First, there may occur a rapid decrease in concentration due to adsorption on the walls of the cylinders or in the case of certain reactive gases by reaction with the container. Second, slow long term decreases in concentration may result from reaction within the cylinder. Third, an increase in concentration may occur as cylinder pressure drops with use and previously adsorbed material desorbs in keeping with changing equilibria inside the cylinder. The second effect, slow long term decrease, can be recognized by comparison of freshly prepared standards with standards that have been stored within the container for a long period of time. Short term changes can be recognized by transferring an analyzed sample to an empty container and comparing the composition of the two. The possibility of increase of concentration due to desorption is observed by deliberately blowing down a cylinder and observing the change or lack of change in concentration. If no significant changes are observed due to the above causes then one can feel some assurance for the stability of the mixture.

In addition to gravimetric data it is desirable to measure the pressure of the various components as they are added to a cylinder. Analytical blunders are easily recognized when the pressure data and gravimetric data do not agree to within one percent of each other.

The use of dynamic dilution methods to generate standards at the time of use can provide an independent confirmation of the accuracy of primary standards prepared by gravimetric or pressure techniques. The dynamic dilution method involves the preparation of a mixture by blending two streams of gas of individually known composition. It is necessary to measure the volume flow of each gas with an accuracy of better than 99 percent if the resulting mixture is to have an uncertainty of composition similar to the gravimetric or pressure standards.

The primary standards may or may not be prepared in the same type of container in which the Standard Reference Material will be contained and it is necessary to independently assess the stability of the mixture in both containers. This stability can only be verified with confidence by observing the change, or lack of change, with time over the period of time during which stability is required. Some prediction of the long term stability of a sample may be based on observed behavior of a sample immediately after preparation but only long term experience yields the degree of confidence required of a Standard Reference Material.

PREPARATION OF CARBON MONOXIDE STANDARD REFERENCE MATERIAL

The major difficulty associated with carbon monoxide standards is the tendency of the carbon monoxide concentration to decline with time. Carbon monoxide mixtures prepared and stored in stainless steel cylinders remain constant for very long periods of time but similar mixtures prepared in mild steel cylinders, either DOT specification 3A or 3AA, show unpredictable and often disastrous reduction in carbon monoxide concentration. Figure 1 represents data obtained on analysis of four samples of carbon monoxide in nitrogen. The samples were prepared from the same materials and at the same time and under essentially identical conditions at concentrations of 5, 10, 25 and 50 ppm. The samples were analyzed periodically over a period of one year. The behaviour shown is typical of what has been observed with carbon monoxide mixtures stored in cylinders. The reason for the decline has not been definitely established but is probably due to either oxidation to carbon dioxide or carbonyl formation. In any case, the individual container is critical relative to the stability. Stainless steel containers are not an economically practical solution to the problem but a simple treatment of mild steel cylinders has resulted in adequate long term stability. The treatment consists of applying a thin coat of ceresin wax to the interior surface of the cylinder. The wax is applied hot to a heated cylinder, which is subsequently allowed to drain thoroughly. Table 1 shows the results of analysis of several samples of carbon monoxide in nitrogen stored in these wax-lined cylinders. It is obvious that over a period of one year the composition has not changed.

The primary standards were prepared gravimetrically in stainless steel cylinders. It was determined by comparison of numerous samples prepared over a period of years that no decrease in concentration of carbon monoxide occurs in stainless steel. The accuracy with which a typical set of gravimetric standards of carbon monoxide can be prepared is indicated in Table 2. This table shows the results of intercomparison of two samples each at six concentrations between 10 and 1300 ppm. The comparison was made by a method in which the carbon monoxide was catalytically reduced with hydrogen to methane with subsequent measurement of the methane using a flame ionization detector. The precision of intercomparison was between 0.1 and 0.2 percent relative. The agreement between pairs of samples is indicated by the agreement in the values "Division per unit of concentration" which is simply the total signal due to carbon monoxide divided by the concentration calculated from the gravimetric data. It is obvious that the accuracy of the standards may approach the precision with which they can be intercompared

but in general does not equal it. It should be noted that a direct comparison between different pairs of samples is not possible in this case because the separate pairs were analyzed at different times under slightly different instrumental conditions.

Analysis of large numbers of samples would require quantities of primary standards that would be inconvenient to produce. Consequently, a series of secondary standards were prepared in large stainless steel cylinders. The concentration of carbon monoxide in these samples was determined by numerous comparisons with primary standards. At least three primary standards were prepared at concentrations bracketing the concentration of the secondary standards. New primary standards were prepared periodically to confirm the stability of the secondary standards.

Two hundred and eighty cylinders consisting of five lots of five different concentrations of carbon monoxide in nitrogen were obtained from a commercial supplier. The cylinders were wax-coated as previously described prior to filling. All samples in each lot were analyzed by comparison with the secondary standards in a sequence of the standard followed by five samples followed by a repetition of the standard. Two separate measurements were made of each sample and standard. Some instruments drift may occur between the analysis of the standards and if this occurs it is necessary to interpolate the value of the instrument calibration between the standards. This resulted in some additional imprecision in the intercomparison. This is illustrated by Figure 2 where the measured value for 55 samples at the 950 ppm level is shown in the sequence of analysis. In addition, the manner in which the instrument calibration changed, as evidenced by the change in the absolute value of the signal generated by the standard, is shown. It is obvious that the calibration was changing rapidly early in the analysis and the exact value was less certain than during the period of stable operation. A second analysis of at least ten samples from each lot was performed one month after the first analysis. All samples that appeared to deviate from the average as well as a number at the average were included in the second analysis except that all samples at the 10 ppm level were reanalyzed. The total results are summarized in Figure 3 which is a frequency distribution plot of the observed concentrations.

All cylinders in each lot were filled from a single batch of material and it is reasonable to assume that the variation of the individual values for a lot represent imprecision in the measurement rather than actual differences in samples. The average for a lot, therefore, represents the actual concentration of any sample in the lot and the

uncertainty of the average represents the imprecision of the measurement.

The uncertainty assigned to the final value of the Standard Reference Material is a combination of four errors which are as follows:

1. The inaccuracy of the primary standard which is estimated to be ± 0.4 percent of the calculated value.
2. The imprecision of intercomparison of the primary and secondary standard which is ± 0.2 percent relative.
3. The imprecision of intercomparison of the secondary standard and the samples which is ± 0.2 percent relative.
4. The heterogeneity of the analytical values which is equal to the one half the range of the values.

The estimated upper limit for the total error of the average is given simply by the square root of the sum of the squares of the individual errors. Table 3 is a summary of the estimated upper limit for the total error for the five mixtures. The range of values for each lot is also shown.

The somewhat higher error for the second lot, 482 ppm, is due to the fact that the overall precision of intercomparison for this lot was 0.6 percent relative. This resulted from an attempt to use a second instrument of lesser precision for some of the analyses. Twenty-two samples analyzed by the more precise instrument with which all other lots were analyzed gave an average of 482 ppm with a total estimated error of 3 ppm. The average for the lot, 482, is considered accurate to within the ± 1 percent limit placed on the final certified value.

NITRIC OXIDE IN NITROGEN

Nitric oxide is not a particularly reactive gas in the chemical sense but it is difficult to prepare and store as a gas mixture in cylinders at pressure. Two major sources of error are recognized. These involve an apparent reaction with resulting decrease in concentration. This can be minimized by vigorous pretreatment of the container with nitric oxide mixtures of higher concentration than will ultimately be stored in the cylinder. This treatment, however, may result in a second source of error, which is the desorption of nitric oxide from the walls of the container after a period of use in which the cylinder pressure is reduced and which results in an increase in concentration.

Figure 4 is an illustration of this latter effect and was encountered in a study of nitric oxide stored in small steel cylinders. The cylinders had all been previously used

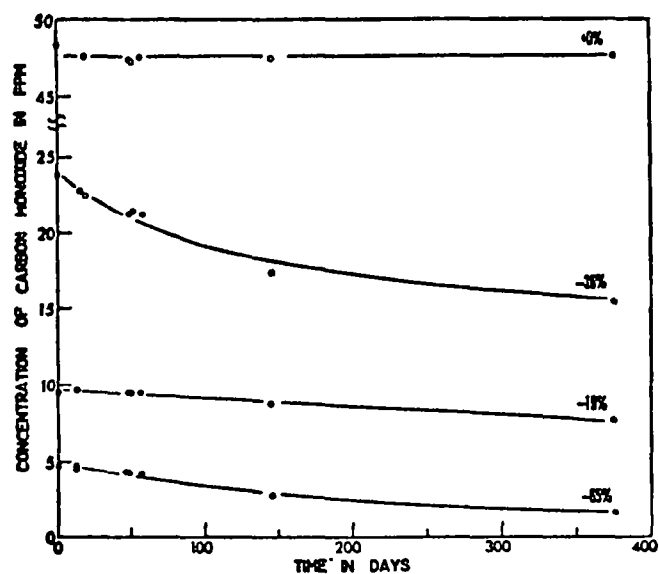


FIGURE 1. STABILITY OF CARBON MONOXIDE MIXTURES IN CYLINDERS (DOT-3AA)

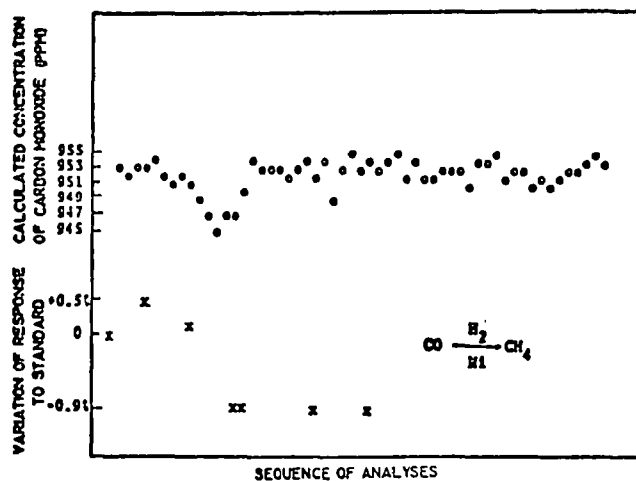


FIGURE 2. ANALYSIS OF 55 SAMPLES OF CARBON MONOXIDE ILLUSTRATING THE EFFECT OF INSTRUMENT RESPONSE ON PRECISION

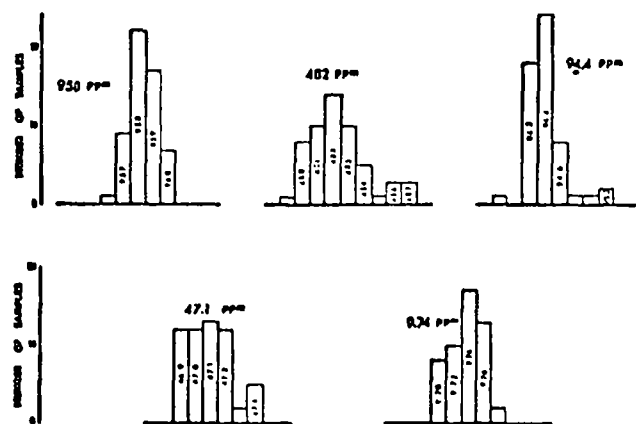


FIGURE 3. DISTRIBUTION OF CARBON MONOXIDE IN NITROGEN CONCENTRATIONS

**Table 1. Comparison of Carbon Monoxide Concentration
at One Year Intervals**

<u>Number of Samples</u>	<u>Average Concentration in ppm</u>	
	<u>6/73</u>	<u>6/74</u>
7	958.*	954.
4	482.	481.
4	94.4	94.4
3	47.1	47.0
5	9.74	9.74

*The maximum error is one percent or less at
all concentrations.

Table 2. Intercomparison of Carbon Monoxide Standards

<u>Sample Number</u>	<u>Calculated Concentration in ppm</u>	<u>Signal in Divisions</u>	<u>Divisions Per Unit of Concentration</u>
1	9.33	1128	121.0
2	10.30	1241	120.5
3	47.1	5260	111.7
4	51.5	5750	112.1
5	94.5	10915	115.5
6	103.6	11945	115.3
7	478.	54958	115.0
8	518.	59431	114.8
9	1007.	116913	116.1
10	1008.	116524	115.6
11	1275.	147900	116.0
12	1368.	159646	116.7

**Table 3. Estimated Upper Limit for Total Error of
Five Lots of Carbon Monoxide in Nitrogen**

<u>Measured Average in ppm</u>	<u>Range in ppm</u>	<u>Error in ppm</u>
958.	5.	±5.
482.	9.	±5.5
94.4	1.5	±0.9
47.1	0.5	±0.3
9.74	0.09	±0.7

FIGURE 4. STABILITY OF NITRIC OXIDE MIXTURES

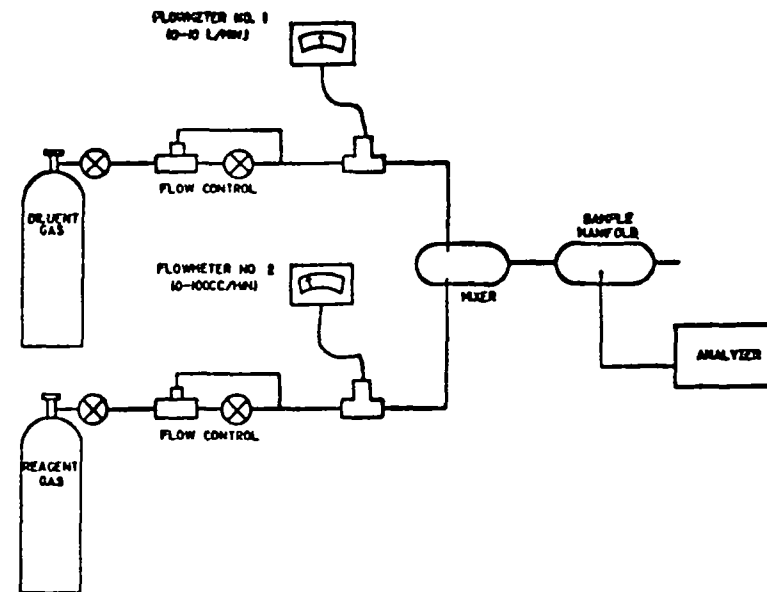
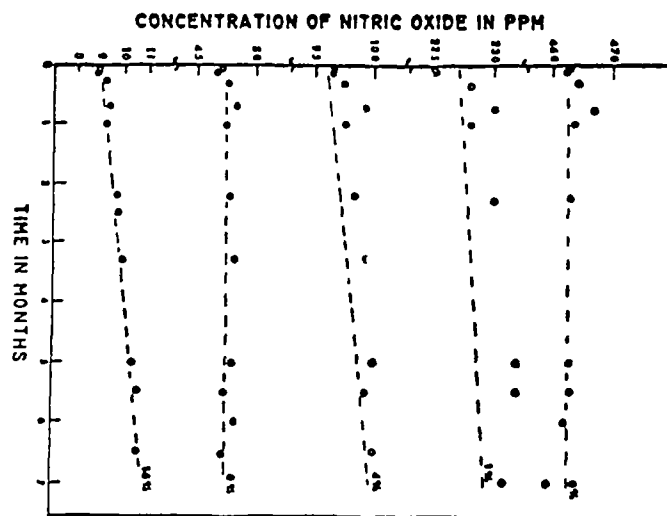


FIGURE 5. DYNAMIC DILUTION SYSTEM FOR NITRIC OXIDE MIXTURES

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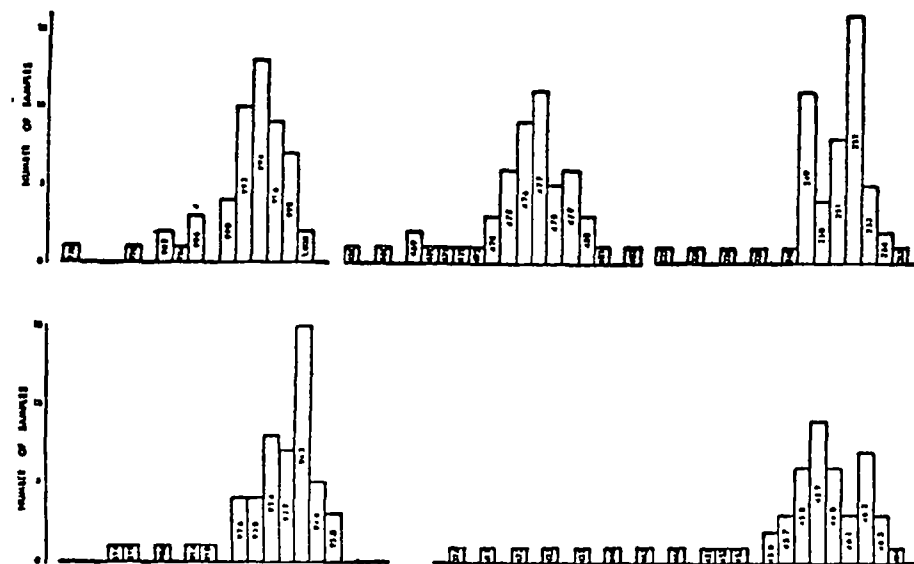


FIGURE 6. DISTRIBUTION OF NITRIC OXIDE IN NITROGEN CONCENTRATIONS

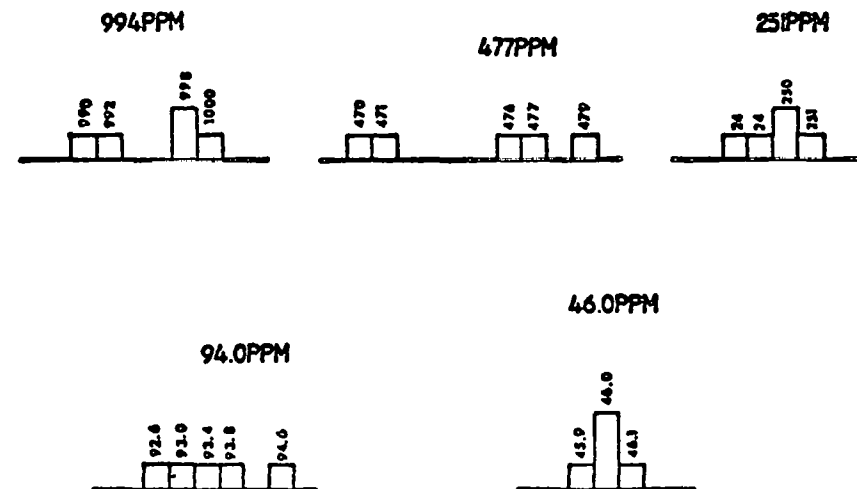


FIGURE 7. CONCENTRATION OF NITRIC OXIDE MIXTURES IN ALUMINUM CYLINDERS (5 SAMPLES AT EACH CONCENTRATION)

to store mixtures of nitric oxide or had been specially conditioned by "soaking" with a mixture of a high concentration of nitric oxide prior to use. The soaking appears to reduce or eliminate the decrease in concentration that had been observed to occur when new or untreated cylinders were used but it is obvious that increases in concentration can occur with time. Unfortunately, no exact record was kept of the cylinder pressure during this series of experiments but the frequency of analysis and the pressure observed at approximately seven months indicate that a steady decline in pressure occurred from about 500 psi to essentially zero pressure. The single points on Figure 4 are the results obtained on analysis of a single sample at each concentration while the broken line is the estimated average for a total of four samples analyzed at each concentration.

Neither wax lining of cylinders nor the use of stainless steel cylinders appeared to offer any advantage over steel cylinders of DOT 3AA specification. Aluminum cylinders which have recently become commercially available and which meet Department of Transportation requirements for interstate shipment may constitute a more satisfactory container for mixtures of this sort. However, considerable work has yet to be done to prove the feasibility of aluminum cylinders. This work is currently in progress simultaneous with the preparation of nitric oxide mixtures in nitrogen as Standard Reference Materials.

Primary standards for nitric oxide mixtures have been prepared by gravimetric, pressure and dynamic dilution techniques. Because of the potential instability of these mixtures it is necessary to prepare primary standards more frequently than with most other gaseous systems investigated.

Gravimetric mixtures can be prepared with an error of about ± 0.2 percent relative. This is shown in Table 4 where the results obtained on comparison of 15 gravimetric mixtures at five different concentrations are shown. The samples were compared with an instrument utilizing the chemiluminescent reaction between nitric oxide and ozone.

In this case the difference between samples approximates the imprecision in the measurement of the sample and the error in the gravimetric samples is considered to be this imprecision. Secondary standards were prepared for analysis of the Standard Reference Materials for the same reason mentioned for the carbon monoxide mixtures. Intercomparison of these mixtures with the primary standard has been done with maximum error of ± 0.6 percent relative.

The pressures of the components added to the gravimetric mixtures were measured dur-

ing preparation of the gravimetric standards. In addition, the gravimetric standards were compared to standards generated with a dynamic dilution system. The system is shown in Figure 5. The major source of error in the composition of mixtures generated by gas blending systems of this type lies in the uncertainty in calibration of the flow measuring devices. Mass flowmeters of the thermal conductivity type were used in the system described in Figure 5 and each was calibrated. The high flowmeter (0-10 l/min) was calibrated at several points by passing a measured weight of nitrogen through the meter. A weighed cylinder of nitrogen was attached to the system and nitrogen was allowed to flow at a constant rate for a measured time. The weight loss of the cylinder gives the value of nitrogen directly and after appropriate minor corrections for response time of the flowmeter the relationship between indicated flow and actual flow was determined. The effect of very small leaks in the calibration of the high flow system are negligible. This is not so in the case of the low flow system and a somewhat less direct technique was employed. A one liter per revolution wet test meter was first calibrated by passing a known weight of nitrogen through the meter. The meter was then attached to the dilution system at the outlet of the mass flowmeter and a constant flow was established. The volume flow per unit time was then determined from the time required for passage of one liter of nitrogen.

The estimated error in the calculated concentration of a mixture prepared by blending two streams of gas of known composition is about 0.8 percent relative. This is based on the uncertainty in the composition of the stream containing the nitric oxide (0.2 percent), the error in calibration of flowmeter number 1 (0.5 percent) and the error in calibration of flowmeter number 2 (0.6 percent). The error in calibration of flowmeter number 1 is based on the agreement between six separate gravimetric determinations of the flow. The error in calibration of flowmeter number 2 is the combined error in the calibration of the wet test meter and the flowmeter.

Table 5 is a summary of results obtained by the three methods. The calculated value is based on both the measured pressure and the measured weights. The analyzed value was obtained by measurement of the sample using a chemiluminescent analyzer calibrated with mixtures of nitric oxide generated by the dynamic dilution system. There is generally good agreement between all samples with the exception of the value calculated from the pressure data for sample #133. The agreement between the gravimetric result and the analyzer values suggest an error in reading or

Table 4. Intercomparison of Primary Standards
of Nitric Oxide in Nitrogen

<u>Sample No.</u>	<u>Cal. Conc. in ppm</u>	<u>Signal in mv.</u>	<u>Div. Per Unit of conc.</u>	<u>Δ^*</u>
140	949.	929.	0.979	0.0
139	951.	929.	0.977	-0.2
133	960.	943.	0.982	+0.3
132	449	438	0.976	-0.1
143	446	436	0.976	-0.1
142	451	441	0.979	+0.2
145	226	215	0.951	-0.5
131	225	215	0.956	0.0
144	227	218	0.960	+0.4
149	95.2	96.2	1.011	0.0
148	94.5	95.4	1.010	-0.1
147	94.4	95.5	1.012	+0.1
150	45.4	45.0	.991	-0.3
151	46.2	45.9	.994	0.0
152	45.2	45.1	.998	+0.4
Average = 0.2				

*Relative difference of the value from the average for the set.

Table 5. Summary of Results Obtained by Three Methods for Concentration of Nitric Oxide Standards

<u>Mixture No.</u>	<u>Calculated Concentration</u>		<u>Observed Concentration</u>
	<u>Weight</u>	<u>Pressure</u>	
133	960.	(942)	962.
139	951.	951.	948.
140	949.	950.	948.
132	449.	445.	443.
142	451.	449.	447.
143	446.	446.	447.
131	225.	225.	223.
144	227.	229.	225.
145	226.	227.	222.
147	94.4	93.1	94.3
148	94.5	93.5	93.9
149	95.2	94.3	95.1
150	45.4	45.0	45.3
151	46.2	46.0	45.9
152	45.2	45.2	45.3

(All concentrations are in parts per million)

recording the pressure data for this particular sample.

The value assigned to the primary standards is the value calculated from the gravimetric data. The internal self consistency of the set of gravimetrics shown in Table 5 is used to describe the accuracy of these standards and the pressure data and analysis against the dynamic dilution standards is considered confirmatory.

A total of 265 cylinders of five different concentrations of nitric oxide in nitrogen were prepared commercially and have been analyzed by comparison with the secondary standards. The results are shown in Figure 6. The wide range of values around the average is not entirely due to imprecision of intercomparison but rather, may represent real differences between samples. It has already been established that the several very low values in each lot represent true differences. It has not yet been determined exactly how wide is the imprecision around the average but previous experience with the method suggests a maximum value of ± 0.6 percent relative but the exact value is probably lower. For instance, a single sample in the 46 ppm lot was analyzed on several different days during the analysis of the entire lot. The value for this sample was found to be 46.0 ppm with a standard deviation of the average of twelve measurements of 0.1 ppm or 0.2 percent relative.

The final upper limit of the error on the certified value will be determined by the reason for the wide range of values. If the range represents imprecision in the measurement then the total uncertainty will be somewhat larger than if the differences are real. Table 6 is an estimate of the error derived for the two cases. The first value of the error is based on the same considerations as were applied to the carbon monoxide samples except that the obviously low values have been omitted. The second value assumes real differences in the samples and the error is the expected imprecision of analysis based on prior experience in the intercomparison of the primary and secondary standards. Both values are conservative and work in progress is intended to more clearly define the error. First the nature of the wide variation of results will be determined by reanalysis of a representative group of samples from each lot. However, this analysis will not be performed until a time interval has passed sufficient to recognize any further deterioration of samples. The analyses described here were performed approximately one month after the cylinders were filled. If the disparate results are due to progressive reaction of nitric oxide in the cylinder then those samples originally found to be

low will on reanalysis be even lower. If the differences in concentration are due to a fast reaction dependent on the individual cylinder then the relationship between samples will be approximately as shown by the first analysis.

The cylinders in which the Standard Reference Materials were packaged were first treated by soaking with a mixture of nitric oxide in nitrogen at about the concentration with which they were to be finally filled. All cylinders were new and unused and were carefully prepared by drying, evacuating, and flushing with oxygen-free nitrogen. The long term stability is expected to be adequate and will be confirmed by further analyses as described above.

The possibility of an increase in concentration due to desorption of nitric oxide is being investigated by analysis of a number of cylinders from each lot in which the pressure is decreased stepwise from 2000 psi to about 500 psi. Thus far, analyses do not indicate that any serious desorption occurs but further analyses over a longer period of time will be necessary to confirm this.

Several samples in each lot were examined for other oxides in nitrogen. No evidence of any other oxides within the limits of precision of the measurement were observed. The limits of measurement for this analysis is considered to be about ± 0.2 percent relative.

Each lot of fifty-three samples included five samples packaged in aluminum cylinders. The results for these cylinders is shown in Figure 7. Compare this to Figure 6 where the results for all samples are shown and it is obvious that the aluminum cylinders offer some advantage. While the spread of values among the aluminum samples is approximately that of the majority of samples, there are no low values of concentration among the 25 aluminum cylinders. Statistically, it is unlikely that a distribution of this sort would have occurred if the differences between samples represented imprecision rather than selective reaction in specific cylinders.

In summary concerning the nitric oxide mixtures, it appears that a stable series of standards at concentrations between 50 ppm and 1000 ppm will result. A maximum error of between ± 1 or 2 percent appears reasonable and the shelf life and quantity available appear adequate.

PERMEATION TUBES

Permeation tubes consist essentially of a tube of porous material, usually Teflon, containing a liquid such as sulfur dioxide or nitrogen dioxide. The material in the

tube permeates through the walls of the tube at a rate determined by the vapor pressure of the substance, and at constant temperature the permeation rate is constant. The devices are used to generate atmospheres containing a known quantity of the substance by placing them at fixed temperatures in a stream of air or other gas flowing at a known rate.

In order to serve as a satisfactory standard a permeation tube must permeate at a predictable and unchanging rate throughout its useful lifetime. The rates are determined by measurement of the weight loss per unit time at a number of fixed temperatures. The rate (R) is described by the equation, $\log R = mT - b$ where T is the temperature in degrees absolute and m and b are empirically determined constants. The tubes are calibrated by periodic measurement of the weight while maintaining the tube at a constant temperature. The value of the constants, a and b , are determined by calibration at several different temperatures. Permeation tubes must maintain a predictable rate even after subjection to varying temperature excursions both of use and storage.

Sulfur Dioxide Permeation Tubes

Sulfur dioxide permeation tubes have been studied in detail and no significant problems have been recognized in either use, storage, or calibration. Sulfur dioxide permeation tubes are available as Standard Reference Materials in three lengths, 2, 5 and 10 cm. The permeation rate of these SRM's is about 0.25 $\mu\text{g}/\text{minute}$ per centimeter of tube length. The relative accuracy with which the rate is known at 25 °C is ± 0.5 percent for 5 and 10 cm tube and one percent for 2 cm tubes. The relative accuracy at the 20 ° and 30 ° calibration points is one percent for 5 and 10 cm and two percent for 2 cm tubes. These values are considered conservative and are based on at least nine measurements of the rate of each tube at three different temperatures.

A long term investigation of the behavior of sulfur dioxide permeation tubes is continuing. The normal lifetime of a tube stored at room temperature is about nine months but the lifetime can be extended by low temperature storage between periods of use. A number of tubes fabricated as long as three years ago and retained from calibrated batches of Standard Reference Material have recently been recalibrated. The results of the recalibration and the rates measured before storage at low temperatures are shown in Table 7.

In addition to these tubes a number of tubes manufactured in 1969 are being studied. Early rate data for most of these tubes is not available but the rates measured recent-

ly are consistent with rates measured earlier for other tubes in the same batch. One tube that was calibrated was found to have a rate of 2.58 ± 0.2 microgram per minute in 1970 and in June of 1974 the rate was measured at 2.61 ± 0.2 micrograms per minute at the same temperature.

The results obtained thus far are all reassuring and it appears that no problems arise with sulfur dioxide permeation tubes from the effects of storage. Further, there is no evidence of changing rate as the quantity of sulfur dioxide decreases in the tube with use. It has been observed that the rate for a sulfur dioxide permeation tube remains constant as long as any liquid remains in the tube no matter how small the quantity may be. Tube 7-36 shown in Table 7 is a good example of this. The value at 25 °C measured during 6/74 represents the last useable measurement because the liquid disappeared shortly after the weighing used to determine this rate. The rate at 25 °C remained constant over a period of two years, which time included both use at 25 ° and storage at low temperatures.

Nitrogen Dioxide Permeation Tubes

Permeation tubes appear at present to be the most practical method for conveniently preparing mixtures of nitrogen dioxide in air of accurately known concentration. Nitrogen dioxide permeation tubes, however, are not as predictable in use as sulfur dioxide tubes have proven to be. There are two primary difficulties associated with nitrogen dioxide permeation tubes. First, a tube constructed similarly to a sulfur dioxide tube has a permeation rate several times faster with a resulting shorter lifetime. Second, the rate has been found to decrease significantly with time. The solution to the problem of a high rate has been solved through the design shown in Figure 8. The device consists of a glass reservoir connected to what is in effect a short permeation tube. This design has the advantage over other designs in that the thickness of the permeation wall is such that equilibrium is established rapidly and that the total weight of the tube is small enough to allow rapid calibration through measurement of small changes in weight.

The solution to the problem of declining rate appears to lie in drying of the nitrogen dioxide with which the tube is filled and protecting the tube from subsequent exposure to high concentration of water vapor.

Nitrogen dioxide permeation tubes can be calibrated with an accuracy equal to sulfur dioxide tubes of similar output. However, greater caution must be exercised when weighing tubes because of the hygroscopic nature of the external surface of the

Table 6. Estimated Upper Limit of the Error of the Nitric Oxide Standard Reference Material

Average For The Lot	Range	Estimated Error	
		<u>Imprecision</u>	<u>Real Differences</u>
994.	20.	±13.	±11.
477.	14.	± 8.	± 5.
253.	8.	± 4.	± 3.
94.2	2.4	± 1.5	± 1.0
45.0	0.8	± 0.6	± 0.5

(All values are in parts per million.)

Table 7. Effect of Low Temperature Storage on the Observed Rate of Sulfur Dioxide Permeation Tubes

Tube Number	Storage Time in Months	Rate in Micrograms Per Minute at Indicated Temperature			
		Original Rate		Rate 6/74	
		25 °C	30 °C	25 °C	30 °C
2-45	39	--	2.90	--	2.96
3-9	35	--	3.10	--	3.13
3-10	35	--	3.12	--	3.13
7-36	25	0.58	0.85	0.59	0.85
8-11	24	1.50	2.20	1.49	2.21
8-50	24	--	1.96	--	1.95
14-49	7	3.29	4.82	3.32	4.78
14-50	7	3.17	4.59	3.19	4.64

Table 8. Calibration of Fifteen Nitrogen Dioxide Permeation Devices

<u>Tube Number</u>	<u>Average Rate</u>	<u>s</u>
37-20	1.15	.014
37-21	1.23	.016
37-23	1.33	.015
37-24	1.41	.013
38-2	0.980	.012
38-3	1.15	.012
38-4	1.18	.017
38-6	1.21	.011
38-7	1.05	.008
38-8	1.39	.014
38-10	1.03	.010
38-12	1.21	.012
38-13	1.19	.008
38-14	1.06	.016
38-15	1.24	.013

(The rate and standard deviation are in units of micrograms per minute at 25 °C.)

permeating area. Typical results are summarized in the calibration of fifteen tubes at 25 °C as shown in Table 8. The standard deviation shown is based on fifteen measurements extending over a period of six months.

Nitrogen dioxide permeation tubes of the design described here are intended for use in the range between 20 ° and 30 °C. Exposure to temperatures above 35 °C may permanently increase the rate at lower temperatures by several percent depending on the length of exposure at higher temperature. Storage at low temperatures has no permanent effect on the rate in the useable temperature range but low temperature storage is not advised because of the long lifetime of the tube. These tubes when initially filled to 90 percent of capacity have a useful lifetime of about two years depending on the actual rate for an individual tube.

CONCLUSION

The development of a Standard Reference Material for air pollution measurements involves a detailed study of the accuracy and stability of such standards. The development has been illustrated by reference to several specific Standard Reference Materials which probably represent the median in terms of the total developmental effort. Other systems will be studied but the time required for full development and the necessity for constant surveillance precludes any extensive inventory for some time to come.

ACKNOWLEDGMENT

The author has reviewed what constitutes a major part of the program of the Air Pollution Analysis Section of the Analytical Chemistry Division and wishes to give due credit to all those in the section who were involved. The work described has been supported by the Analytical Chemistry Division and the Measures for Air Quality Office of the National Bureau of Standards and by the Environmental Protection Agency.

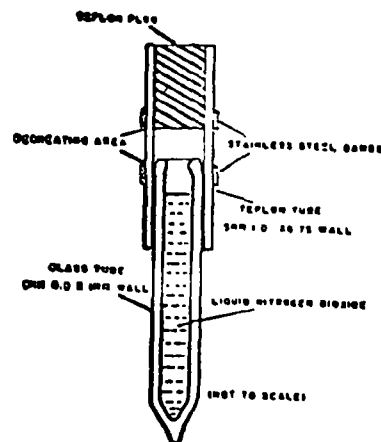


FIGURE 8. NBS NITROGEN DIOXIDE PERMEATION DEVICE

MEASUREMENT OF OZONE AND OXIDES OF NITROGEN IN THE LOWER ATMOSPHERE FROM AN AIRBORNE PLATFORM

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INTRODUCTION

A program^{1/} was conducted during the summer of 1974 in the Ohio River Valley; the objective of the program was to investigate high rural ozone concentrations and their possible relationship to urban hydrocarbon. Data were obtained by sampling for relevant gases at five ground stations and from an aircraft instrumented to measure ozone (O_3), oxides of nitrogen (NO_x - NO - NO_2), air temperature and obtain air samples for subsequent hydrocarbon (HC) analysis.

Two basic flight patterns were to be flown during the field measurement program. These were a box pattern to be flown during stagnation and a square wave pattern aligned with the predicted wind field. Examples of each are shown in a later section of this paper. These patterns were to be flown, in general, at altitudes between 2000 ft to 4000 ft above msl. In addition to these two basic patterns, vertical ascents were to be made to 12,000 ft on days with certain meteorological conditions.

A C-45H aircraft, two pilots, and some instrumentation were provided by the National Environmental Research Center at Las Vegas, Nevada, for the duration of the program. Installation of equipment and test flights were carried out from the Raleigh-Durham airport. During the field phase of the sampling program, mid-July thru September, the aircraft was based at the deactivated Clinton County Air Force Base in Wilmington, Ohio.

This paper describes the instrumenation, the various steps taken to assure valid data, gives some examples of data format and concludes with a brief discussion of recommendations for upgrading of system performance.

AIRBORNE PLATFORM AND INSTRUMENTATION

Aircraft

The aircraft used in the program, a C-45H, is shown in Figure 1. This aircraft has an instrument weight allowance of approximately 750 lbs when operating with a load configuration of two pilots, two instrument personnel, and a full load of fuel. Under these conditions this aircraft has an average cruising speed of 130-150 knots, a climb rate of 500 ft/min, a turning

^{1/} Work performed under contract to the Environmental Protection Agency
Office of Air Quality Planning and Standards



Figure 1. C-45H Aircraft

radius of $1\frac{1}{2}$ miles and a flight range of approximately 5 hrs. Navigation equipment included two VOR units with DME, an ADF, and flux-gate compass. Under normal operating conditions, 10 amps at 28 vdc from the primary power system were available for the instrumentation.

Given an airborne platform and program requirements, it is necessary to consider system parameters, such as: power required by instruments and duty cycle of this power demand; total weight and space requirements of instrumentation and distribution in aircraft; temperature control of equipment in flight and on the ground; electrical noise of instruments and possible adverse effects on communication and navigation equipment; and shock mounting of instruments to reduce vibration problems.

Air Sample Probe

The air intake system is illustrated in Figure 2; it consisted of a 2-in ID aluminum probe permanently mounted on the underside of the aircraft nose approximately 3 ft forward of any point on the plane. The probe was lined with 1-in ID Teflon tubing to prevent or minimize reaction of air pollutants with the manifold wall.

The other end of the Teflon tube emptied inside the aircraft cabin. Two $\frac{1}{4}$ -in Teflon tubes and a temperature-sensing thermister were inserted well into the larger 1-in Teflon tube. One of the $\frac{1}{4}$ -in Teflon lines was connected to a glass sample manifold from which the O_3 and NO analyzers sampled. Ram pressure created by air rushing through the 1-in^x tube forced a steady flow of sample air into the manifold. The pressure in the manifold was essentially that of the unpressurized aircraft cabin, which prevented the pressurization of the instrument sample inlets. The other $\frac{1}{4}$ -inch Teflon line was connected to a stainless steel diaphragm pump used to fill sample bags. The air sample inlet system was designed for a minimum of sample contamination by emissions from the aircraft itself. Ram pressure caused an airflow through the Teflon tube at a velocity sufficient to keep gases found within the aircraft cabin from diffusing into the tube and contaminating the air sample stream. Tests were conducted to insure that contamination from the interior of the aircraft was not getting into the sample manifold.

Instrumentation

A block diagram of the instrumentation installed in the C-45H is shown in Figure 3 and included an RTI solid phase ozone analyzer, a Bendix $NO-NO_2-NO_x$ analyzer, a Yellow Springs temperature sensor, air sample pump, five strip chart recorders, and a 2KW Nova inverter. All instrumentation was shock-mounted with Areoflex twisted steel rope shock mounts. A photograph of the instrumentation is shown in Figure 4.

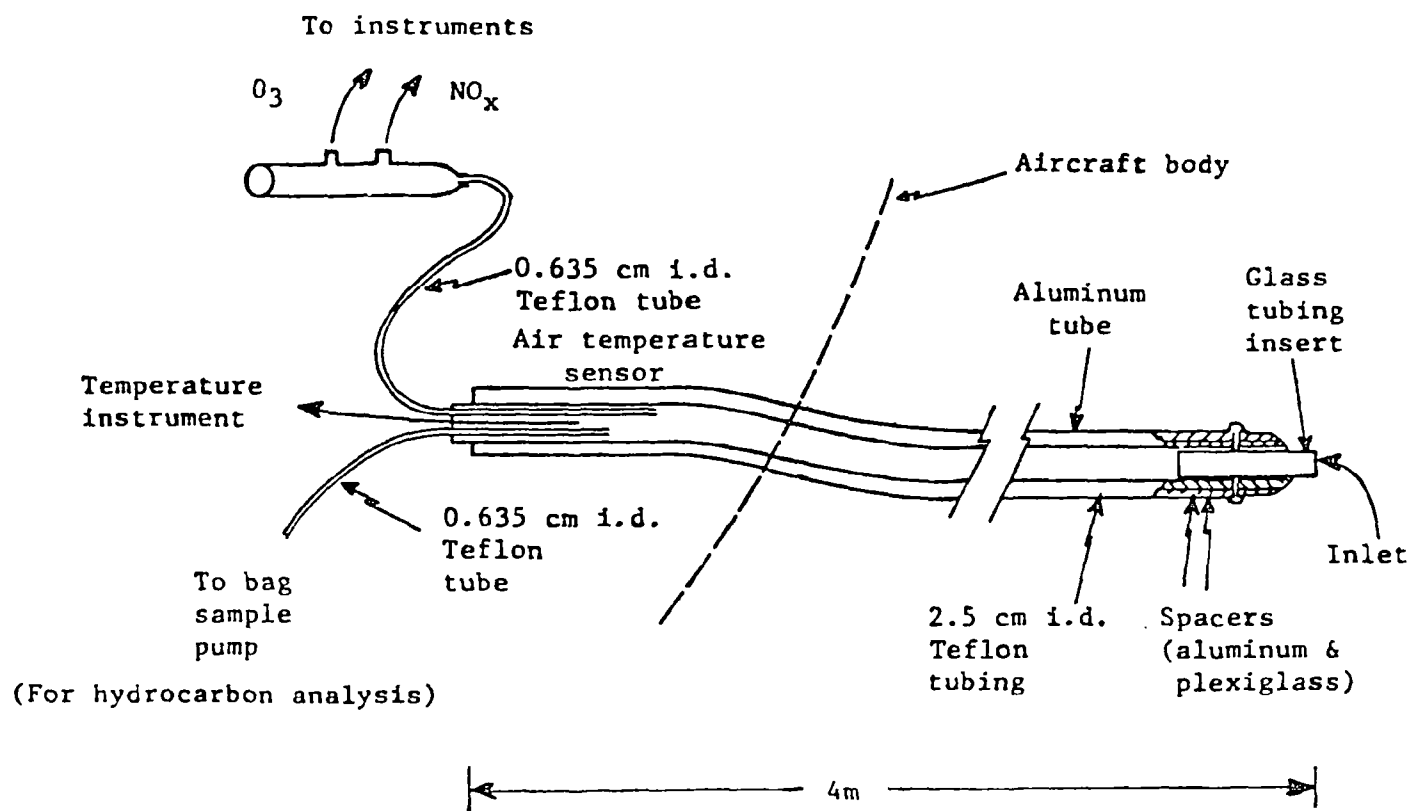


Figure 2. Air-Sampling Probe Used on C-45 Aircraft

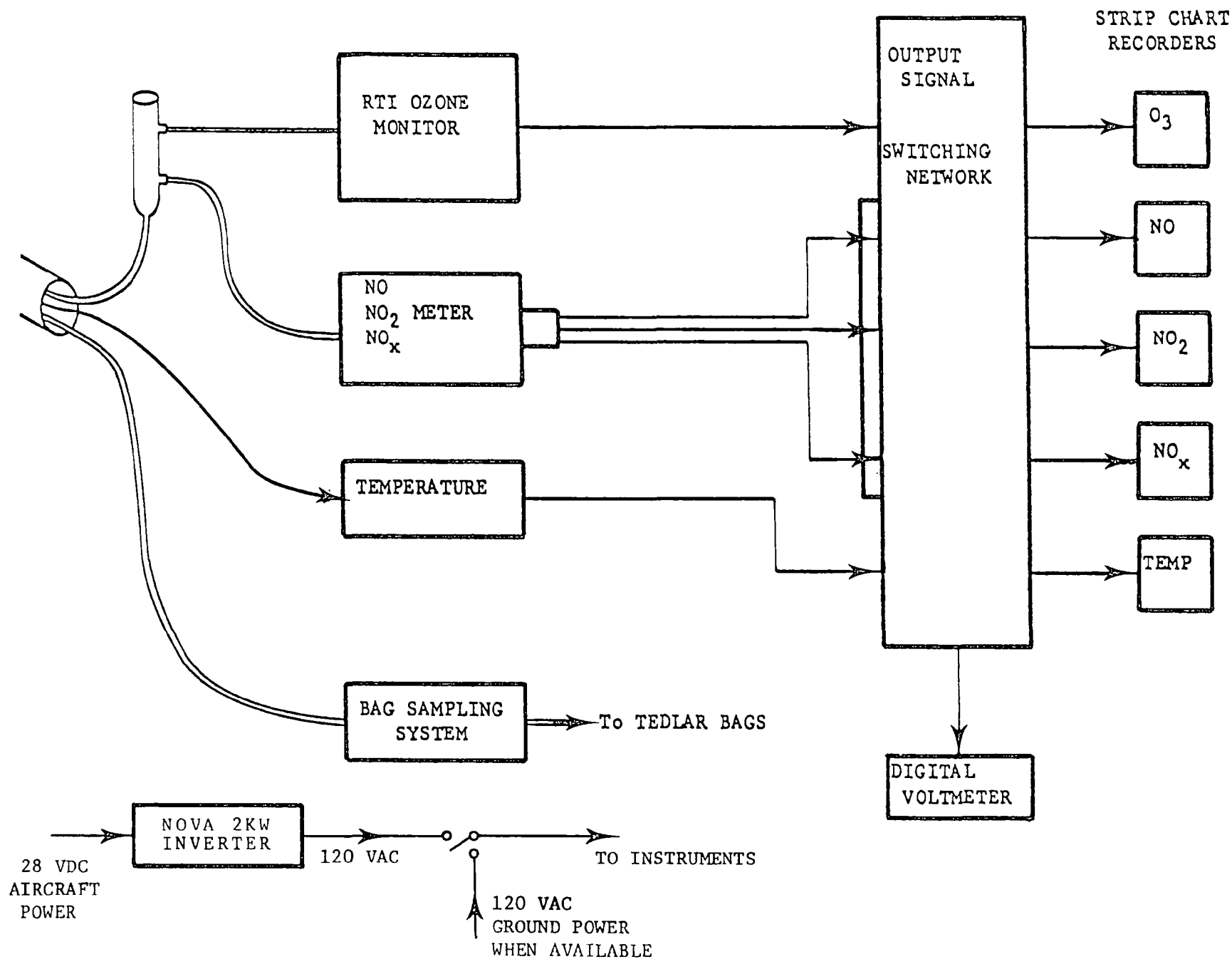


Figure 3. Block Diagram of Aircraft Instrumentation

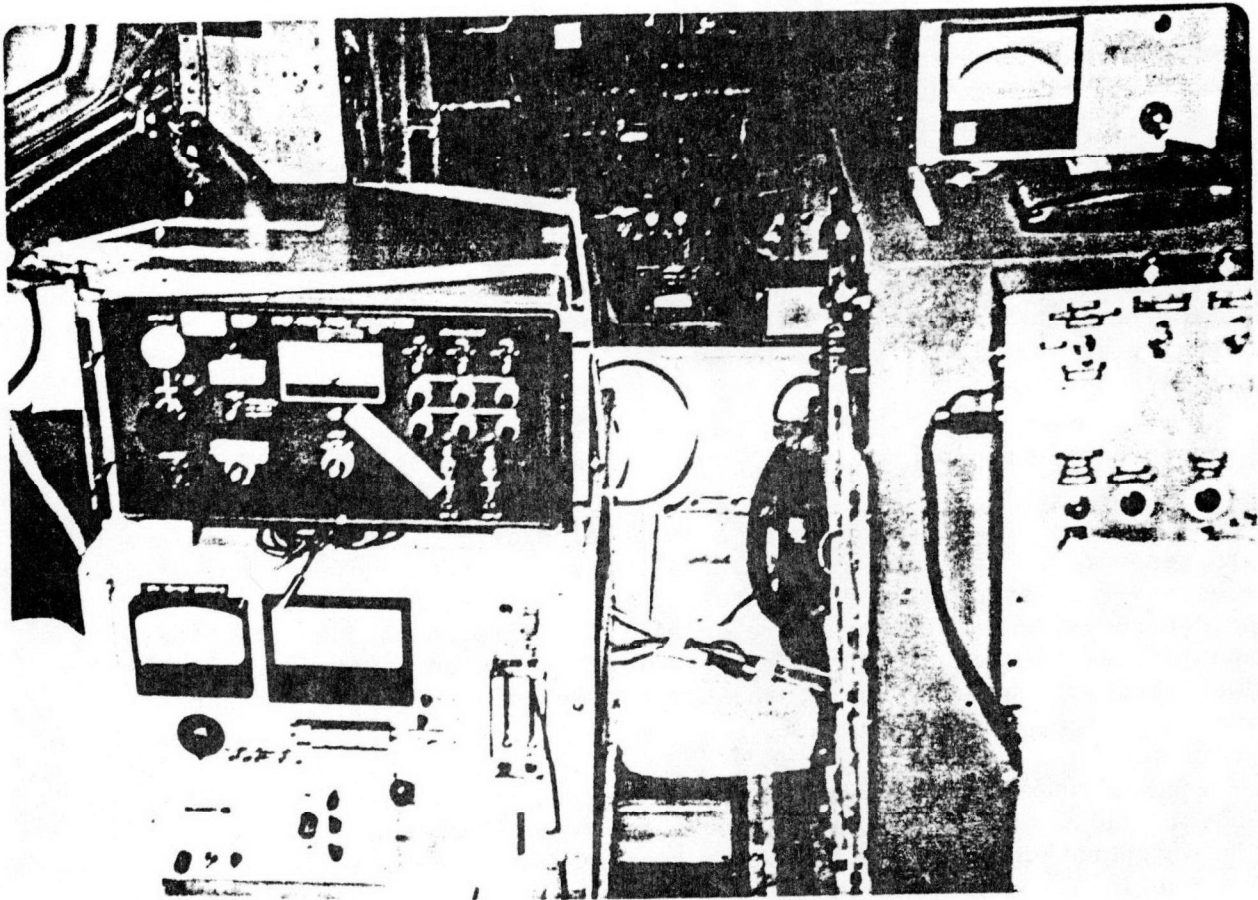


Figure 4. Instrumentation

The ozone analyzer used in the aircraft was a solid phase chemiluminescent instrument built by RTI. It is a self-contained instrument requiring no external pressurized gas supplies of any kind. The analyzer operates in a cyclic mode with a calibration signal response and a measure cycle response output once during each 2-min cycle.

The Bendix 8101-B chemiluminescent analyzer was used in the aircraft to monitor oxides of nitrogen. Support equipment on board for this instrument included a compressed oxygen cylinder and a two-stage diaphragm vacuum pump. The sample inlet for the instrument was from the same manifold as the ozone analyzer.

The system used for collecting grab samples consists of a stainless steel metal bellows pump with a manganese dioxide catalytic converter on the input to convert any ozone to oxygen. The output of the pump is connected to a 20 l Tedlar bag with Teflon lines using stainless steel, quick disconnect fittings.

Primary power was supplied by the aircraft 28 vdc system which was converted to 115 v, 60 Hz, 1 ϕ , by the Nova 2KW inverter. Provisions were incorporated in the system to facilitate rapid switchover from aircraft primary power source to ground power.

DATA VALIDATION PROCEDURES

An airborne platform presents some particularly troublesome problems with respect to operation of ambient air gas analyzers. These include the necessity for essentially continuous supply of power to the instruments; the determination of the pressure or altitude effects on the detection capabilities of each instrument; contamination due to aircraft fuel and power plant of the air sample; and the problem of performing a dynamic calibration of the total system.

Various steps were taken to insure the validity of the data. These included: (1) low altitude passes above the base station with all instrumentation in operation, (2) comparison of readings in the aircraft while on ground to those in the base station located nearby, (3) comparison of readings in the aircraft with readings in another aircraft independently instrumented and operated, and (4) hydrocarbon air sample contamination tests. Data were also obtained during the program to demonstrate the comparability of the RTI solid phase and Bendix gas phase chemiluminescent ozone analyzers.

Operational Procedures

Procedures for the operation of the aircraft instruments were established and documented early in the program so data could be taken under uniform conditions in the event of a change of operators. Also, operating from pre-determined procedures insured more consistent operation with the same operator.

Preflight checks were made in order to insure that all instruments were working and set to the proper range and mode of operation. Also, the strip chart recorders were checked for operation and turned on. The manifold was checked to insure that the instruments were connected properly. These procedures were set to insure that valid data collection began as soon after takeoff as possible and that minimum data were missed due to instruments being improperly set. Routine calibrations were conducted on each of the gas analyzers in the aircraft each day for which a flight was planned. Calibrations were conducted against the instruments in the van which were considered "standards." To accomplish this, two steps were performed: (1) calibration of a portable calibration unit and (2) calibration of the analyzers using the portable calibration units.

During flight, the instrument operator annotated the strip charts with time and observed the instruments for symptoms of normal or abnormal operation. The second observer operated the bag sample apparatus and made pertinent observations of weather conditions and aircraft location. Periodically, analyzer flow rates at given altitudes were measured with a bubble flowmeter.

The instruments aboard the aircraft were operated continuously during the study. Immediately after landing and taxiing to the aircraft tie-down position, a 117 V ac source was connected to the instrumentation before both engines were shut down. Prior to takeoff, at least one engine was started, bringing a generator into operation before ground power was disconnected from the aircraft instrumentation system. Since the aircraft sampling probe system was designed only for operating during flight, an alternate means was needed for supplying sample air to the instruments while on the ground. This was accomplished by connecting $\frac{1}{4}$ -in Teflon lines to the instrument inlet. Each Teflon line extended through the cockpit window and was supported approximately 2 ft above the aircraft. Concentration values of NO and ozone could then be read from the instruments in the aircraft and compared to those values being measured in the RTI base station.

Calibration Methods

Standard operating procedure called for the calibration of all gas analyzer instruments immediately before each flight. The gas analyzers in the mobile van of the same type as those in the aircraft (ozone and NO) were considered standards for the aircraft calibrations. Specifically, the output concentration of a portable calibration unit capable of generating O₃, NO, and NO₂ was determined by connecting it to the analyzers in the base station and observing their response. The portable unit was then carried to the aircraft and operated under the same conditions (flow rates, pressures, line voltage, etc.) as in the base station. The aircraft instruments were connected to the portable calibration unit, and either the span was adjusted to its proper setting (in the case of the Bendix NO-NO₂-NO_x analyzer) or the internal calibration level was determined (in the case of the RTI ozone monitor). The calibration unit operating in this manner is merely a transfer standard imposing the requirement of only short-term stability on it to insure its accuracy.

Zero determinations for the NO instrument were carried out by connecting a clean-up system to the sample input of the analyzer. No zero adjustment was necessary on the ozone analyzer by virtue of the way the output is computed. Multipoint calibrations on the O₃ and NO-NO_x-NO₂ analyzers in the aircraft were performed every two weeks. The temperature-measuring instrument aboard the aircraft did not require as frequent calibration due to its inherent stability. It was calibrated at the beginning and end of the program and twice between. The calibration consisted of a two-point calibration, one at 0°C determined by an ice bath and one at ambient temperature as measured by a lab-type mercury thermometer.

Contamination Tests

On an initial flight, the gas chromatographic analysis of the grab samples indicated a high concentration of gasoline evaporatives. The logical deduction was that air from the interior of the aircraft was being drawn into the sample along with the ambient air. The sample inlet was modified to produce the system described and illustrated earlier. Then during an actual data flight some contents of a lecture bottle of a known hydrocarbon were released continuously in the cabin during the collection of a bag sample. This bag was analyzed and the concentration of the known hydrocarbon observed and compared to levels in normal ambient levels made earlier during the flight. The test indicated that no detectable amount of cabin air containing the high concentration of the released hydrocarbon was evident in the bag sample. Since the sample inlet for the hydrocarbon bag sample was approximately 6 in downstream from the ozone-NO samplet inlet, it was assumed that the ozone-NO sample was uncontaminated as well.

A test for bag permeation was carried out by storing bags of known concentration in the aircraft for long periods of time and reanalyzing them to see if any hydrocarbons permeated the bags.

Instrument Response vs Altitude

Before the airquality analyzers could be used in the aircraft, variations in their response due to pressure changes had to be determined. The environmental test chamber facility at NERC, Las Vegas, was used to determine the effects of change in altitude on instrument response. This facility consisted of a sealable chamber approximately 28' x 32'd x 60'h. Temperature, dew point, and pressure could be set by control units external to the chamber and varied during the test.

A series of tests was run on the RTI ozone monitor and a Bendix NO-NO₂-NO_x analyzer. A functional diagram of the test set-up is shown in Figure 5. Each instrument was placed in the chamber and calibrated. Then a constant concentration of the gas being measured by the instrument was input to the instrument through a port in the side of the chamber. The calibration gas was input to the instrument through a glass manifold open to the inside of the chamber to insure that the pressure on the sample inlet was the same as

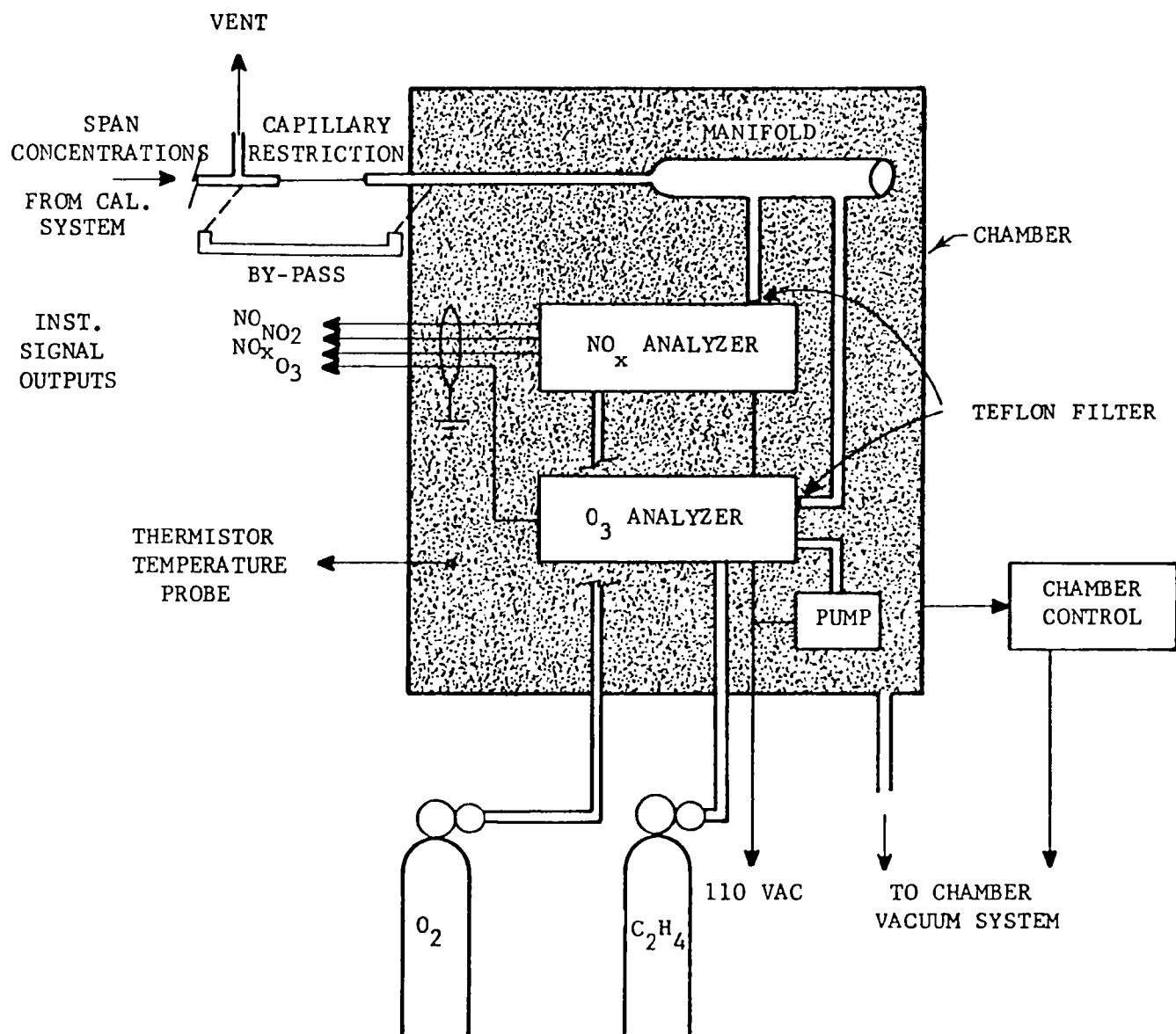


Figure 5. Test Set-up in Pressure Chamber

the chamber pressure. The chamber then was depressurized in increments of pressure up to the pressure equivalent of 12,000 ft (and beyond in some tests) while the response of the instrument was being monitored on two strip chart recorders. Results of multiple runs of this test were processed to produce a curve for each instrument. From this curve the percentage decline in instrument response at a given altitude may be determined and the data compensated for altitude. Curves for the two instruments used in the aircraft are included in Figures 6 and 7.

In addition to the tests run in the chamber, tests of instrument behavior were performed on the ozone instrument while airborne. A standard calibration system using an ultraviolet ozone source and rotameter was used aboard the aircraft with a modification on the output. A restriction was placed on the output, along with a vent controlled by a valve (see Figure 8). By closing the valve, the calibration system could be pressurized. An altimeter was connected to the system so the pressure could be adjusted to the same level as it was on the ground. The flow out the vent was monitored and the length of the 1/8 in Teflon restriction adjusted so that the flow out the vent did not exceed 1 l/min (at standard conditions). This insured that sufficient calibration gas flowed through the manifold to keep it flushed and not contaminated with cabin air.

Flow rates were monitored on the instruments during the tests on the aircraft at the various altitudes. Then during routine flights, the flow rates were checked periodically to insure that the operating conditions were unchanged. This insured that the results obtained during the altitude tests were still valid (including the correction curves).

The results of these in-flight calibration and operational verification tests were in agreement with the tests run in the fixed chamber. Repeatedly it was shown that the response of the instrument declined linearly with environmental pressure.

Ground Comparison of Aircraft and Base Station Measurements

Ground comparison tests consisted of running the aircraft instrumentation and sampling ambient air while the aircraft was parked in close proximity to the base station. The sampling ports in this configuration were located approximately 70 ft apart. The port for the aircraft was approximately 12 ft above the ground while the base station sampled air from about 24 ft above the surface. The comparison of these data was done not so much for quantitative checks of instrument calibration as for a check of the instrument performance. The shape of the ozone concentration curve taken in the aircraft was compared to shape of the one taken in the Mobile Monitoring Laboratory every morning prior to a calibration. The calibration then should correct any discrepancies in instrument readings. A graph of the outputs from both the

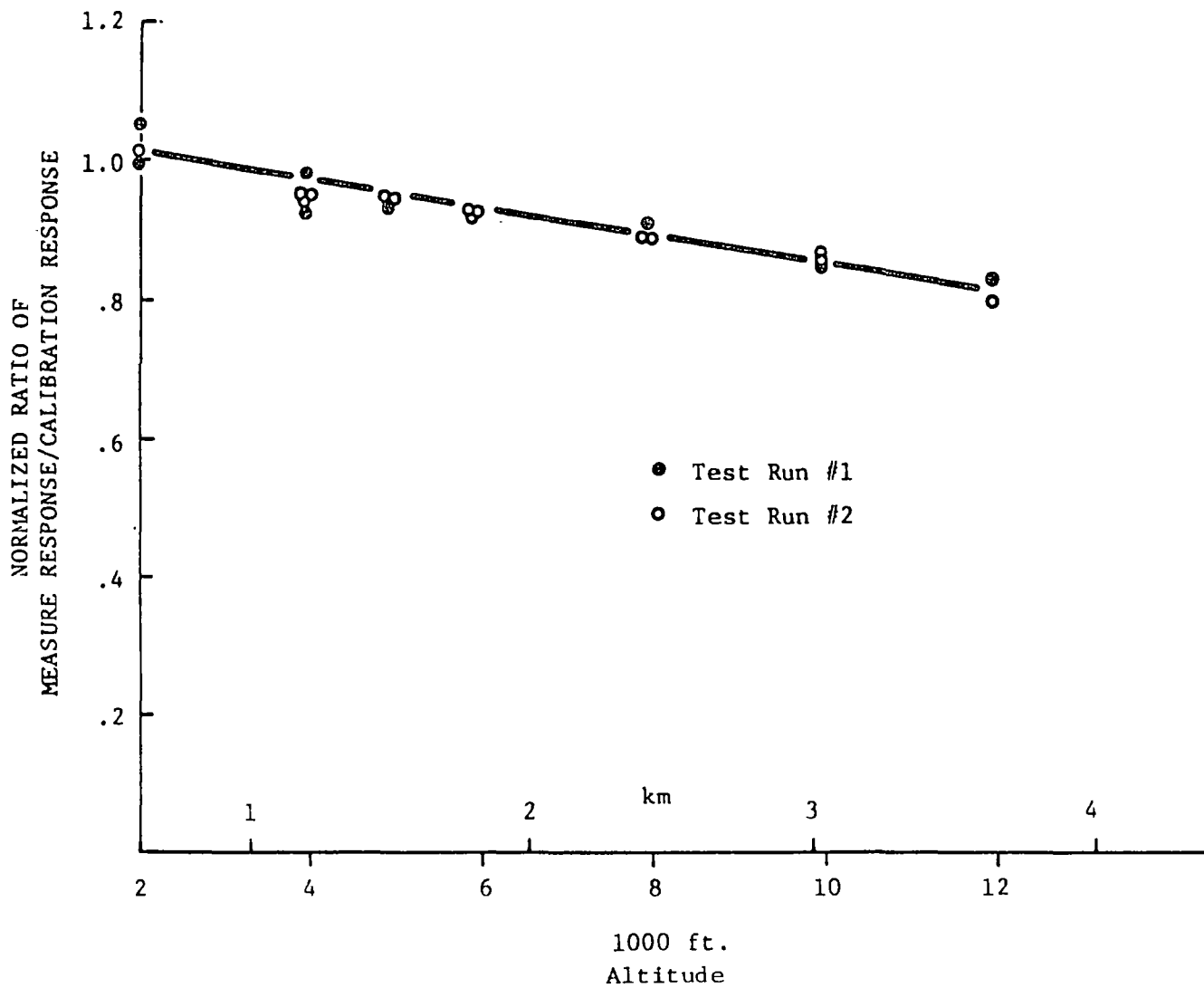


Figure 6. Response of RTI O₃ Instrument vs Altitude

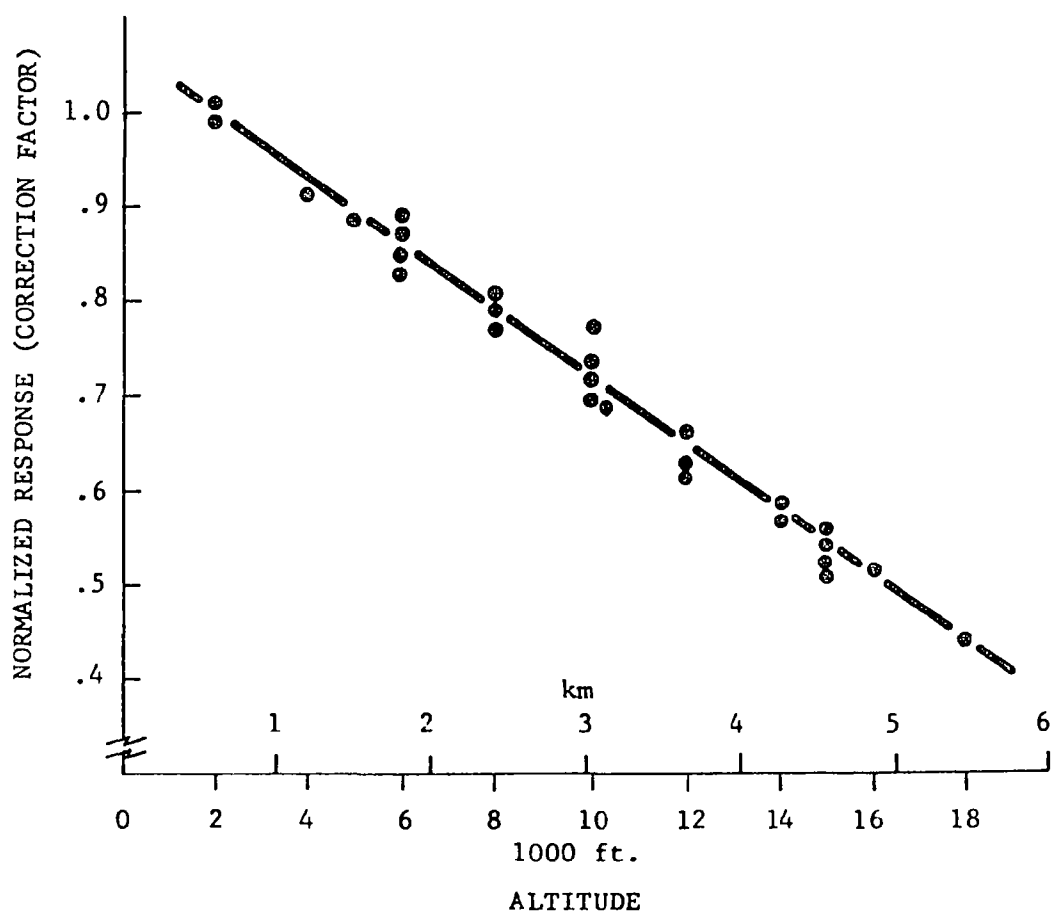


Figure 7. Correction Factor for Bendix NO_x Analyzer to Compensate for Changes in Altitude

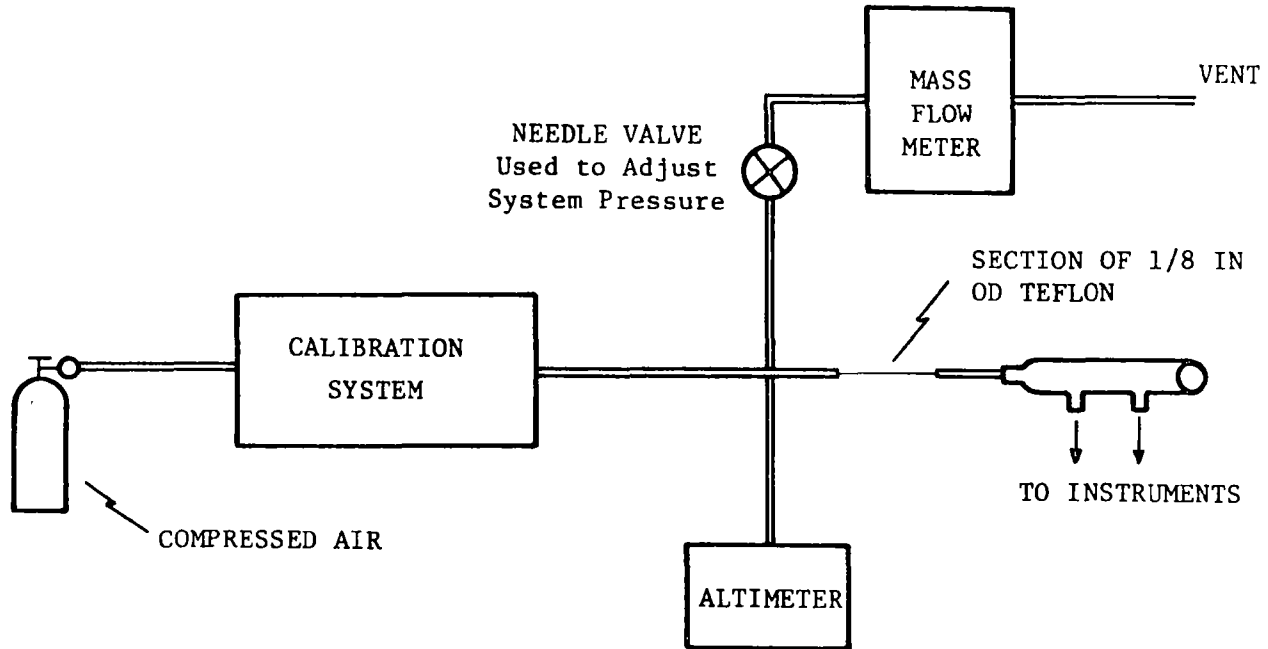


Figure 8. System Used to Calibrate Analyzers While Airborne

the aircraft O_3 instrument and the instrument in the base station plotted against time is shown in Figure 9. Discrepancies in the two as already mentioned may be due to a number of causes, including differences in sample manifold height.

Low-Pass Flights

Fly-bys were conducted by flying the aircraft over Clinton County Air Force Base at an altitude between 50-100 ft above the terrain. Generally, the aircraft approached the field from the end opposite the base station (approach from the northeast end) and flew over the taxiway parallel to the runway. Flying in this manner, the aircraft could safely achieve a lower altitude and hold it longer than flying from another direction over grass or wooded terrain. The time for the aircraft to fly from the end of the runway to the base station took approximately 30 s, which gave the instrument some time to stabilize before a reading was taken.

A plot of the results is included in Figure 10. Here the readings taken from the RTI instrument are plotted on the ordinate against the fixed base station 5-min instantaneous sample readings taken closest in time which were plotted on the abscissa. Perfect agreement between the two instruments would

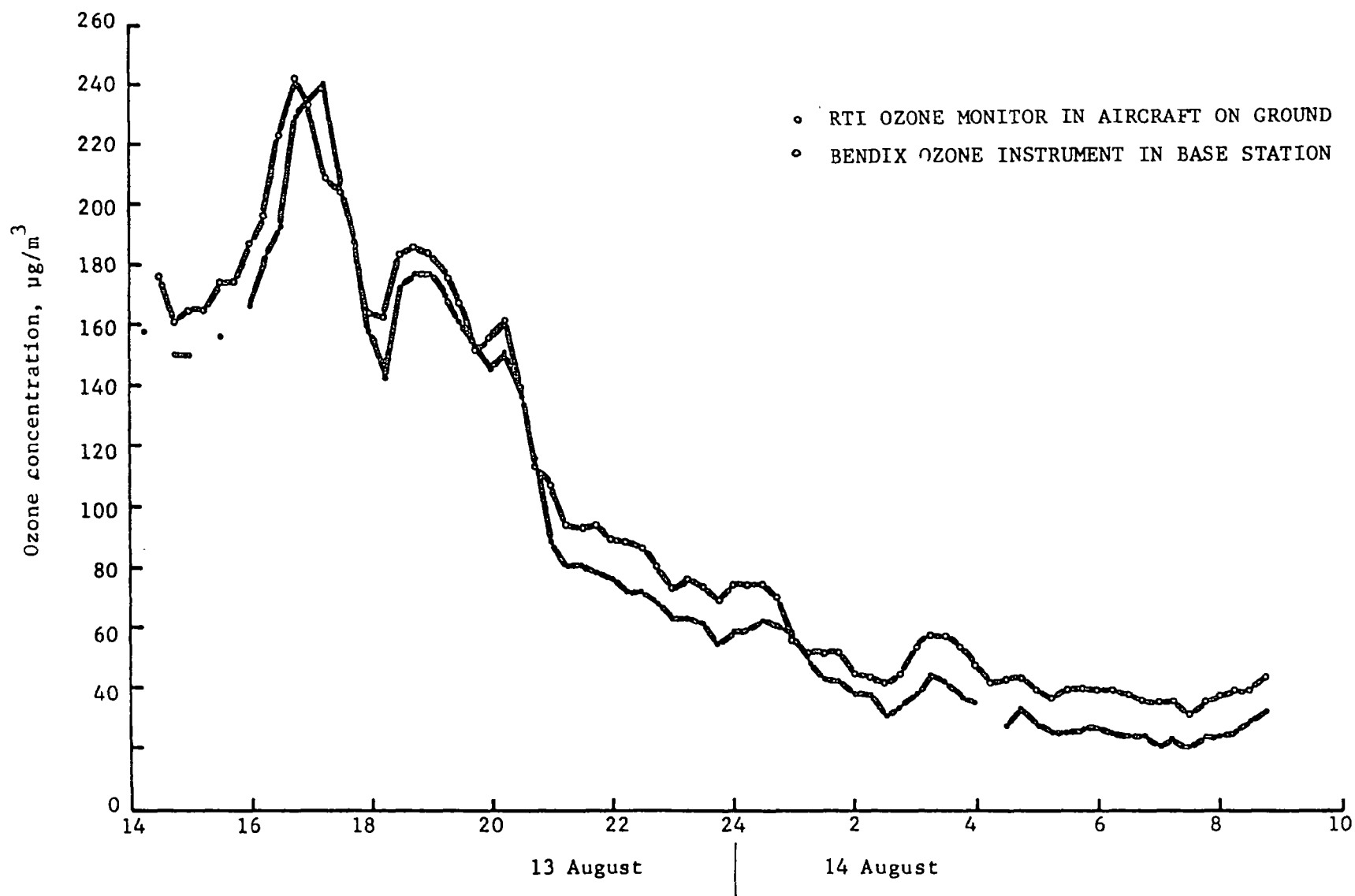


Figure 9. Ground Comparison - Ozone Instruments

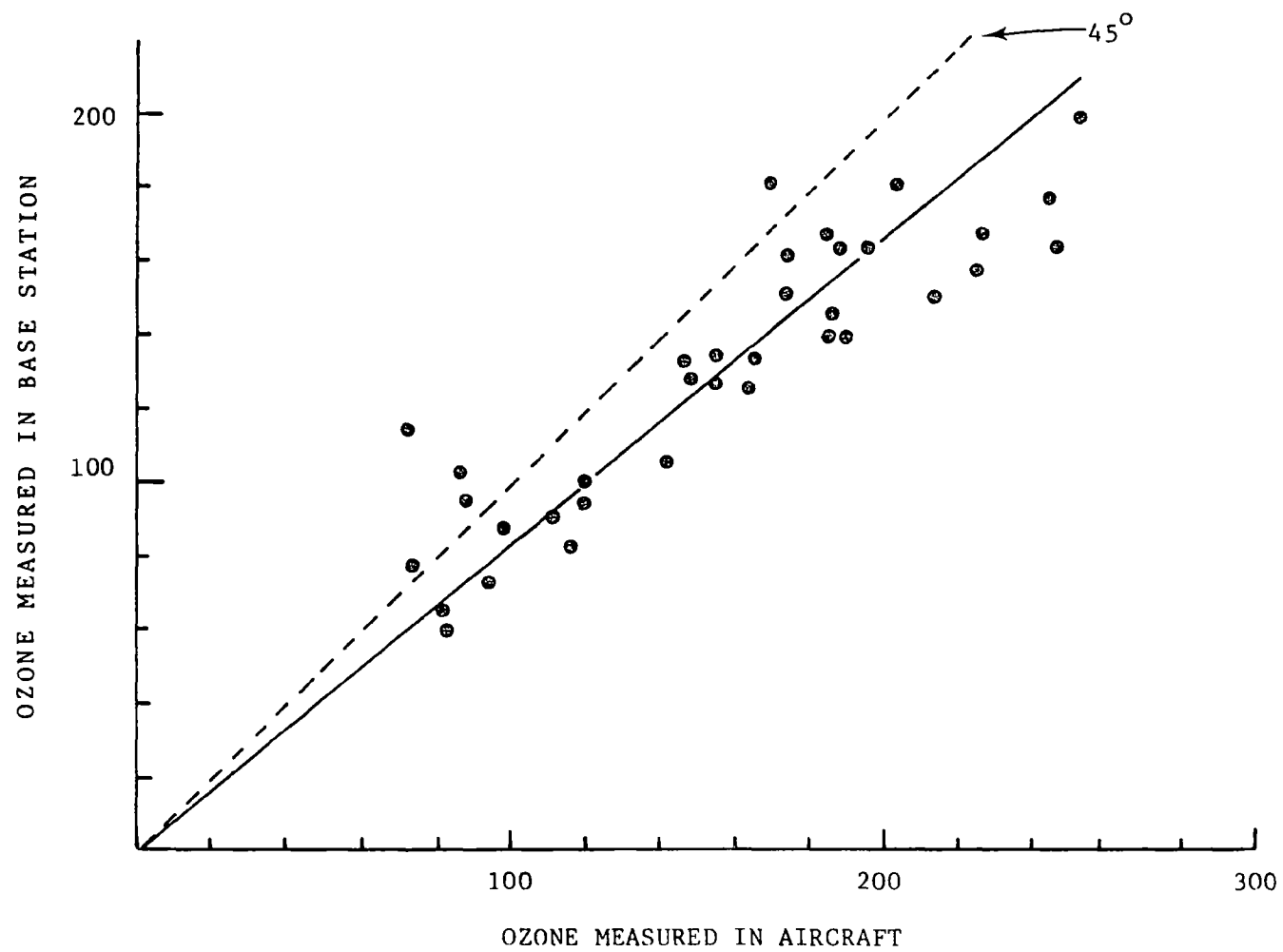


Figure 10. Aircraft Fly-By Data

be indicated by a plot in which all points fell on a line passing through the origin and inclined at an angle of 45° . The departure of the instrument behavior from this ideal is not unexpected. During the early hours of the day at a time when many of these passes were made, a homogeneous concentration of ozone due to mixing had not been achieved. This was borne out by observing the strip chart trace in the aircraft during the measure cycle. It was frequently quite erratic, indicating variations in the concentrations of ozone at different points surrounding the base station. Points taken before 1000 were omitted from the data plot; a rough linear fit is indicated by the solid line in Figure 10. Since the base station sample inlet was at 30 ft above ground level, it is reasonable that the values should differ to some extent.

Comparison Flight

Another means of insurance of valid data lies in comparison of results of two independent similar systems operating in the same environment with no interaction. This type of test was conducted in conjunction with Battelle Memorial Research Institute. They were operating a Cessna 173 aircraft outfitted with a REM gas phase chemiluminescent ozone analyzer and ram pressure bag filling system. The objectives of the test were to fly the C-45H aircraft and the Battelle Cessna through the same air at the same time in such a way as to avoid sampling each other's exhaust. Due to the differences in cruising speed of the two aircraft, a formation flight could not be flown. The pattern shown in Figure 11 was agreed upon. Both aircraft were to fly the pattern twice with the C-45H aircraft starting the flight in front of the Battelle aircraft.

The flight was conducted on 9 August with success. A partial plot of both the RTI-measured ozone levels and those determined by Battelle is included as Figure 12. The readings are plotted versus location along the flight path; consequently, there was a time difference between the times that data at the same point was taken, and the amount of time difference varied with position of the flight plan.

The plot shows good agreement between the RTI instrument and the REM instrument over the duration of the flight path, the difference being typically less than 10%.

Gas Phase Chemiluminescent vs Solid Phase Chemiluminescent Ozone Measurements

The ozone meter used in the aircraft was one built by RTI, under a previous contract with EPA, using a Rhodamine B disk which chemiluminesces with ozone. This instrument requires no ethylene bottle aboard the aircraft. In addition, it incorporates an internal calibration source which is measured once each cycle.

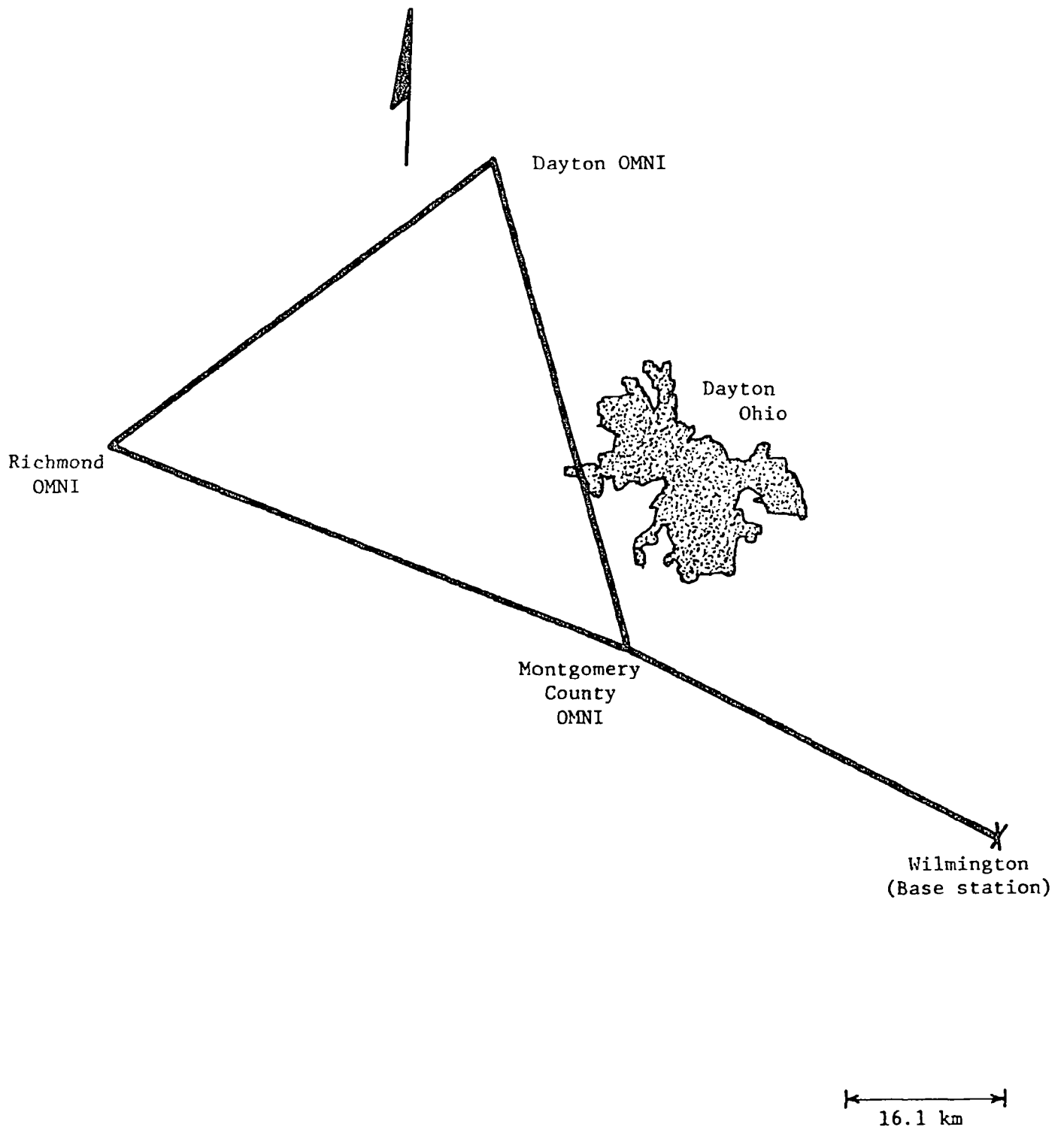


Figure 11. Ozone Instrument Comparison Flight Pattern

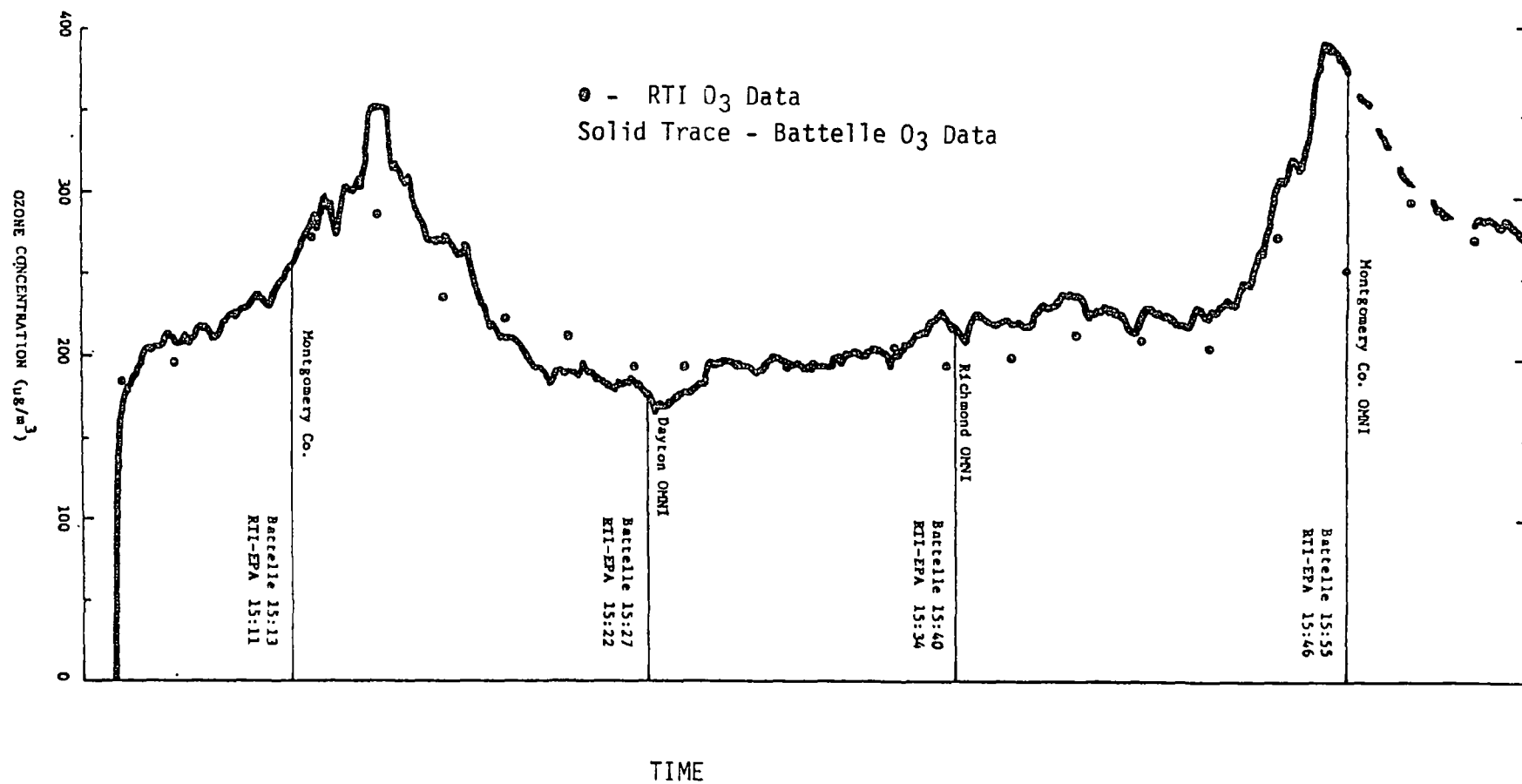


Figure 12. Comparison Flight - O₃ Data - 9 August 1974

Tests were run using the RTI instrument alongside the Bendix gas phase chemiluminescent ozone monitor to demonstrate the comparability of the two methods. These tests were run in the RTI Mobile Monitoring Laboratory with the two instruments located side by side and connected to the sampling manifold through which ambient air was being aspirated. The output of each was sampled once every 5 min, 24 hr per day and recorded on a magnetic tape. The RTI ozone monitor used for this test had a set of three sample and hold modules and electrical analog subtraction and division circuitry which carried out the function of comparing the measure signal level with the known internal calibrate. The magnetic tape data was processed by computer and the data output in concentration units.

Tests were run on these instruments on two occasions: once in the spring of 1974 (April 17, 18, 19 and May 2, 3) and again in late summer 1974 (August 9-September 1), yielding ample data for comparative analysis. A statistical analysis was performed on the data (spring and summer) to numerically evaluate the similarity of the readings. Results of this analysis are shown in Table 1. For the April and May data, 15 min averages consisting of three 5-min data points were used for the analysis; in the August data, individual 5-min data points were used. An example of a three-day period is shown in Figure 13. These data substantiate that the two instruments are comparable.

Data Acquisition and Reduction

The data acquisition system used consisted of six electric writing strip chart recorders rack-mounted in a single unit. Also included in the unit was switching circuitry which allowed the input of the recorders to be shorted without shorting each instrument output. This facilitated the zero adjustment check of the recorders by allowing this operation to be carried out with a single switch. A digital voltmeter (DVM) was included for checking the instrument levels (and therefore checking the operation of the strip chart recorders by checking the correctness of the deflection). The DVM could be switched to any instrument output with no movement of test leads.

Since there were up to five individual records represented -- concentrations of O_3 , NO , NO_2-NO_x and temperature -- some means had to be utilized to correlate the five with each other and with the corresponding location on the ground. The zero adjust switch was used for this purpose. Each time a significant point was crossed in the flight pattern, the switch was activated causing all recorders to simultaneously trace to zero and return to normal leaving a distinguishable mark. The time of the event was marked on the ozone recorder to the nearest minute. The operator maintained a separate log of the times and the event which occurred.

After the data were converted to micrograms per cubic meter, it was placed on a map illustrating the flight path at the point corresponding to its origin. The flight path was drawn immediately after the flight considering recollections of the pilot and co-pilot and notes made by the second instrument operator. The data was then put on the map by observing where the

Table 1.

STATISTICAL COMPARISON OF THE
RTI SOLID PHASE INSTRUMENT VERSUS BENDIX GAS PHASE INSTRUMENT

Time Period Day	N*	Correlation	Means		Ratio of Means RTI/Ben
			RTI	Ben	
April 17	20	.9644	159.1	150.7	1.06
18	20	.9958	136.9	133.6	1.02
19	20	.9567	158.1	151.7	1.04
May 2	30	.9981	74.1	66.4	1.12
3	64	.9987	65.3	59.4	1.10
Aug. 7-9	547	.99	85.7	81.1	1.06
14-16	632	.99	94.1	95.4	.99
22-24	849	.98	121.8	120.2	1.01
28-30	617	.97	63.7	61.6	1.03

* Number of data points included in comparison.

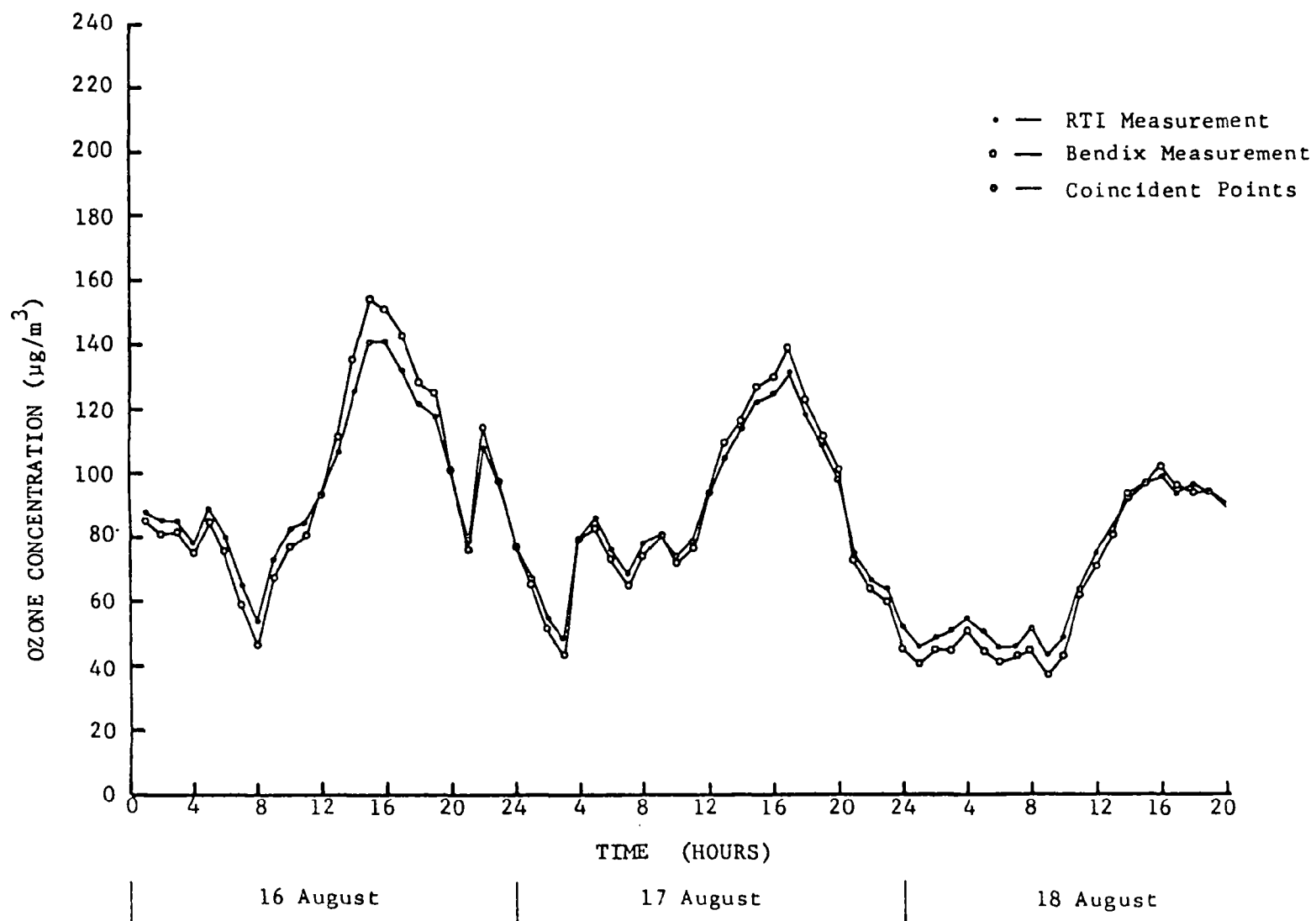


Figure 13. Gas Phase and Solid Phase Ozone Instrument Comparison

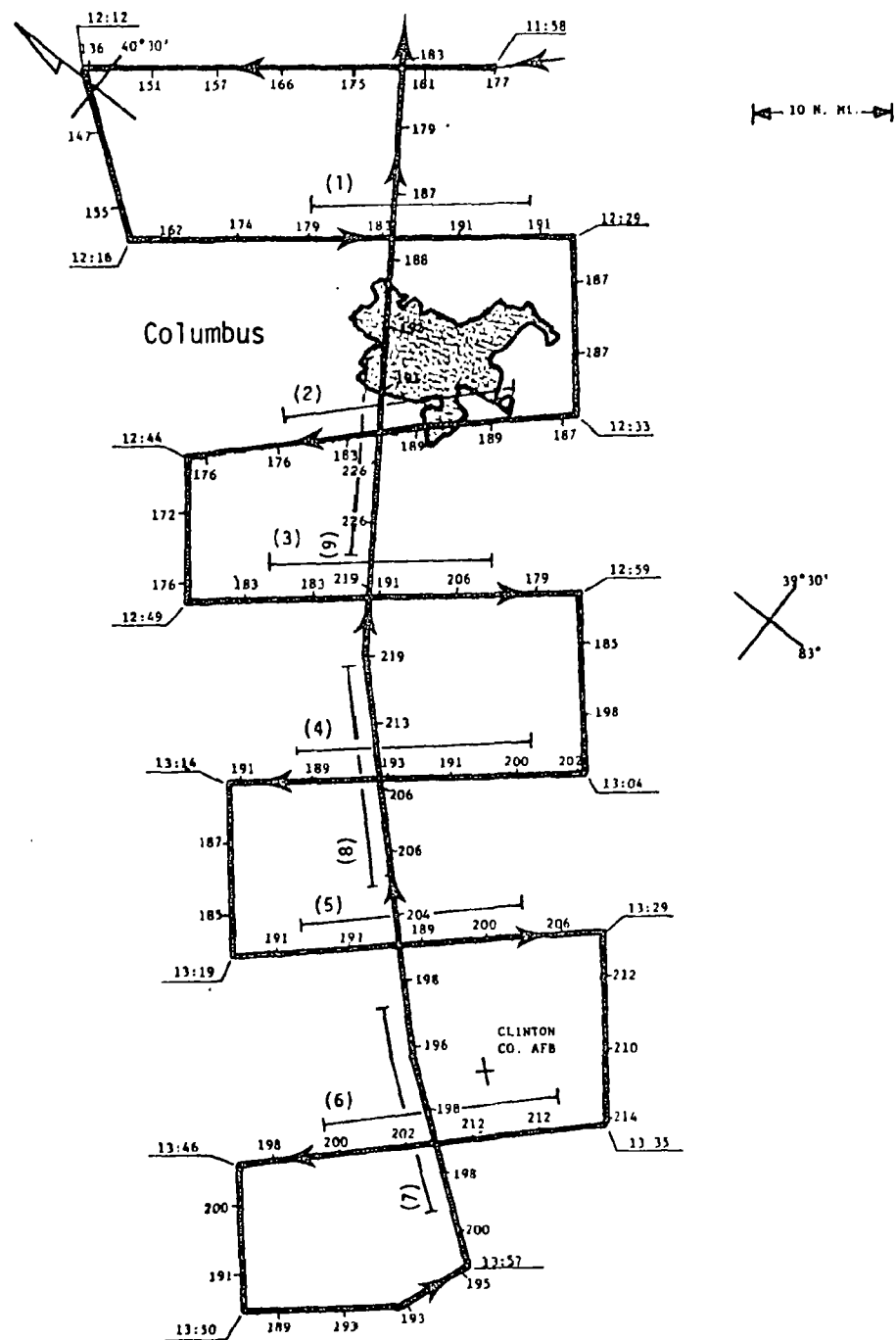
particular data point fell on the strip chart in relation to noted significant events in the flight path (turns, prominent landmarks, etc.) and placing it on the pertinent portion of the flight path at proportionant distance between the two nearest significant features. The times of all turns were placed on the maps as an aid to those who analyze the data. NO and NO₂ data were omitted from the flight plan due to the fact that they were nearly always below the detectable limits of the instrument, but were put in tabular form along with the temperature data.

Examples of the aircraft's data may be found in Figures 14, 15, and 16. The latter example was taken from flights flown subsequent to the Ohio River Basin study and are given to show a third type of flight pattern.

SUMMARY AND RECOMMENDATIONS

There are several improvements one would consider in a system of the type described, most of which are practical to implement, assuming the necessary time, facilities, and funds are available. These improvements are as follows:

- (1) Although continuous measurement, with compatible response times, of each of the pollutants is practical at this time with state-of-the-art analyzers, an improvement is needed in the minimum detection level of NO_x-NO-NO₂ analyzers. At least an order of magnitude improvement in detection sensitivity is needed for detection and measurement of NO more than 500 ft above ground. Also, it would be desirable to have improved flow-rate control and/or monitoring; especially for flights involving altitudes varying over a range of several thousand feet.
- (2) A small, light weight, simple, and reliable calibration system for in-flight measurements would be very useful in routinely verifying the instrumentation system operation and calibration. Such a system would have to be usable over the range of altitudes covered in data flight, a requirement not imposed on typical calibration systems currently available.
- (3) Testing of the sample inlet system should be tested for dynamic characteristics in a wind tunnel initially, if possible. In addition, in-flight tests should be conducted to compare the aircraft measurements with those made at a ground-based station. These could be conducted similar to those described in the Low-Pass Flight Section, with more flights being made from several directions, at a time of day when good mixing has occurred and with the ground sample inlet at a height compatible with the permissible aircraft minimum flight altitude. By making several passes from several directions a better statistical sample could be obtained for comparison with the ground-based data system. If possible, a location could be chosen whereby the aircraft could fly at the test altitude for at least a minute before the comparison data point would be taken.



TRUE AIRSPEED: 140 knots MISSION ALTITUDE: 3,200 ft above msl

Figure 15. Square Wave Pattern Flight - 21 July 1974

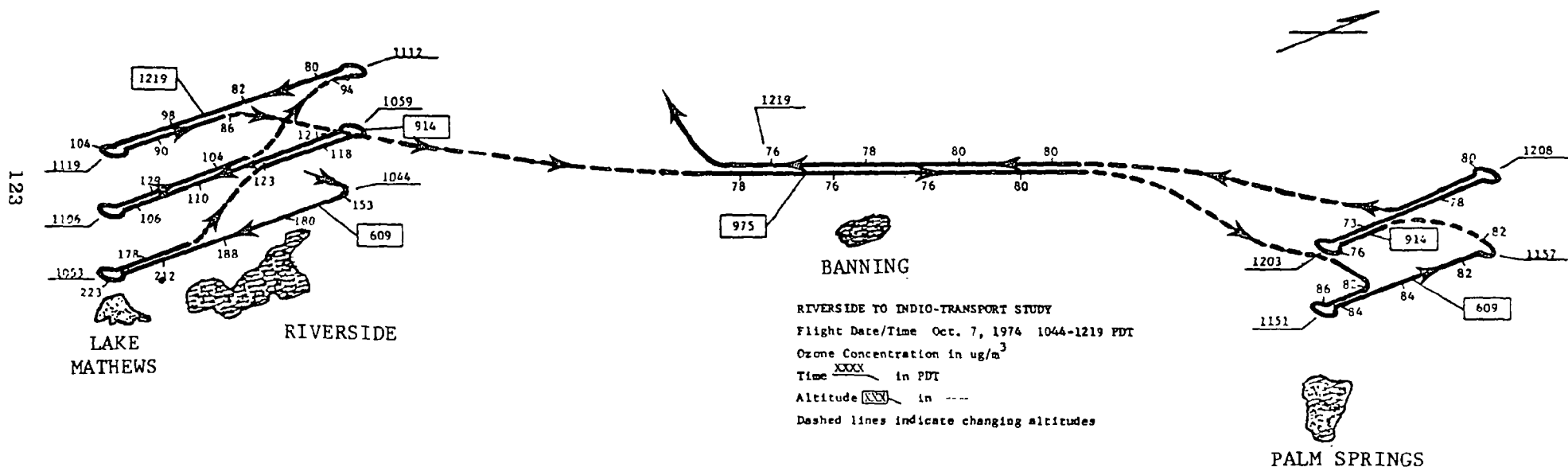


Figure 16. Los Angeles Basin and Vicinity

- (4) Incorporate automatic recording of altitude and position, along with the primary data and any desirable status information, onto a data acquisition system which is directly compatible with computer processing equipment.
- (5) Redesign of the instruments for aircraft operation for reduction in size, weight and power consumption, and reduced susceptibility to shock and vibration would be desirable. Rapid switchover to a minimum power consumption mode would provide for the maintenance of power to the critical subsystems during times of refueling, etc. with a minimum battery back-up system.

INSTRUMENT TIME RESPONSE AND ITS IMPLICATIONS

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Introduction

It is well known that a linear air monitoring instrument with a finite response time, defined as the time required to reach a percentage of a unit step input signal, will not produce an exact record of the atmospheric concentration being sampled. Data taken by ground based monitoring stations are recorded, reported and analyzed without correction for the response time characteristics of the instruments. Neglect of this effect is justified in most cases, by the fact that air quality standards and health effects are related to averages of one-hour or greater which are relatively unchanged by this effect. However, for aircraft sampling, where the purpose of the monitoring is to obtain spatial variability, or to measure the manner in which a plume is dispersing these effects can and do become significant. This paper discusses a technique by which the concentration input to the instrument can be estimated from the recorded output using linear systems theory and the instrumental transfer function.

Theoretical Development

A previous publication by the author, included as appendix A, developed the theory and the use of the transfer function to provide a rigorous relation of input to output. The details will not be discussed in this presentation since they are available in the literature. A simplified model may be set up for an arbitrary detector placed within a chamber of volume V liters with a flow of pollutant in and out at a rate of v liters/minute. If we assume the chamber is perfectly mixed, the outflow will have an identical concentration C , to that in the chamber, and we can write a mass balance

$$vC_i - vC = \frac{VdC}{dt} \quad (1)$$

where C_i is the input concentration which we desire to measure. This equation is a first order linear differential equation and can be written as

$$C_i = C + \tau \frac{dC}{dt} \quad (2)$$

where $\tau = V/v$ is the time constant for the system. For the case of zero lag time, this equation means that to the output C we must add τ times the slope of the curve to get the input concentration C_i at the time the recorder is reading C . For example, let us assume the instrument with time constant τ measures a sinusoidal signal of period T as $C = C_o + \sin \frac{2\pi}{T} t$. The input to the system which produced this output is $C_i = C_o + \sin \frac{2\pi}{T} t + \frac{2\pi \tau}{T} \cos \frac{2\pi}{T} t$. At $t = 0, T, 2T, \dots$ when $C = C_o$, $C_i = C_o + \frac{2\pi \tau}{T}$.

For the simple case where $T = 2\pi \tau$ and $C_o = 2$, the input and output curves are shown on Figure 1.

These two curves have the same period only because of the choice of $T = 2\pi \tau$. In general the input and output curves will be out of phase. The most obvious effect is the decrease in amplitude of the fluctuations about the mean from 1.414 to 1, a difference of about 30%. The following sections discuss these corrections in relation to aircraft measurements.

Response Time Effect on Aircraft Monitoring

For an aircraft moving at 150 knots ground speed, one second of time corresponds to 77 meters (253 ft) of travel. To demonstrate the effect of the response time, assume the plane is carrying an instrument which has a first order linear response with a time constant $\tau = 2$ seconds and a lag of 1 second. If the plane were to pass through a plume of pure pollutant (10^6 ppm) .077 mm wide, this would correspond to a delta function input of area 1 ppm-second. The response of the instrument is shown as Figure 2. The

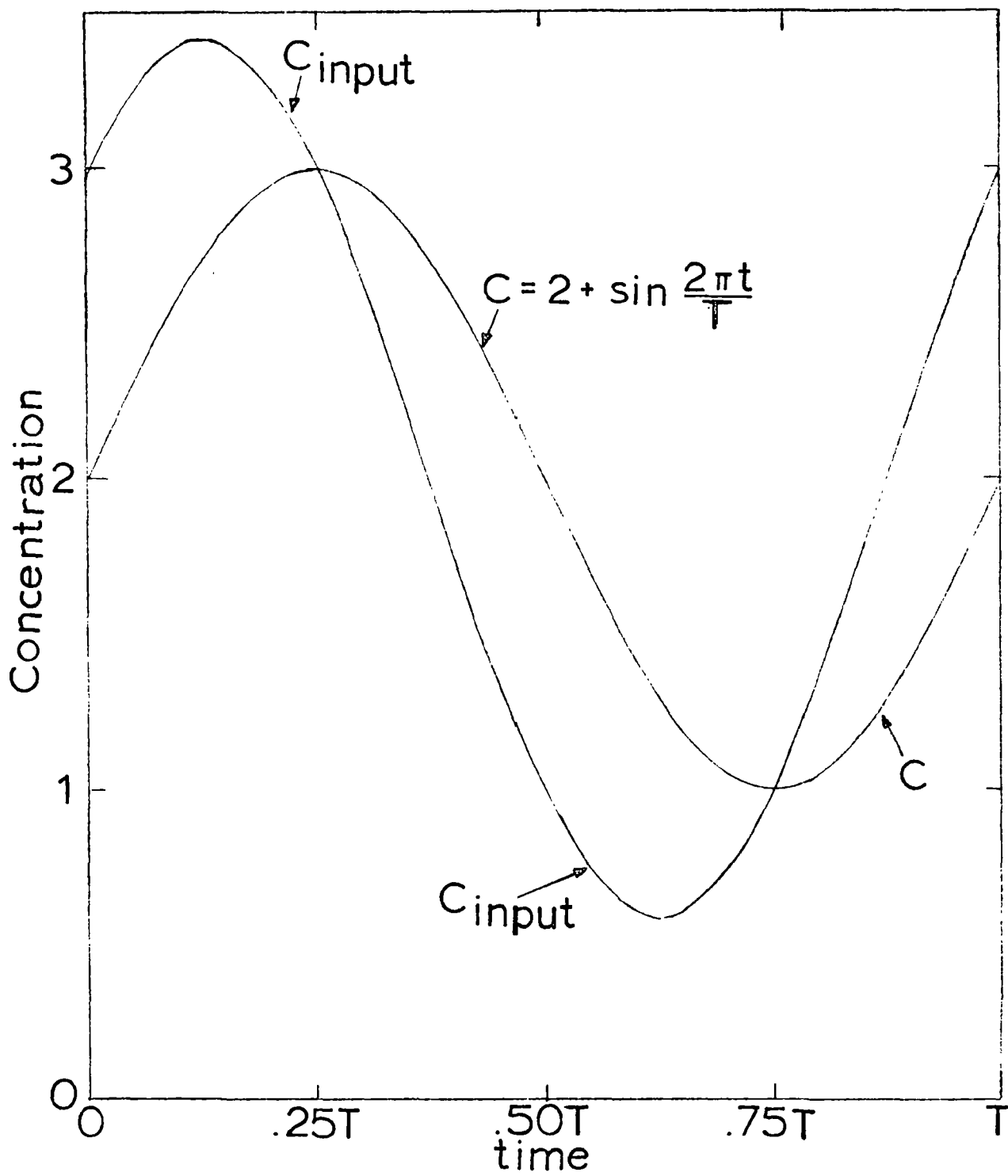


FIGURE 1

aircraft would observe the exponential curve $e^{-t/\tau}$ rather than the delta function. The instrument would not respond until the aircraft had traveled 77 meters beyond the plume and the reading would be spread out over approximately 1/2 kilometer of travel. The difference between input and output shown here is the maximum possible and points out the need for making the time-space correction when sampling from high speed aircraft.

In the following section reference is made to the figures in the appendix. Let us assume the instrument is being flown at 150 knots and it responds 60 times faster than the instrument analyzed in the appendix. The figures A4, A5 and A6 could then be changed simply by changing the time scale from minutes to seconds, as shown in Figures 3 and 4. The instrument would have a 2 second lagtime and it would take an additional 5 seconds to reach 90% of a change in signal. The technique of using the convolution integral in finite difference form is equivalent to treating the output as a general autoregressive-moving average process of order m, where the transfer function is divided into m increments. The transfer function of this particular instrument is shown in Figures 3 and A-4. It is of interest to note that this function is no longer the ideal exponential response and no apparent analytical expression can be used to represent it. In Figure A-6 and 4, the instrument is assumed to have recorded the output marked as I, the response $R(t)$ curve caused by the disturbance $D(t)$ curve, marked as II. The disturbance is damped out over 100% and is spread over almost twice the distance. If this were a horizontal pass through a plume, the spread of the recording would change a computed σ_y from the order of 50 meters to about 100 meters. Another area where these corrections might be necessary is that of vertical measurements. The recorded concentrations can be used to obtain the flux in horizontal crosswind flight

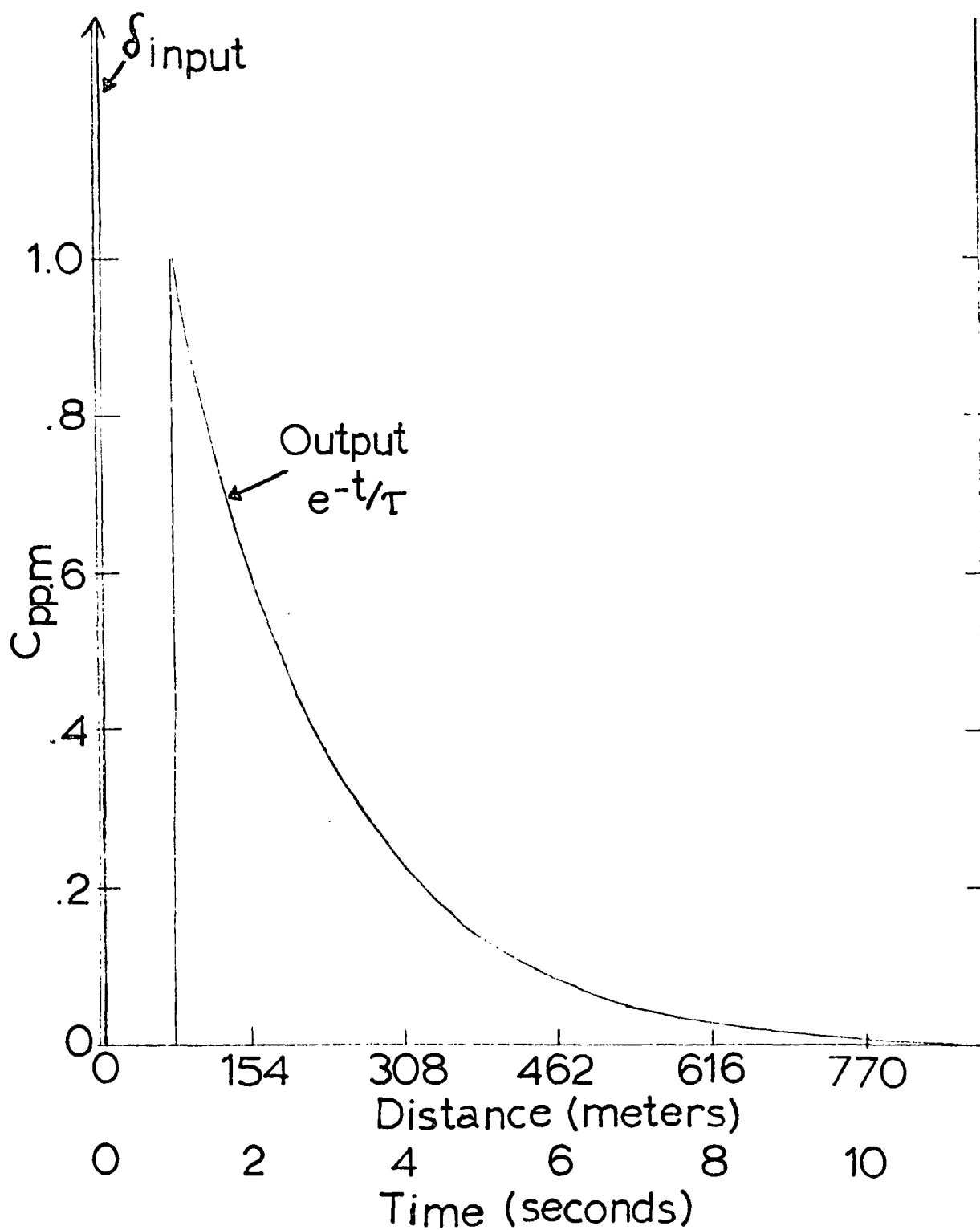
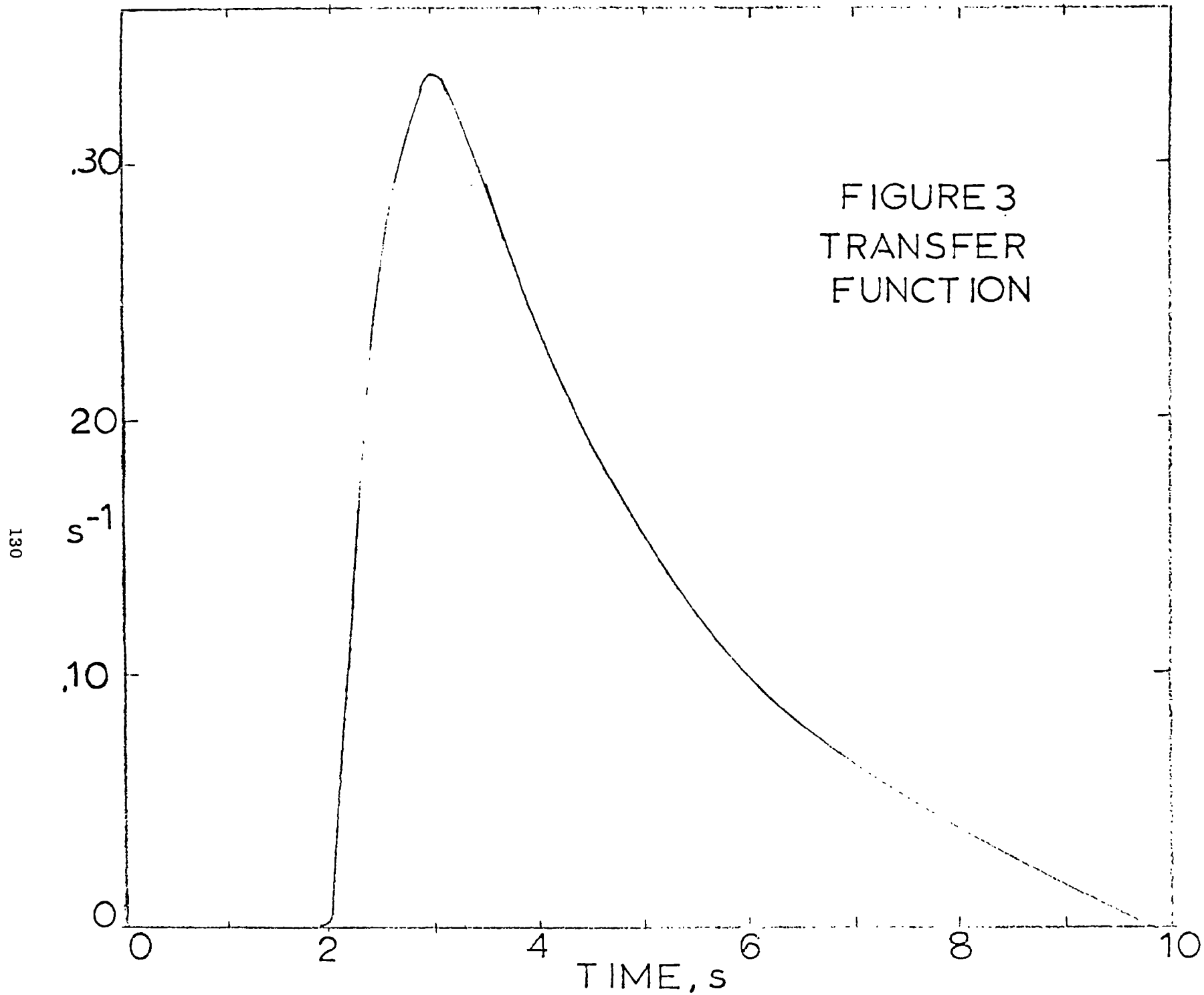
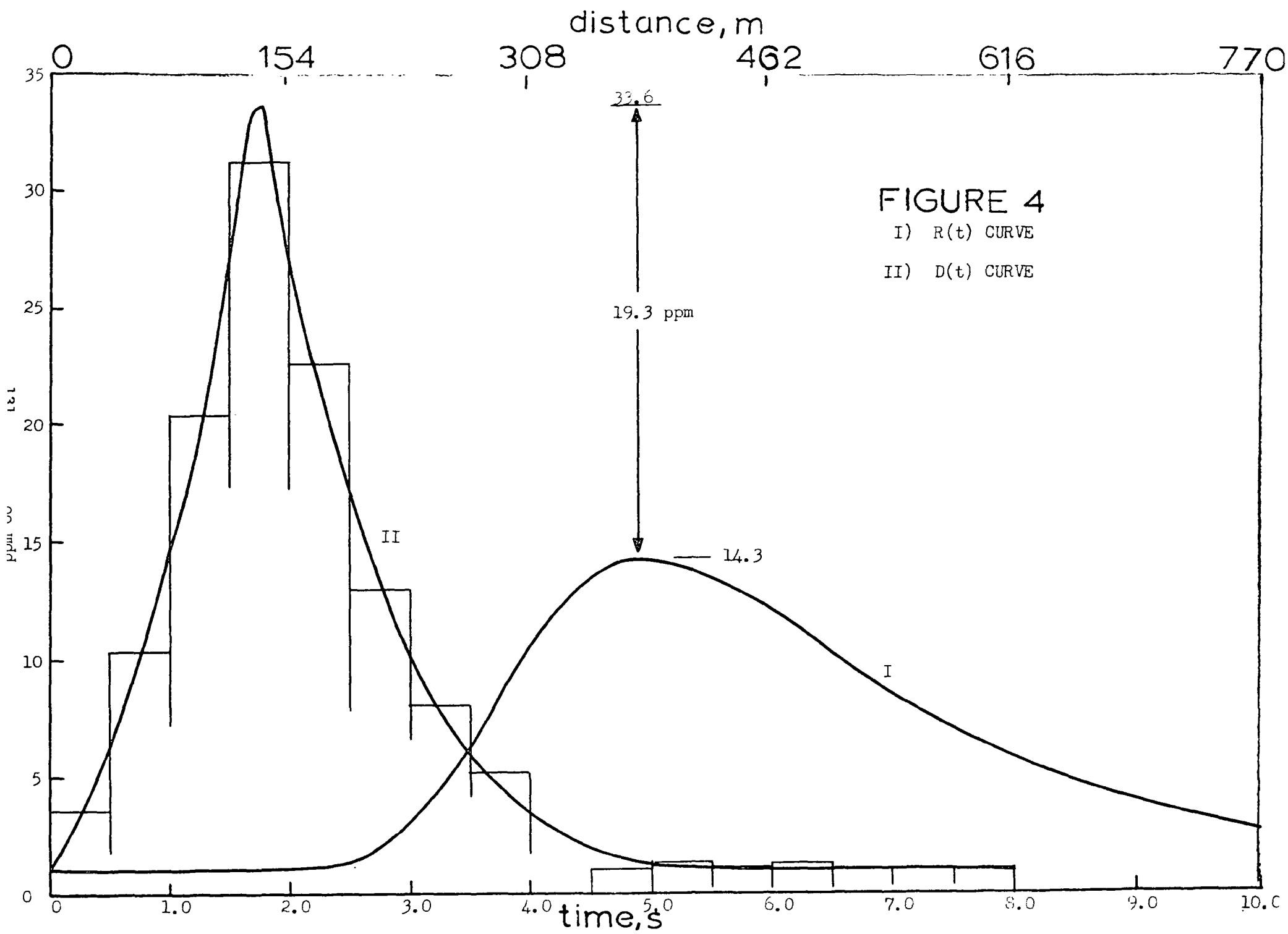


FIGURE 2





since the wind velocity will not change noticeably in the horizontal over a small distance and the flux $\dot{Q} = \int_Y C U \Delta Z dy$. However the computation of vertical flux requires use of the wind velocity U as a function of height and the equation for the flux $\dot{Q} = \int_Z C U \Delta y dZ$ cannot be used with the recorded data directly. Turning the previous figure 90° we have what may correspond to a vertical sounding as the plane is descending. The plume at the higher altitude would give a greater flux than the recorded plume at the lower altitude where the winds are diminished. This effect can be minimized by utilizing a slow rate of descent such as 500 ft/min used by the RAPS helicopters in the St. Louis area.

Summary and Conclusions

In using high speed aircraft and instruments with response times on the order of seconds, high frequency disturbances may be spread over relatively long distances. For those situations where gradients of properties, rather than the averages of the properties are required, a correction for the response of the instrument system may be necessary. This paper reviews the theory of linear systems and presents a technique by which any linear instrument may be modeled and corrections made.

True Atmospheric Pollutant Levels by Use of Transfer Function for an Analyzer System

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Air pollution analyzers, because of inherent lags and response times, will not produce an exact record of pollutant concentrations. A procedure is described for determining the transfer function for an analyzer system. This transfer function is applied to the recorded output to produce a record of the actual atmospheric pollutant concentration at the inlet to the system. This procedure is applied to the carbon monoxide analyzer of the Bay Area Air Pollution Control District monitoring station in San Jose. Results show that variations in peak heights of more than 50% can exist between actual and recorded values.

It is a well known fact that most air pollution monitoring instruments do not respond instantaneously to the actual levels of pollutants entering their intakes. In ventilation type instruments (i.e., instruments in which air is pumped through a detector), it takes a finite time for a gas sample to reach the detector. In this time the sample may become mixed with other gas samples which previously have entered the system in a similar manner. As a result of this system behavior, a sudden, abrupt change in an atmospheric pollutant level will not be recorded instantly, and the instrument output will show a gradual increase to the new level after a delay which is characteristic of the system.

Such an abrupt change of the input of a system is commonly referred to as a "step" input, while the resulting output is called the "step response" of the system. Figure 1 for example, shows the step response of a sulfur dioxide (SO_2)

measurement instrument to a three minute input step of 2 ppm SO_2 .¹ There are four important factors to observe:

1. It took 60 sec before the instrument first began to respond.
2. It took another 114 sec for the output to reach 1.51 ppm.
3. The maximum recorded value was 1.9 ppm not the true value of 2.0 ppm.
4. During a period of 1.85 min the recorded value is above 1.5 ppm.

The inability of the monitoring instrument to record the actual pollutant level in the atmosphere can be a serious obstacle for those responsible for air pollution monitoring. In the San Francisco Bay Area, this occurrence of 2 ppm for a 3-min period would constitute a violation of the local air quality standards. Regulation 2 of the San Francisco Bay Area Air Pollution Control District

(BAAPCD) states, in part "No person shall cause, let, permit, suffer or allow any emission of sulfur dioxide which results in ground level concentrations of sulfur dioxide at any given point in excess of 1.5 ppm (vol) for three consecutive minutes . . ." Thus, for the purpose of monitoring a suspected violator of this air quality standard, this instrument would not be satisfactory because the recording is not an exact copy of the concentration present in the atmosphere.

If one is seeking to control emissions from a process to prevent a violation of a regulation, the violation may be discovered after it has occurred. If an episode exists, it may be over before it is discovered. This effect can become even more significant for air monitoring with some other wet-chemistry instruments. For example, the California Air Resources Board uses a Beckmann K-76 Analyzer for the measurement of NO_x and NO_2 in Santa Rosa, Calif. This instrument exhibits a 15-min delay before initially responding and a total elapsed time of 30 min before reaching 90% of the maximum value in response to a step input. Thus, this type of instrumentation would be inadequate for measurement of NO_2 levels as part of an emergency alert network both because of the large delay and the reduction of maximum values which would be produced.

The method described in this paper allows one to take into account the instrument delay and response and thus allows the more accurate analysis of true time variations of air quality.

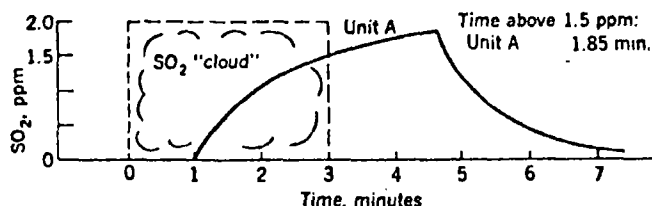


Figure 1. Response check.

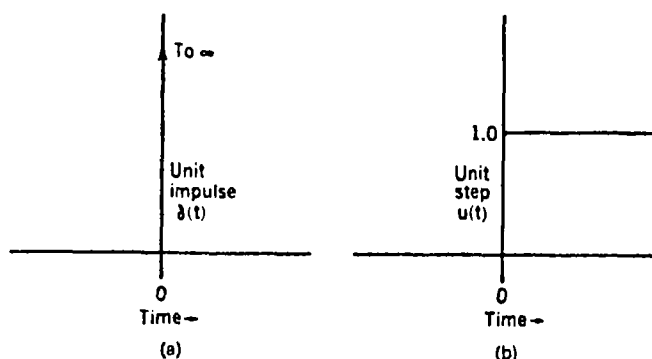


Figure 2. Idealized inputs for system analysis.

Theory of Transfer Functions for Linear Systems

A linear system is one which exhibits various linear properties, one of the most important of which is the principle of superposition illustrated by Table I. The functions $y_1(t)$ and $y_2(t)$ are the output responses for each of two different input excitations, $x_1(t)$ and $x_2(t)$. When the input function $x_3(t) = x_1(t) + x_2(t)$ is introduced into the system, the output then must be equal to the sum of the previous two outputs, $y_3(t) = y_1(t) + y_2(t)$. A more detailed description of the characteristics of linear systems may be found in the literature.^{2,3}

From our investigations with air monitoring instrumentation, it appears that many such instruments can be treated, to a good approximation at least, as linear systems. Each linear system has its own unique transfer function, and, from this transfer function, the system's response to an arbitrary input can be determined. The development of such a transfer function usually involves the use of Laplace transforms. If $f(t)$ is a function of t defined for values of $t \geq 0$, its Laplace transform is obtained as follows:

$$L[f(t)] = \int_0^{\infty} f(t)e^{-st} dt \quad (1)$$

Two inputs which are common in the discussion of linear systems are the unit impulse $\delta(t)$ and the unit step $u(t)$. The unit impulse is defined to be zero for all values of t except at $t = 0$, at which point it has the value of infinity; it is defined to have the area of unity. The unit step is a function which is 0 for all values of $t < 0$ and 1 for $t > 0$. These two functions are depicted in Figure 2. The Laplace transform of the unit impulse is simply unity.

The response of a system to a unit impulse excitation is called the transfer function for the system, $C(t)$, with Laplace transform $C(s)$.

The transform of the output $R(s)$ will be the product of the system transform $C(s)$ and the input transform $X(s)$.

$$L[R(t)] = R(s) = X(s) \cdot C(s) \quad (2)$$

To obtain the actual output as a function of time, it is necessary only to take the inverse Laplace transform of the resulting output transform:

$$R(t) = L^{-1}[R(s)] = L^{-1}[X(s) \cdot C(s)]. \quad (3)$$

For a complex air monitoring instrument, we usually cannot write the system transform $C(s)$ directly from a knowledge of the working of the instru-

ment. We can, however, observe the systems behavior to a known input and, from this derive $C(s)$. The ideal input to use is the impulse function $\delta(t)$ shown in Figure 2(a), since its transform is unity and the transform of the output thus will be equal to the transform of the system. In practice it often is difficult to generate a true impulse function, and an alternate approach is to use the step function as the input; since this is the integral of the unit impulse, one only needs to differentiate the step response to arrive at the true impulse response. From this the overall system transform $C(s)$ may be derived, and then it will be possible to calculate the output to any input function.

Since the resulting transform of a complex instrument can sometimes be unwieldy to write and handle, one can choose a more simple approach which makes use of the convolution integral. Here, the unit impulse response is used to estimate the output to any arbitrary input without the necessity for writing an analytical expression of the transfer function of the system. A rigorous solution to the system the time response $R(t)$, with zero initial condition, can be obtained by use of the convolution integral

$$R(t) = \int_0^t C(\lambda)X(t - \lambda)d\lambda \quad (4)$$

where λ is a dummy variable used for the convolution integration.⁴

A physical explanation for the process involved in use of the transfer function may be given by looking at an example of a system response to the unit impulse, $C(t)$, as shown in Figure 3. Figure 3 shows the mass flow rate divided by total mass input plotted vs time. The area under the curve $R(t)$ must be equal to unity if the total mass leaving the system is equal to the total mass put into the system $X(t)$. In this case, the input curve is the delta function $\delta(t)$ and the output is the transfer function. For a 1 l/min flow rate and a 2 l volume of the sampling and detector system, if no mixing took place, the entire gas sample would appear as a unit impulse, $\delta(t)$, at the detector 2 min after it entered the system. However, due to by-passing and turbulence, mixing does take place in the flow system resulting in a reduction in amplitude of the signal.

Table I. Superposition property of linear systems.

Input	Output
$x_1(t)$	$y_1(t)$
$x_2(t)$	$y_2(t)$
$x_1(t) + x_2(t)$	$y_1(t) + y_2(t)$

From Figure 3 it is observed that such a gas sample may take 1 min to reach the detector and 3 min to pass through it completely.

In practice, the solution to the convolution integral of equation (4) is quite involved and a finite-difference method may be used to approximate the solution. The following describes the computational method for obtaining the output response, $R(t)$, to an arbitrary input function $X(t)$ by such a finite difference approach, in which ΔT represents an arbitrarily small increment of time, and T represents the time required for the unit impulse to clear the system (3 min in Figure 3.)

$$R(t) = \sum_{n=1}^{n=T/\Delta T} C(n) \cdot X(t - n\Delta T) \cdot \Delta T \quad (5)$$

and

$$R(t) = C(1) \cdot X(t - \Delta T) \cdot \Delta T + C(2) \cdot X(t - 2\Delta T) \cdot \Delta T + \dots \quad (6)$$

A more detailed example of this type of computation is given later. It is also possible, as in the following, to obtain $X(t)$, the input, when the recording $R(t)$ and transfer function $C(t)$ are known. In both cases, the accuracy of the result depends upon the size of the time increment ΔT .

Equipment and Procedure

Three instruments were installed at the Bay Area Air Pollution Control District air monitoring station in San Jose, in parallel, for measurement of concentration of hydrocarbons, oxides of nitrogen (NO_x), and carbon monoxide (CO) in the surrounding atmosphere. Each instrument is equipped with a small vacuum pump to circulate air through the unit. The CO analyzer has a 5 l jar in the inlet line to produce an "averaging effect," and reduce the magnitude and frequency of traffic spikes.

Air is circulated through a $\frac{3}{4}$ in. glass

pipe and then is distributed to each instrument by $\frac{1}{4}$ in. tubing. The CO analyzer is the conventional nondispersive infrared (NDIR) unit (MSA LIRA), with desiccant, found in most air monitoring installations. The sample flow rate through the CO detector is 1 l/min. An 82 ppm CO span gas was passed into the sample inlet abruptly, to generate the "step response" of the CO analyzer system. The span gas flow rate was throttled down to prevent pressurization of the glass sample intake pipe. Consequently, additional air from the surrounding atmosphere also was passing into the sample inlet tube during the experiment, bringing the equilibrium value of the CO finally recorded down from 82 to 57 ppm. It is necessary to pass the span gas into the atmospheric sample intake as it actually exists, rather than into the instrument intake, because the length of $\frac{3}{4}$ and $\frac{1}{4}$ in. pipes serves to delay and modify the instrument response because of additional mixing which occurs in these tubes.

A high speed strip chart recorder permits an accurate recording of the shape of the response, which is similar to curve shown in Figure 1. Figure 4 is the $C(t)$ curve obtained by differentiation of this step response. The curve shows that the CO monitor tested has a 2 min delay time, and that it takes 10 min for the gas to clear the system in its entirety.

In order to develop the transfer function in a finite difference form, for use in equations (5) or (6), a value of $\Delta T = .5$ min was chosen, corresponding to 20 equal increments between 0 and 10 min. The series $C(1) \dots C(20)$ has values as below,

$$\begin{aligned} C(1) &= 0 \\ C(2) &= 0 \\ C(3) &= 0 \\ C(4) &= 0 \\ C(5) &= 0.162 \text{ min}^{-1} \\ C(6) &= 0.316 \text{ min}^{-1} \end{aligned}$$

etc and

$$\sum_{n=1}^{20} C(n\Delta T) \cdot \Delta T = 1 \quad (7)$$

To demonstrate the procedure for solution of the convolution integral to determine the input function $X(t)$, the CO span gas was reconnected to the system input as previously described. This gas was turned on briefly to simulate a significant atmospheric level of CO at the intake probe. The BAAPCD carbon monoxide instrument recorded the rise and fall of carbon monoxide as shown on Figure 5. Expanding this figure, as shown in Figure 6, the $R(t)$ curve was obtained. This curve is

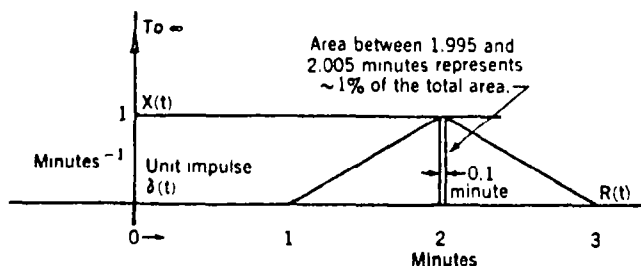


Figure 3. Hypothetical response to a unit impulse.

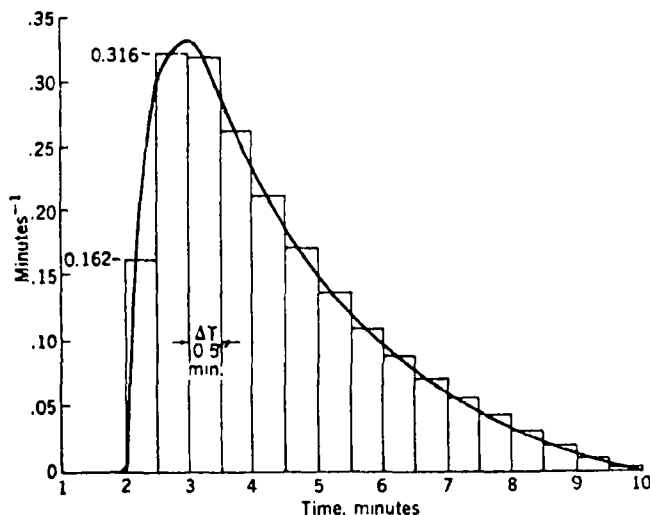


Figure 4. Normalized $C(t)$ curve for MSA Infrared CO analyzer system.

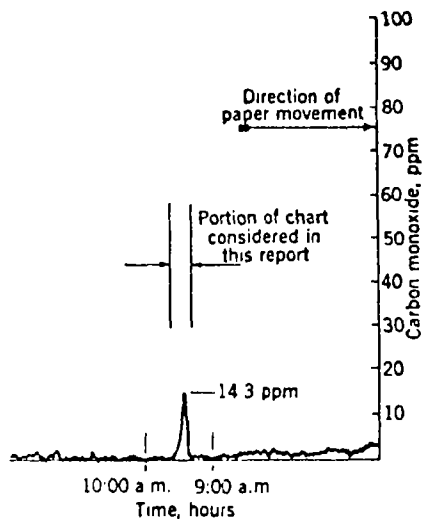


Figure 5. Ppm CO vs time, BAAPCD, San Jose.

broken into equal increments of 0.5 min each, corresponding to the same increment used in determining the transfer function.

For purpose of computation, the atmospheric carbon monoxide was assumed to be constant at 1.1 ppm for the preceding 10 min, as shown on Figures 5 and 6. The curve $R(t)$ can then be broken up into increments as follows:

$$\begin{aligned} R(1) &= 1.1 \text{ ppm} \\ R(2) &= 1.1 \text{ ppm} \\ R(3) &= 1.1 \text{ ppm} \\ R(4) &= 1.1 \text{ ppm} \\ R(5) &= 1.3 \text{ ppm} \\ R(6) &= 2.2 \text{ ppm} \end{aligned}$$

etc

By utilization of equation (6), the $X(t)$ curve can be solved for as follows:

$$\begin{aligned} R(t) &= C(1) \cdot X(t - \Delta T) \cdot (.5) + \\ &C(2) \cdot X(t - 2\Delta T) \cdot (.5) + \\ &C(3) \cdot X(t - 3\Delta T) \cdot (.5) + \\ &C(4) \cdot X(t - 4\Delta T) \cdot (.5) + \\ &C(5) \cdot X(t - 5\Delta T) \cdot (.5) + \\ &C(6) \cdot X(t - 6\Delta T) \cdot (.5) + \dots \end{aligned}$$

noting

$$C(1) \dots C(4) = 0 \text{ and}$$

$$R(t) = 1.1 \text{ ppm, } t < 0$$

$$R(4) = (2.0 \text{ min}^{-1}) \cdot (.5 \text{ min}) \cdot$$

$$(1.1 \text{ ppm}) = 1.1 \text{ ppm}$$

In this analysis, $X(t)$ is the unknown, and can be solved for by a stepwise procedure as follows:

$$\begin{aligned} R(t) &= C(5) \cdot X(t - 5\Delta T) \cdot (.5) + \\ &C(6) \cdot X(t - 6\Delta T) \cdot (.5) + \dots \end{aligned}$$

$$\begin{aligned} R(5) &= C(5) \cdot X(5 - 5\Delta T) \cdot (.5) + \\ &C(6) \cdot X(5 - 6\Delta T) \cdot (.5) + \dots \end{aligned}$$

noting $R(5) = 1.3 \text{ ppm}$ and $X(5 - 6\Delta T) = X(5 - 20\Delta T)$ are equal to 1.1 ppm one can apply the equations above using the experimental values for $C(5) \dots$

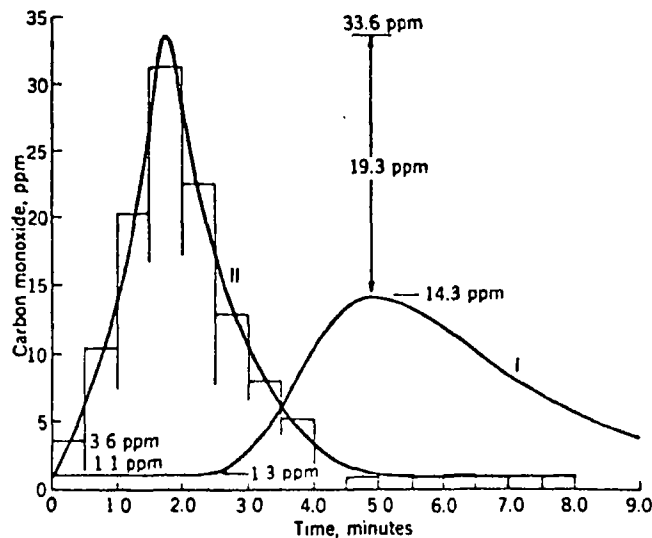


Figure 6. I. $R(t)$ curve. II. $X(t)$ curve.

$C(20)$ to solve for the remaining unknown, $X(5 - 5\Delta T)$.

$$1.3 \text{ ppm} = 0.162 \text{ min}^{-1} \cdot X(5 - 5\Delta T) \cdot$$

$$(.5 \text{ min}) + \sum_{n=6}^{20} C(n) \cdot X(5 - n \times \Delta T) \cdot (.5 \text{ min})$$

$$1.3 \text{ ppm} = .081 \cdot X(5 - 5\Delta T) + 1.838 \text{ min}^{-1} \cdot (1.1 \text{ ppm}) \cdot (.5 \text{ min})$$

solving for $X(5 - 5\Delta T)$, it is found to be equal to 3.6 ppm.

Continuing the procedure, advancing time by ΔT , one again solves for $X(5 - 6\Delta T)$ but now $X(5 - 6\Delta T)$ is no longer equal to 1.1 ppm, but the previous value determined 3.6 ppm now becomes the value for $X(5 - 6\Delta T)$. This procedure is repeated, continuously indexing the determined values and solving for the single unknown concentration. The results of this process are shown in Figure 6 as curve II. The maximum recorded value of 14.3 ppm was quite different from the true maximum input value of approximately 34 ppm.

In conclusion, where air quality standards are based upon a timed exposure to certain air pollution levels which are believed to be injurious to health, it may be necessary to calibrate the instrument as described herein to determine the true atmospheric values. Once the transfer function is obtained, one can write a computer program which will give the output of the instrument for any arbitrary input, as was done here. By doing so, it is then possible to obtain a feel for the true nature of the input by examination of the recorded output of the instrument. When the data acquisition system is part of an air pollution alert system for a community, a computerized data transmission system can make these corrections which will aid the calling of alerts at the earliest possible moment.

Acknowledgment

We wish to thank the Bay Area Air Pollution Control District for its co-operation in this research and the use of the CO analyzer at the San Jose Air Monitoring Station in undertaking the analysis and calibration technique described in this paper. We also wish to thank Mr. Wayne Ott of the Office of Air Programs, U. S. Environmental Protection Agency for many valuable and helpful discussions and suggestions concerning this work.

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