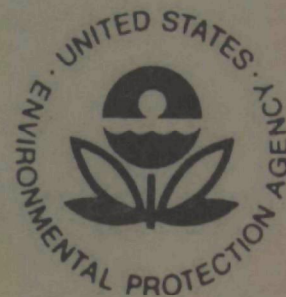


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February 1975

Environmental Monitoring Series

**COLLABORATIVE TEST
OF THE CONTINUOUS COLORIMETRIC
METHOD FOR MEASUREMENT
OF NITROGEN DIOXIDE IN AMBIENT AIR**



U.S. Environmental Protection Agency
Office of Research and Development
Washington, DC 20460

COLLABORATIVE TEST OF THE CONTINUOUS COLORIMETRIC METHOD FOR MEASUREMENT OF NITROGEN DIOXIDE IN AMBIENT AIR

by

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Prepared for

U. S. ENVIRONMENTAL PROTECTION AGENCY
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WASHINGTON, D. C. 20460

February 1975

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FOREWORD

This program, "Collaborative Testing of Methods for Measurement of NO₂ in Ambient Air," is being conducted under the Environmental Protection Agency (EPA) Contract No. 68-02-1363, which is Midwest Research Institute's (MRI's) Project No. 3823-C. The program is concerned with the evaluation of the following four methods with regard to their precision and accuracy:

1. Sodium-Arsenite,
2. TGS-ANSA,
3. Continuous-Colorimetric, and
4. Chemiluminescence.

The collaborative study covered by this report is of the continuous-colorimetric procedure, which is a tentative instrumental method. In summary, MRI's responsibility was to develop an NO₂ ambient-air sampling system for use with the four methods, provide the test site and facilities thereon where the collaborative tests would be conducted, select the collaborators with regard to the program, prepare a plan of test for the collaborative test, schedule testing, coordinate the test, retrieve field data and results from the collaborators, statistically analyze their results, and report its findings to EPA. The 10 collaborators who participated in the continuous-colorimetric collaborative test are:

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This report of test summarizes MRI's and the collaborators' activities. It describes the development of the NO₂, ambient-air sampling system, which covers the general concept of the system, design considerations, the design of the system and the system checkout. Following this, there are discussions on the test site, the selection of collaborators, the formal statistical design including the presentation of factors and parameters that were considered, the collaborators' field sampling at the test site, the collaborators' analysis results, MRI's statistical analyses of the collaborators' results, conclusions and recommendations. Appendices contain a copy of the tentative, continuous-colorimetric method, information on the permeation tubes prepared for this program by the National Bureau of Standards, written communiques with collaborators, instructions for collaborators, and MRI's field, operational, and data-log sheets.

These individuals named above with the collaborating organizations are acknowledged for their excellent work in the continuous-colorimetric collaborative test.

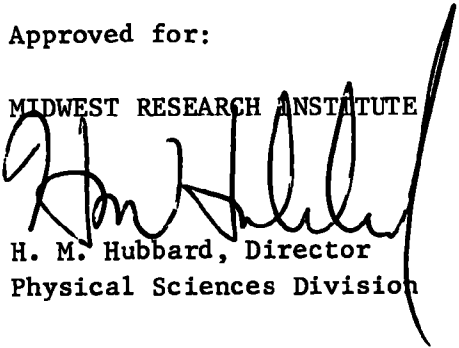
Special acknowledgements are made to the National Bureau of Standards and to Mr. Ernest E. Hughes and Dr. John K. Taylor of NBS who provided the NO₂ permeation tubes for this collaborative test; and to Dr. John B. Clements, Chief, Methods Standardization and Performance Evaluation Branch, National Environmental Research Center, Environmental Protection Agency, and

Mr. John H. Margeson, Government Project Officer, Methods Standardization and Performance Evaluation Branch, for their valuable suggestions in planning and design.

This MRI collaborative program is being conducted under the management and technical supervision of Mr. Paul C. Constant, Jr., Head, Environmental Measurements Section of MRI's Physical Sciences Division, who is the program manager. Those who contributed to this test are: development of the NO₂, ambient-air sampling system - Dr. Chatten Cowherd, Jr., Mr. Fred Bergman, Mr. Emile Baladi, and Mr. Wallace Yocum; experimental design and statistical analysis - Mr. Michael C. Sharp; and preparation and operation of test facilities - Dr. George W. Scheil, Mr. John LaShelle, Mr. Donald Cushing, and Mr. Edward Cartwright, Jr.

Approved for:

MIDWEST RESEARCH INSTITUTE



H. M. Hubbard, Director
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14 May 1975

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SUMMARY

A collaborative test was conducted by MRI in the Greater Kansas City Area during the week of 29 July to 2 August 1974. Ten collaborators participated in this test of the "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (Continuous-Colorimetric Procedure)." All collaborators sampled from the NO₂, ambient-air sampling system that was developed by Midwest Research Institute specifically for this collaborative test program. For each of the four test days, a different average NO₂ challenge (spike) level was used: 47.1, 102, 187, and 288 µg/m³. These levels were obtained from permeation tubes that were developed by the National Bureau of Standards.

The collaborators sampled from both the spiked and unspiked (ambient) lines of the NO₂, ambient-air sampling system, providing three sets of collaborators' results. The first set of data per 24-hr period (a test day) comprised results where all 10 collaborators sampled from the spiked line for approximately 14 hr (1800 to 0800). The second set of data per test day comprised results collected for approximately 3 hr and 20 min (0930 to 1250) by the collaborators when they were divided into two groups of five collaborators each, with one group sampling from the spiked line while the other group sampled from the unspiked line. The third set of data per test day would be collected for approximately 3 hr and 40 min (1250 to 1630) with the two groups interchanging sampling lines. These 12 sets of results were used for determining the bias and precision of the method.

In general, the relative measurement errors are stable over the range of NO₂ measured (approximately 50 to 400 µg/m³) and are not very large (approximately 6% true value). The collaborator-collaborator relative standard error is also fairly stable but larger ($\sigma_c \approx 12\%$ true value and $\sqrt{\sigma_e^2 + \sigma_c^2} \approx 13\%$ true value).

However, the bias is not stable with respect to NO₂ level, and is not consistent within collaborators either. Although the overall average bias is only about +10%, individual collaborators produced biases as great as +80% (at some levels). Thus, it is fair to say that the continuous-colorimetric method may produce extremely inaccurate readings in an unpredictable fashion (even though the overall average results are fairly accurate).

About half of the collaborators did achieve fairly stable results throughout the experiment. A subjective interpretation of this fact is that the continuous-colorimetric method is difficult to use, but will produce reliable results in some hands.

Two methods of estimating the lower detectable limit (LDL) were used. From the results of these calculations, it is reasonable to state that the LDL within a collaborator is probably $\leq 13 \mu\text{g}/\text{m}^3$, and the LDL from a set of collaborators $\leq 19 \mu\text{g}/\text{m}^3$.

INTRODUCTION

The Methods Standardization and Performance Evaluation Branch, National Environmental Research Center of the Environmental Protection Agency (EPA) is engaged in a program to evaluate four methods for measuring NO₂ in ambient air. Midwest Research Institute (MRI) is working for EPA under Contract No. 68-02-1363 to provide EPA data on the precision and bias of the following four methods: sodium-arsenite and TGS-ANSA, which are manual methods, and continuous-colorimetric and chemiluminescent, which are instrumental methods.

To achieve this objective, a collaborative testing program is being conducted that will assess interlaboratory as well as intralaboratory variation. In summary, MRI in the execution of this program, selects the collaborators, provides sampling locations and facilities thereon, orients the collaborators relative to the program, prepares a plan of test for each method tested, schedules testing, coordinates the collaborative tests, retrieves field data and results of the collaborators' chemical analyses of their field samples, statistically analyzes results received from the collaborators, and reports results of the program to EPA.

These activities were performed by MRI on its third test undertaken on the contract. The method investigated was the "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (Continuous-Colorimetric Procedure)," dated June 1974. A copy of the write-up of this method is given in Appendix A.

The program was initiated on 30 June 1973, and this collaborative test took place at MRI's field station in Kansas City, Missouri, during 29 July to 2 August 1974, with 10 different collaborators. The interim period was devoted to the preparation for this test and conduction of the first two collaborative tests, which covered the sodium-arsenite and TGS-ANSA procedures. A major task of the preparation activity was the development of a precision NO₂, ambient-air sampling system that could be housed indoors and be suitable for all four methods.

The two major phases of the test program were sampling and analysis. The sampling phase covered the field test where the collaborators obtained continuous analog NO₂ readings from the ambient-air sampling system. The analysis phase covered the calculations of average hourly NO₂ levels from the collaborators' recorder charts and the statistical analyses of their results by MRI. After the field test, the collaborators returned to their home laboratories where they analyzed their recorder charts and reported their results to MRI. Then MRI performed its statistical analysis and prepared this report of the continuous-colorimetric collaborative test.

This report covers the collaborative test of the tentative continuous-colorimetric method in the following order: the second section discusses the NO₂, ambient-air sampling system MRI developed for this program, covering the general concept of the system, the design considerations, the system design, and the system checkout. The third section describes the test site and the facilities that were used at this site. The fourth discusses how the collaborators were selected and who they are. The fifth section presents the factors and parameters that were considered in the formal experimental design as well as the formal design. The sixth section summarizes the test activities during the collaborative test. The seventh section discusses the analyses that were performed by the collaborators. The collaborators' results are presented in this section on MRI's test data. The eighth section discusses the statistical analysis of the collaborators' results and presents the results from this analysis, which includes biases and components of variance. The ninth and 10th sections present conclusions and recommendations, respectively. The appendices contain a copy of the tentative continuous-colorimetric method, data on the permeation tubes that were used as the source of NO₂ in the spiked section of the sampling system, information concerning the calibration of the venturi and dry-gas meter, copies of written communiques MRI had with the collaborators, a copy of the test instructions that were given to the collaborators, the NO₂, ambient-air sampling system's operational data, collaborators' comments, results of MRI's analyses, and additional statistical-analysis information.

NO₂, AMBIENT-AIR SAMPLING SYSTEM

GENERAL CONCEPT

Primary requirements for the evaluation of an ambient-air method by on-site collaborative testing are: (a) that all collaborators sample the same air, (b) that the samples be representative of ambient air, and (c) that the concentration of NO₂ in the samples be accurately known and controllable over the region of interest. The first requirement can be met by using a manifold system with each collaborator taking samples from a common stream of air. The second and third requirements are somewhat antagonistic to one another and not as easily solved.

Ideally, these requirements can be met by obtaining actual ambient samples over a wide range of concentration. However, this approach would require that each level be obtained at a different location with the additional requirement of fortuitous weather conditions, since weather conditions have a strong effect on ambient NO₂ concentrations. An additional problem with this approach is that no accepted primary reference method exists for the analysis of NO₂ in ambient air.

However, gravimetrically calibrated NO₂ permeation tubes are available which generate a stable, precise rate of release of high purity NO₂ over a period of a few years. By using a set of these tubes, different levels of NO₂ can be generated by adding the NO₂ from the permeation tubes to a stream of air with a known flow rate. Since the test conditions must relate to actual ambient-air conditions, the NO₂ from the permeation tube can be added as a known addition or spike to the ambient air stream. The method under test should show a difference in concentration between samples of ambient and spiked air equal to the spike level. To ensure that the NO₂ concentration of the spiked sample does not exceed the maximum level of interest--350 µg/m³--and to allow control of the spiked air NO₂ level over a reasonably broad range, the average ambient levels must be well below the lowest NO₂ concentration to be tested, in this case 50 µg/m³.

To achieve this, the following system is used: outdoor ambient air is drawn into the sampling system through a single tube, as shown in Figure 1. The air is divided downstream into two sections--spiked and unspiked. A controlled flow of ambient air at a specific value exists in the spiked section. A comparable ambient-air flow exists in the unspiked section, but the latter is uncontrolled. Temperature-controlled permeation tubes provide the source of NO_2 which is injected into the spiked section at a desired level. The NO_2 is then thoroughly mixed with the ambient air in a mixing unit--a diffuser. The mixture is then equilibrated before it reaches the sampling station where the collaborators sample from identical ports--subjected to the same gas flow (spiked plus ambient). A continuous monitor is attached to the spiked and unspiked sampling manifolds to monitor the integrity of the spike. The collaborators sample ambient air simultaneously at an identical sampling manifold that is at a similar location in the unspiked section. The gas in both sections is then exhausted to the outdoors.

DESIGN FACTORS

The design of the NO_2 , ambient-air sampling system was based on the following factors:

1. The flow rate of each of the four methods to be tested is approximately 0.2 liter/min, with a maximum of 1 liter/min for some of the instruments that would be used in the instrumental methods.
2. The sampling period of each instrumental method is preferably 24 hr, but could be less.
3. NO_2 permeation tubes whose rates are approximately 1 $\mu\text{g}/\text{min}$, which are furnished by the government, are the source for the spiked levels of NO_2 . These tubes are to be operated at $25.1^\circ\text{C} \pm 0.2^\circ\text{C}$.
4. The number of collaborators for each collaborative test is to be 10.
5. The NO_2 range of concern is 50 to 350 $\mu\text{g}/\text{m}^3$, which is representative of ambient conditions.
6. There are four different NO_2 spiked levels: high, low, and two medium. Each level is maintained throughout the run's period, within the accuracy of the system.
7. The test period is to be no more than 6 days, which is based upon the consensus of potential collaborators surveyed.
8. The overall NO_2 sampling system accuracy is to be 5% or better.
9. The flow control in the spiked section is to be 2% or better.

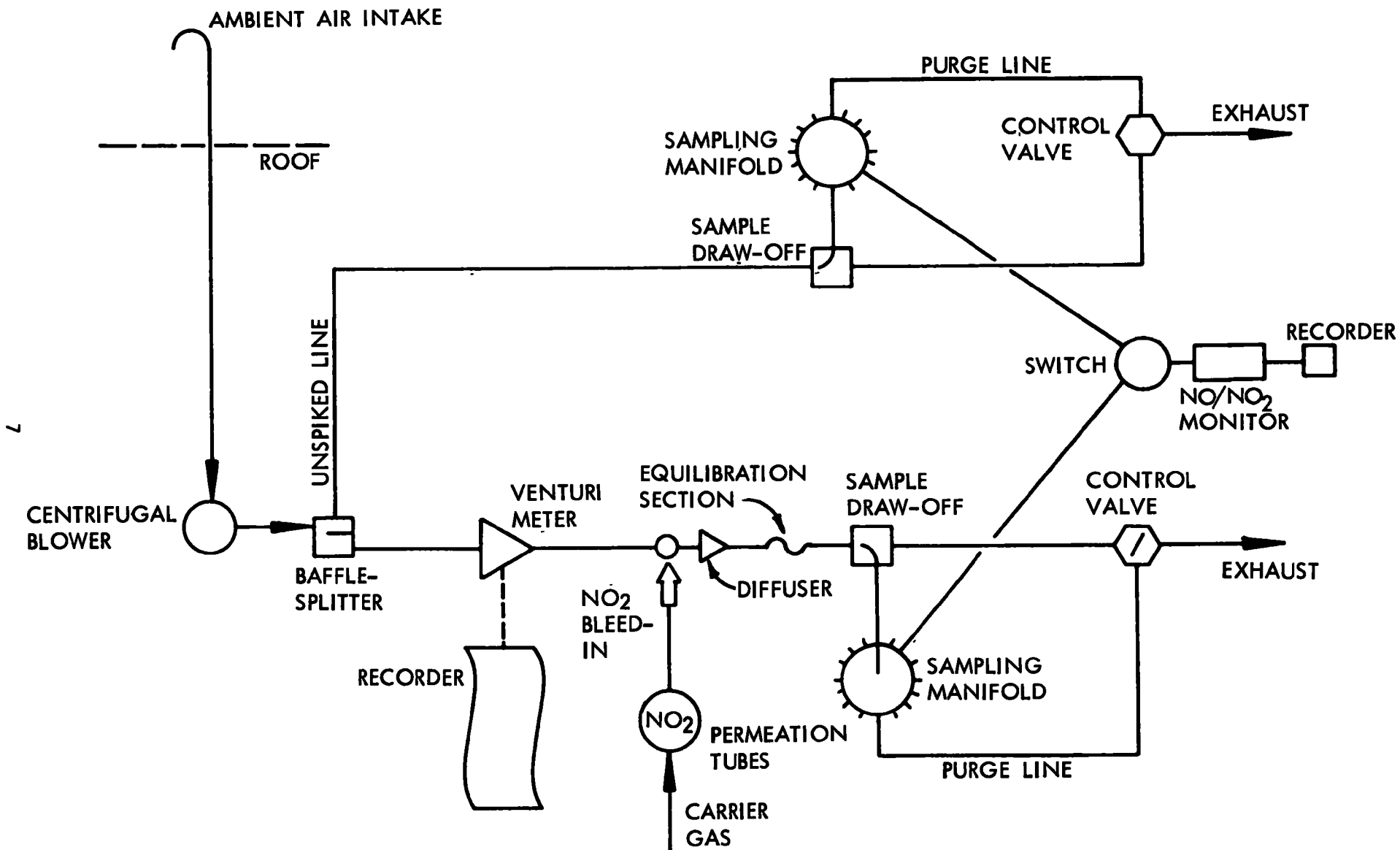


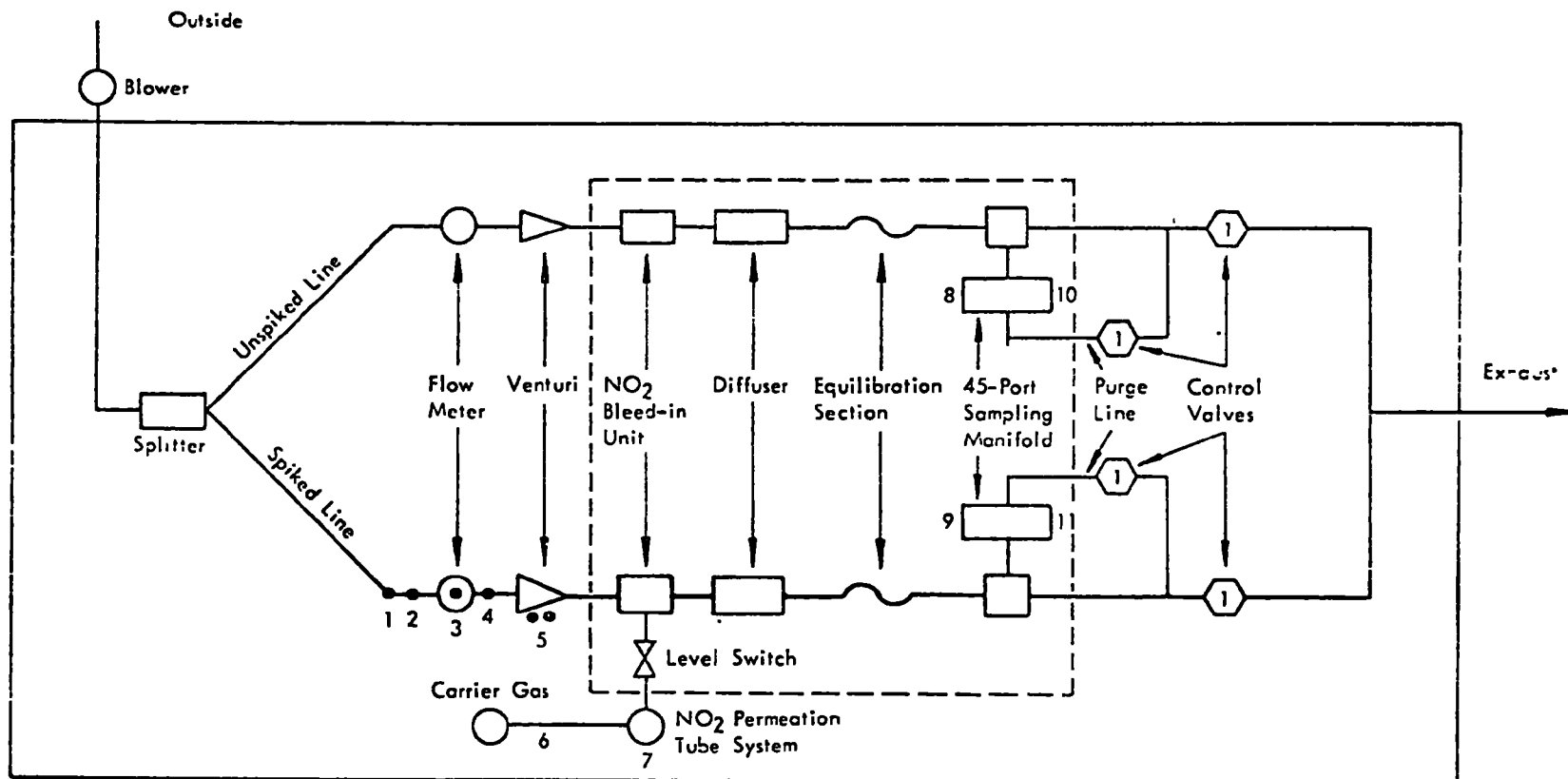
Figure 1. NO_2 , ambient-air sampling system concept.

10. Flow parameters of the spiked section are to be measured.
11. One NO₂/NO chemiluminescent device, switched between spiked and unspiked sampling manifolds (or stations), is to be used as a monitoring instrument.
12. Only one person from each collaborators' organization will be needed in the field for each method.
13. There is turbulent flow in the spiked section between the point of injection of the spiked levels of NO₂ and the diffuser to provide mixing of the spiked NO₂ with the ambient air. The diffuser insures proper mixing. Up to 20% of the stream in each section--spiked and ambient air--can be sampled to (a) insure that there is capacity in the main stream to provide each collaborator with his needs in case there is a problem with one or more collaborators drawing an excess amount, and (b) allow the quantity of spiked flow to be drawn from the center of the spiked line where there is assurance of equilibration. There is to be a minimum amount of adsorption of the spiked NO₂ on surfaces, from its source to and including the sampling manifold. By using Teflon or glass as the material in which the gases come in contact and by maintaining a high gas flow rate, which allows for extremely short residence times, adsorptivity of NO₂ on surfaces and reaction with water vapor and other losses are insignificant.
14. Each section--spiked and unspiked--is to be similar, including material and geometric aspects.
15. Each section is to be under positive pressure so that no unwanted air will be pulled into the system in case there was a leak.
16. Collaborator's equipment size, configuration and power requirements must be met.
17. Environmental effects on operation of sampling system must be considered.

SYSTEM DESIGN

The final design of the NO₂, ambient-air system is shown in a general schematic form in Figure 2. Annotated photographs of this operational system are given in Figure 3.

The input to the system is located outdoors about 2 m above ground level and approximately 30 m from the building. A valve at the intake of the 2-in. aluminum tubing provides resistance to the flow of ambient



Monitoring Points:

- | | |
|--|-------------------------------------|
| 1. Flow Temperature | 6. Carrier Gas Flow |
| 2. Flow Pressure at Input to Flow Meter | 7. NO ₂ Flow Temperature |
| 3. Ambient Air Flow | 8. Port Pressure |
| 4. Flow Temperature | 9. Port Pressure |
| 5. Pressure Drop of Venturi & Temperature of Pressure Transducer | 10. NO ₂ & NO |
| | 11. NO ₂ & NO |

Notes:

1. Component within Dashed Area Made of Teflon
2. Piping Out Side Dashed Area made of Aluminum
3. Venturis made of Stainless Steel
4. Spiked & Unspiked Lines Symmetric with Respect to Geometry & Material

Figure 2. Final design of the NO₂, ambient-air sampling system.

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air to keep the Model 8700 DMP "Tornado" blower at a stable revolutions per minute, and to serve as a gross flow control. A Variac inside the building serves as an operational flow control. A blower is located at the input end of the system to provide positive pressure in the system. It is located outdoors to keep out the intensive noise it generates and is housed as shown in Photographs 1 and 3 of Figure 3 to protect it from the elements.

The line from the blower to the splitter is 2-in. diameter, aluminum pipe. It is sufficiently long to serve as a trap for any excess moisture and to bring the ambient air to room temperature. The splitter is also made of aluminum. This splitter, shown in Figure 4, reduces large-scale turbulence from the blower and divides the ambient air stream between the spiked and unspiked 1-in. diameter, aluminum lines. A controlled flow goes to the venturi where the air flow in the spiked line is continuously measured and recorded. This flow is determined by the following equation:

$$\text{Flow in liters/min} = \frac{\text{method sampling rate (number of samples} \times \text{number of collaborators} + \text{monitor number} + \text{purge number})}{\text{percent flow drawn through sampling manifold}}$$

$$= \frac{0.2 \text{ liters/min} \times (4 \text{ samples} \times 10 \text{ collaborators} + 1 \text{ NO/NO}_2 \text{ monitor} + \text{purge-line flow})}{\text{percent flow drawn through sampling manifold}}$$

$$= \frac{0.2 (4 \times 10 + 1 + 4)}{0.15} \frac{9}{0.15} = 60$$

The monitor number and the purge number are flows attributable to the continuous monitor and the purge line of the system, respectively. The flow on each line--the spiked and the unspiked--is turbulent--Reynolds No. > 2,100 --with the Reynolds number being

$$R = \frac{Q}{\alpha \nu D} = \frac{Q \text{ liter/min} \times 1,000 \text{ cm}^3/\text{liter}}{0.785 \times 0.15 \text{ cm}^2/\text{sec} \times D \text{ sec} \times 60 \text{ sec/min}}$$

$$= \frac{1,000 Q}{7.065 D} = \frac{1,000 \times 60}{7.065 \times 2.1} = 4,000$$

Since the spiked and unspiked sections are identical except that the spiked section also contains the monitoring points 1, 2, 3, 4, and 5 identified in Figure 2 and the NO₂ permeation tube system, only the spiked section will be discussed.

From the splitter, the spiked line connects to a Singer AL-175 dry-gas meter, which is made by the American Meter Company. (See Photograph 9

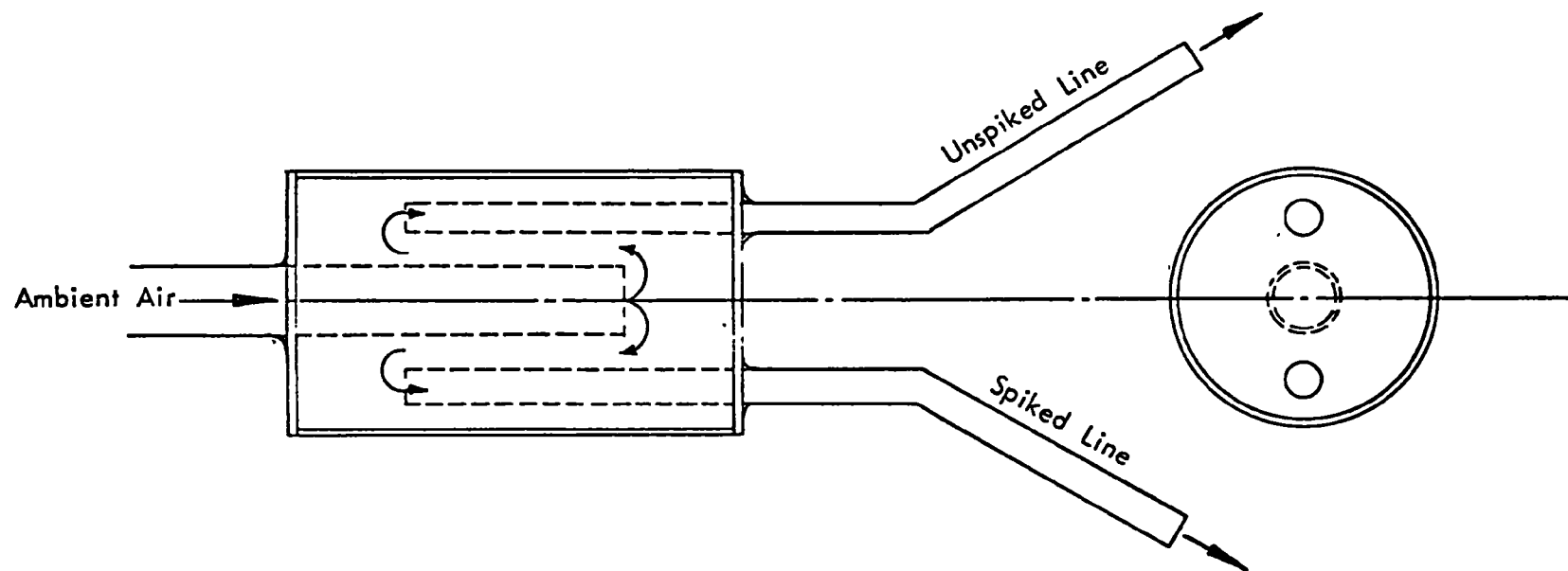


Figure 4. Ambient-air stream splitter.

of Figure 3.) This flow meter has a pressure drop of 10 mm of water and is temperature-compensated. Thus, only the gas pressure is measured to correct the flow readings to obtain the true flow rate of ambient air delivered during a test run. This flow rate is determined hourly by measuring the time required for a known quantity of air to pass through the meter.

The output of the flow meter is connected, as shown in Photographs 7 and 9 of Figure 3, to a stainless steel venturi, which was designed for a flow of 60 liters/min. This venturi is used as a general flow control device, and provides a continuous record of flow rate using a strain gage pressure transducer and thermocouples--see Point 5 of Figure 3(A). Both the pressure drop of the venturi and the temperature of the pressure transducer are recorded on analog recorders. Control of the flow rate is handled by monitoring the venturi pressure drop. When the value deviates from a reference value, 60 liters/min, the flow rate can be changed appropriately by making an appropriate adjustment of the Variac control to the blower.

The flow temperature measurement (Point 4 of Figure 3(A)) is actually the gas-flow temperature at the output of the gas meter and at the input to the venturi, since those two units are physically close together (about 12.5 cm apart). Tests have shown that the temperature at this point is identical with the temperature at the gas flow meter inlet. The gas temperature at this point is normally within 0.5°C of room temperature. This temperature measurement is used to obtain accurate gas-flow values.

To provide more accuracy, the thermocouples at Points 2 and 4 of Figure 3(A) were replaced for this test by a 0 to 50°C bimetallic dial thermometer that is located at Point 4 of Figure 3(A).

The output of the venturi is a few centimeters from the input of the NO₂ bleed-in unit as shown in Photograph 9 of Figure 3. These two units are connected by 1.0-in. diameter, aluminum tubing. From the input of the NO₂ bleed-in unit through the sampling manifold, the system is made of Teflon.

The NO₂ bleed-in unit, as shown in Figure 3(A) and Photographs 7 and 9 of Figure 3, receives ambient air from the venturi and a level of NO₂ (a spike) from the NO₂-permeation tube assembly (see Figures (A) and (B), and Photographs 8 a-c of Figure 3). Detailed photographs of this bleed-in unit are given in Figure 5. Photograph 1 of Figure 5 is a closeup showing the assembled Teflon unit with its metal holding/mounting plates. The gas stream, or ambient air, enters the opening to the right and passes through the unit, mixing with the spiked level of NO₂ which exits through the tapered smaller tubing shown as concentric to the output of the bleed-in unit at the left of Photograph 1 of Figure 5.

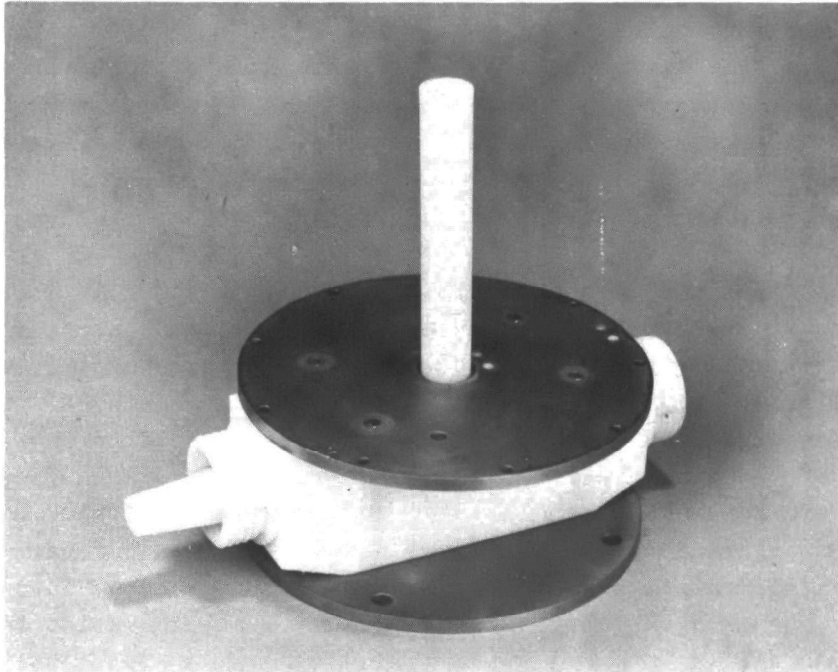


Photo 1 - Detail of NO₂ Bleed-In Unit with Vertical Tube from Permeation Assembly, Chamber with Central Tapered Pickup Tube and Stainless Steel Mounting Components.

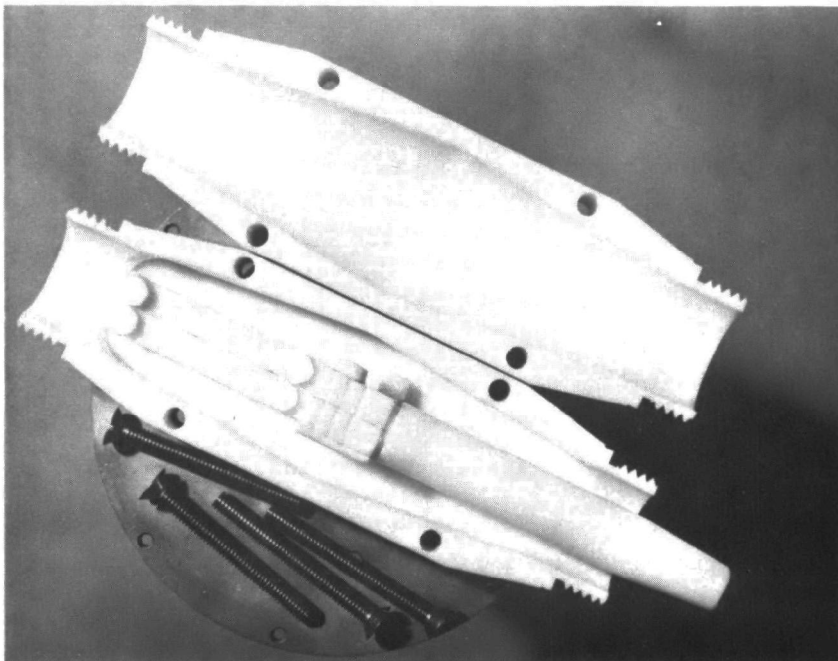


Photo 2 - Close-Up Showing Machined Chamber with Pickup for Bleed-In in Place.

Figure 5. Photographs of the NO₂ bleed-in unit--assembled and disassembled.

The vertical tube of this bleed-in unit accepts the NO₂ gas from the permeation tube assembly. This spiked gas flows downward through this tube, which is inside the unit (see Photograph 2 of Figure 5), and after a short run, mixes with the ambient air as stated before.

The NO₂-permeation system is shown in Figure 6 and Photograph 8 a-c of Figure 3. Details of the system are given in the captions of these photographs. The nitrogen carrier gas is used to flush the NO₂ into the system. It is passed through a charcoal and soda-lime scrubber before it is delivered to the NO₂ permeation tubes. Also, the flow is set by means of control valves and rotameters. This flow is monitored during system operation. The carrier gas is then fed into four separate branches to achieve different levels of NO₂. (More detail on the permeation tubes and their arrangements in the branches is given in Appendix B.) The NO₂ permeation tubes* are arranged in these four different branches to provide NO₂ spike levels of approximately 50, 100, 200, and 300 µg/m³. Branch 1 has four permeation tubes, Branch 2 has five permeation tubes, Branch 3 has two permeation tubes, and Branch 4 has two permeation tubes. An ASTM calibration thermometer (0.1°C or better accuracy) is an integral part of each permeation tube branch. Each set of permeation tubes is enclosed in a glass tube which has an inlet for the nitrogen carrier gas and an outlet for the nitrogen carrier gas/NO₂ mixture. These NO₂ permeation tube, enclosure units are immersed in a temperature-controlled, water bath for operating at 25.1°C. If the temperature of this bath were to vary more than 0.2°C, a correction would be made from the following relationship:

$$\log r = 0.034857 (273.12 + T) - 10.29198$$

where T = temperature in °C of the permeation tube environment, and

r = the permeation rate.

Flow meters of the permeation tube assembly that measures the nitrogen flow were calibrated by the manufacturer to 1% accuracy. Thermometers that were used to measure the gas temperature in the permeation tube holders are ASTM type that are accurate to within 0.1°C. The permeation tubes used were calibrated by the National Bureau of Standards and checked by EPA. (See Appendix B.) The entire permeation assembly from the tube holders to the pickup fitting, where the spiked gas enters the main gas stream, was checked for leaks with Snoop and found to be airtight.

* "Operation Characteristics of NO₂ Permeation Device," by Harry L. Rook, Ernie E. Hughes of NBS, Washington, D.C., and Robert S. Fuerst and John Margeson of EPA, Research Triangle Park, North Carolina. A paper presented before the Division of Environmental Chemistry, American Chemical Society, Los Angeles, California, 31 March to 5 April 1974.

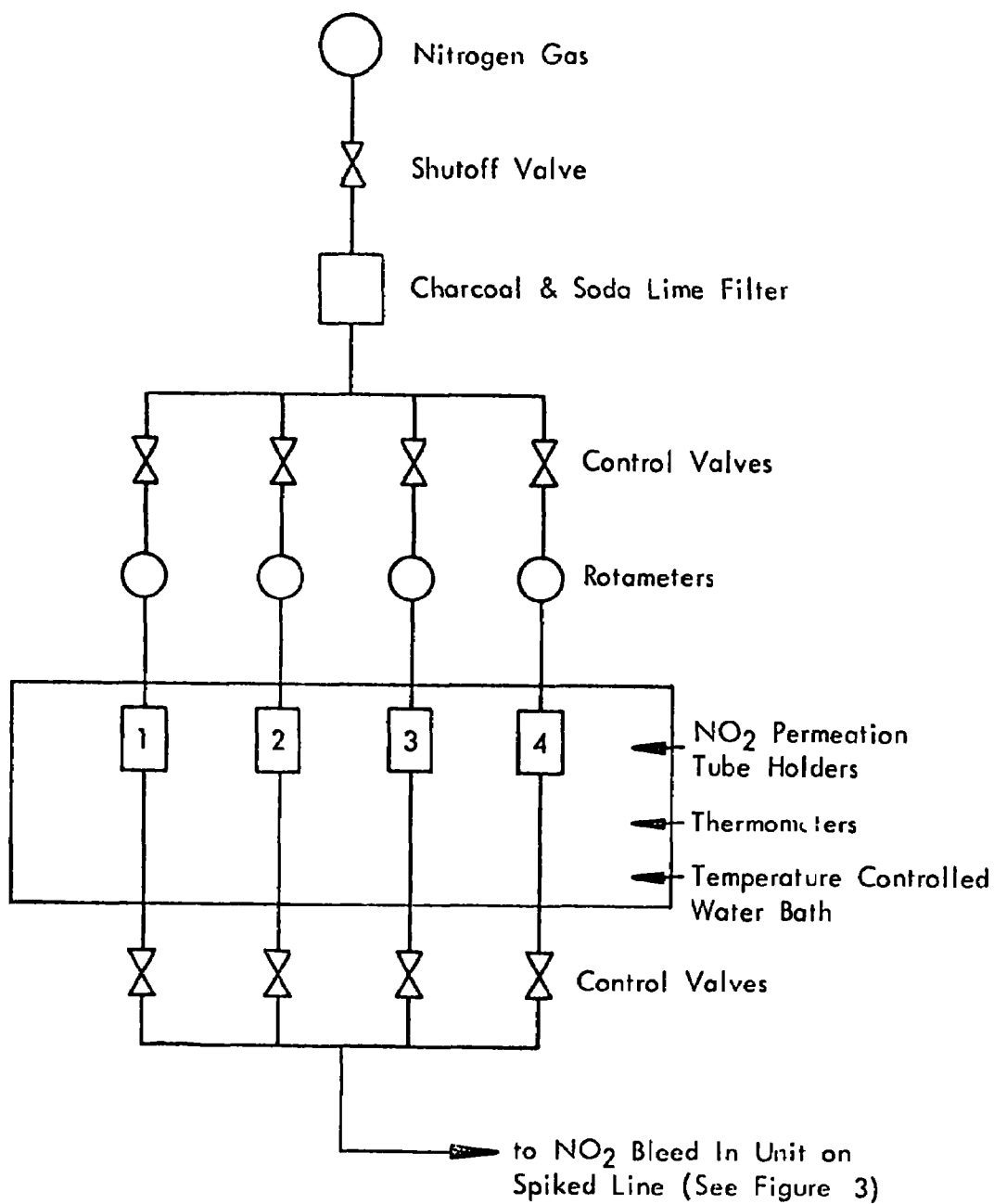


Figure 6. Schematic drawing of the NO₂ permeation tube assembly.

The ambient air and the NO₂ spike flow from the bleed-in unit to the diffuser where they are well mixed. The diffuser is a few centimeters downstream from the bleed-in unit, as shown in Photograph 9 of Figure 3. At the diffuser, shown schematically and in the photograph in Figure 7, the gases enter the diffuser through the Teflon tubing (Section A of the schematic drawing of Figure 6), pass into the spiraled tube and through its angled holes into the space outside the tube. The flow continues through the holes in the prescreen block, Item D of the schematic, and then through a series of Teflon screens, Item E.

The homogeneous mixture passes through an equilibration section that is Teflon tubing 1.0 m long. This section of tubing provides the final equilibrated concentration. This tubing is connected to the input of the sampling manifold. (See Photographs 10 and 11 of Figure 3.)

The 45-port sampling manifold is constructed of Teflon except for its metal plates which are entirely external. Photographs 1 to 3 of Figure 8, which show external and internal views of the sampling manifold and a schematic drawing, describe the operation of the manifold. The stream of the homogeneous mixture of ambient air and a spiked level of NO₂ flows through the bottom portion of the manifold, into the exhaust line. Section A of the manifold is in the pickup tube through which flows the total volume of gas sampled by the collaborators. The inlet to this pickup tube is located such that this volume is drawn from the central portion of the main stream. The sampled volume flows past a mixing impeller (B) and then into the main chamber of (C) of the manifold. In this chamber, the flow is spread evenly to the 45 symmetrically located exit channels (D). The gas in the main chamber that is not drawn through the exit channels to the collaborator ports flows out the exhaust duct or purge line which has a control valve. Both exhaust lines from the manifold join downstream to form a common exhaust tube, which also contains a flow control valve.

One port of each sampling manifold is used to monitor the pressure in the sampling manifold to determine if it remains positive (see schematic drawing of Figure 3). Another port of each manifold is used to monitor the NO₂ and NO levels being sampled by the collaborators and to monitor the integrity of spike during test. A Bendix Model 8101 B chemiluminescence NO-NO₂-NO_x analyzer is used for this and is switched between the spiked and unspiked manifolds. (See Photograph 12 of Figure 3.)

SYSTEM CHECKOUT

Readyng the system for the collaborative test comprised three principal areas of activity: (a) determination of levels of NO and NO₂, both ambient and inside the building; (b) checkout of the sampling system, including monitoring devices and test instrumentation; and (c) checkout of the sampling system as an operational system. These three areas are discussed below.

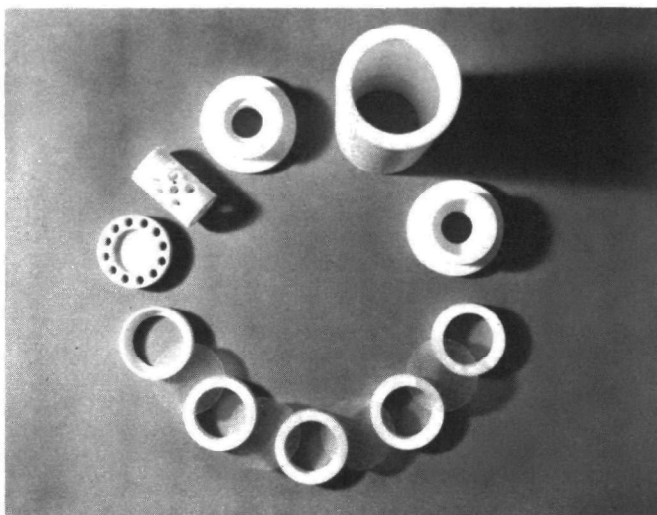


Photo 1 - Top View Diffuser Components: Housing, End Sections, Spiraler Tube, Teflon Screens, Retaining Rings.

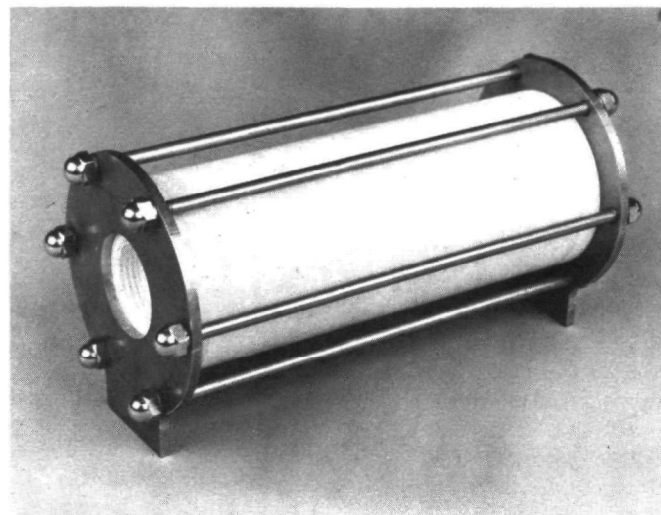
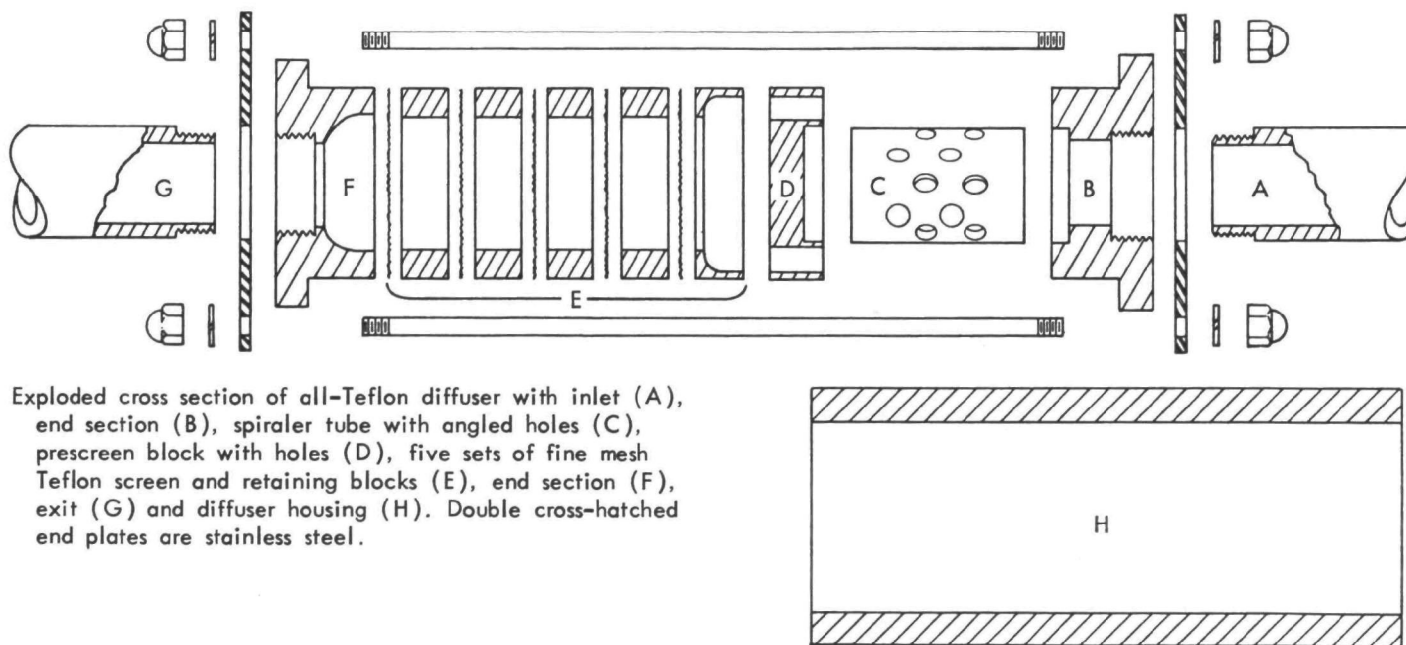


Photo 2 - External View of Diffuser.



Exploded cross section of all-Teflon diffuser with inlet (A), end section (B), spiraler tube with angled holes (C), prescreen block with holes (D), five sets of fine mesh Teflon screen and retaining blocks (E), end section (F), exit (G) and diffuser housing (H). Double cross-hatched end plates are stainless steel.

Figure 7. Schematic drawing and photographs of the diffuser.

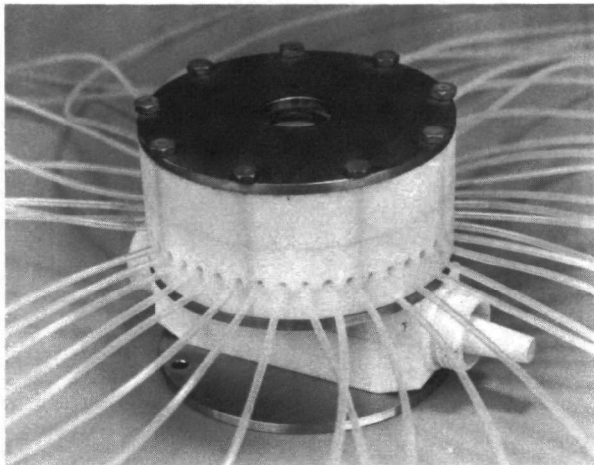


Photo 1 - Sampling Manifold External View.

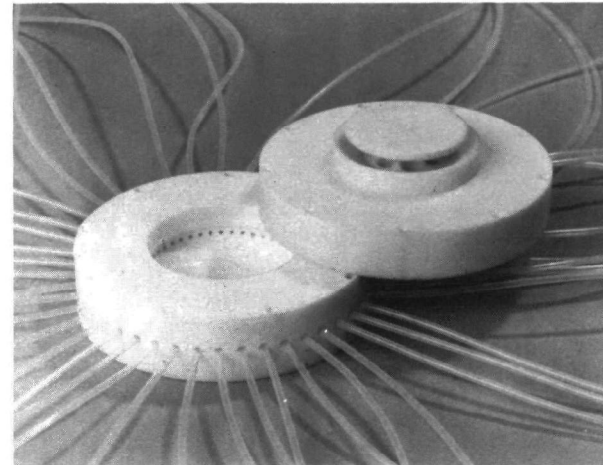
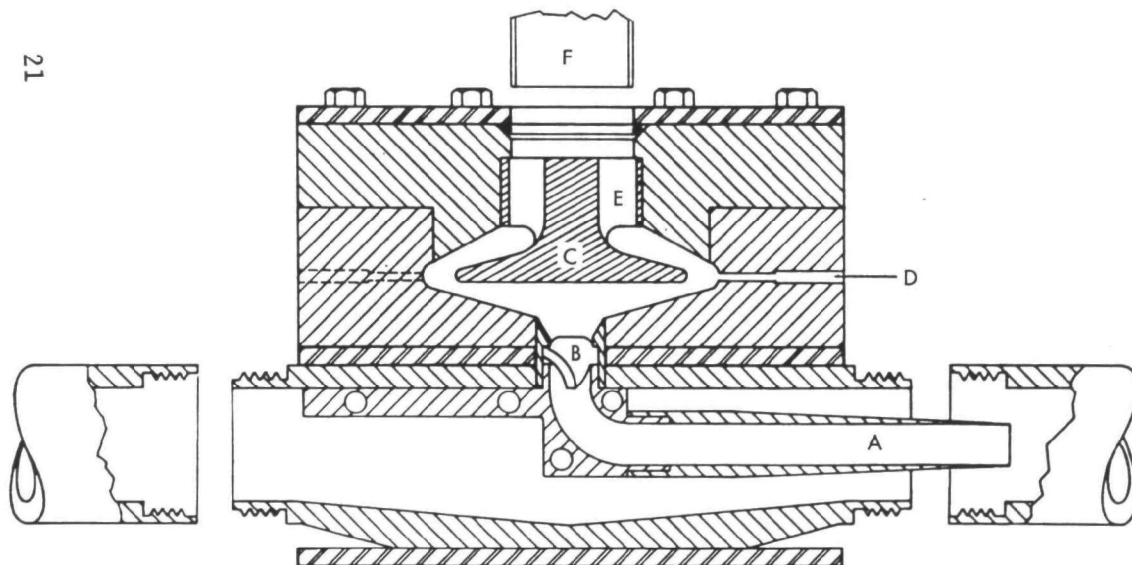


Photo 2 - Internal View (Right Component is Inverted in this Photo).



Cross section of all-TFE Teflon manifold with pickup tube (A), mixing impeller (B), main chamber flow spreader (C), exits to collaborator ports (D), channel to exhaust manifold (E), and manifold exhaust duct (F). Gas not captured by pickup assembly exhausts at left side of manifold base. Double cross-hatched assembly plates at top, middle, and bottom are stainless steel.

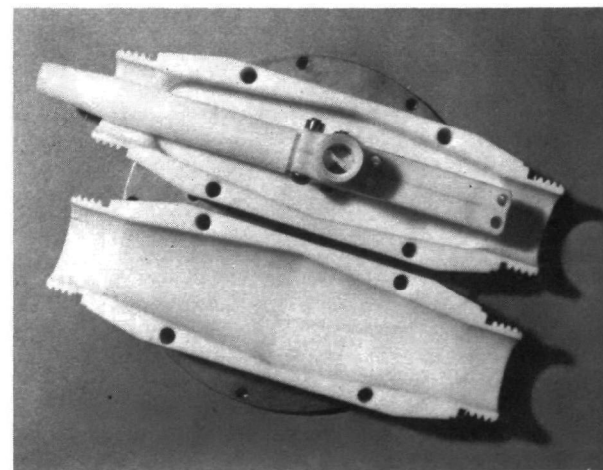


Photo 3 - Internal View of Manifold Pickup Section Showing Flow-Spiraling Impeller.

Figure 8. Schematic drawing and photographs of the sampling manifold.

Ambient Levels of NO and NO₂

Ambient levels of nitrogen oxides at the test site were generally low, but there were considerable variations at these levels. Since the test site is located in a rural area south of Kansas City where there is very little industry, the primary factors that influence NO_x levels at the site are wind speed and wind direction.

During tests of NO_x levels using MRI's Bendix Model 8101 B chemiluminescence NO-NO₂-NO_x analyzer for 24-hr monitoring, the lowest levels were found when the wind was from the south. Both NO and NO₂ seldom exceed 20 µg/m³. Periods of more than 1-hr duration were measured when readings were indistinguishable from the purified zero gas used to calibrate the analyzer.

With northerly winds, NO₂ levels were generally between 30 and 50 µg/m³ and NO levels were approximately 10 µg/m³. As expected, the ambient levels followed an inverse relation with respect to wind speed. The highest daily readings were coincident with the morning and evening rush hours. These peak levels generally began at about 7:00 a.m. and again at 5:00 p.m. and lasted between 2 to 4 hr.

The highest recorded levels of NO occurred under calm wind conditions when the light vehicular traffic in the vicinity of the test station generated levels in excess of 100 µg/m³. NO levels did not exceed NO₂ levels at this site.

Over a 24-hr period, average NO₂ levels were 10 to 50 µg/m³, and NO levels were of the order 10 to 20 µg/m³. During any 24-hr period, maximum NO₂ levels were generally several times higher than the minimum levels. Thus, while NO₂ levels at the test site are lower than those at urban, industrial locations, the NO₂ levels do exhibit the variability found under normal ambient conditions. Indoor readings were similar but did not show the sudden changes often found when monitoring outdoor levels.

Subsystems and Units

The venturi and dry-gas meter were calibrated using a 1.0 ft³/min wet-test meter. Information concerning the calibration is given in Appendix C. The entire system was prepared for the test by bringing all components to normal operating conditions several days prior to the test and running the system continuously in this mode until the beginning of

the test. Water addition to the constant-temperature bath was the only maintenance required. The temperature variation of the permeation-tube bath during this time was less than 0.1°C. A check of NO_x levels in the cylinders of prepurified nitrogen carrier gas found no NO₂ and 40 µg/m³ NO.

The Bendix NO_x Analyzer was checked at MRI by a Bendix field representative. The difference in spiked and unspiked readings of the Bendix analyzer agreed within 10% of the calculated spike levels at all four levels used for the test. The instrument was stable and reliable when operated continuously at the levels found during normal testing. Checks with calibration gases reveal that the catalytic convertor efficiency does fall off sharply above 400 µg/m³.

The symmetry of the sampling ports was checked in two ways. The primary way was that the pressure drop at each port was measured under the normal load of 200 cc/min. This test showed that all ports gave a pressure drop of 1.5 cm of water \pm 0.5 cm. Such a pressure drop should have no effect on normal sample flows and the flow rate from the ports should be identical to that obtained by pulling free room air into the sampling trains. However, since some of the analyzers used for this test required flow rates on the order of 1.0 liter/min, 10 larger diameter Teflon tube connections were provided on each manifold. These larger diameter Teflon lines were capable of supplying more than 2.0 liters/min without developing a pressure drop of 1.5 cm of water.

A second way was to connect the NO₂ monitor to ports of the spiked and unspiked sampling manifolds and measure the level of NO₂ in micrograms per cubic meter. This was done in two ways: the system under a load, e.g., a spiked level of approximately 350 µg/m³; and an unloaded condition where just ambient air was passed through each section--spiked and unspiked--of the NO₂ sampling system. In both cases, the NO₂ monitor showed no variation between four ports spaced equally around the manifold.

System Operation

Identical materials and dimensions are used on the spiked and unspiked sections of the NO₂ sampling system. Handling and treatment of all components were also identical.

Flow rates of the spiked and unspiked sides were within 10% of each other with all dampers open. In normal operation, the exhaust dampers are adjusted to give a positive pressure of 2 to 4 mm water at the sample manifolds. Once set, this pressure is stable.

The rise and fall times to equilibrium in response to changes in a spike level were checked. Rise time was less than 15 min and fall time was less than 5 min (when permeation tubes were disconnected). The fall time is essentially that of the analyzer response time, allowing for the purge time of the sample lines. The rise time is longer than the fall time because of the increased pressure against which the carrier gas stream must work when a set of permeation tubes are connected. Some flow reversal in the permeation-tube holders occurs after connection.

Since the response times were essentially limited by flow rates and instrument response, no observable adsorption effects were noted. Checks of NO_x levels found at the sampling ports agreed, within normal accuracy limits, with those measured outside the building. At the 50 µg/m³ level both readings were within 5 µg/m³ (0.5% of full scale), which is within the accuracy of the monitoring instrument. Thus, the unspiked samples at the sample ports accurately reflect ambient levels and the sampling system may be considered to be inert with respect to NO₂.

TEST SITE

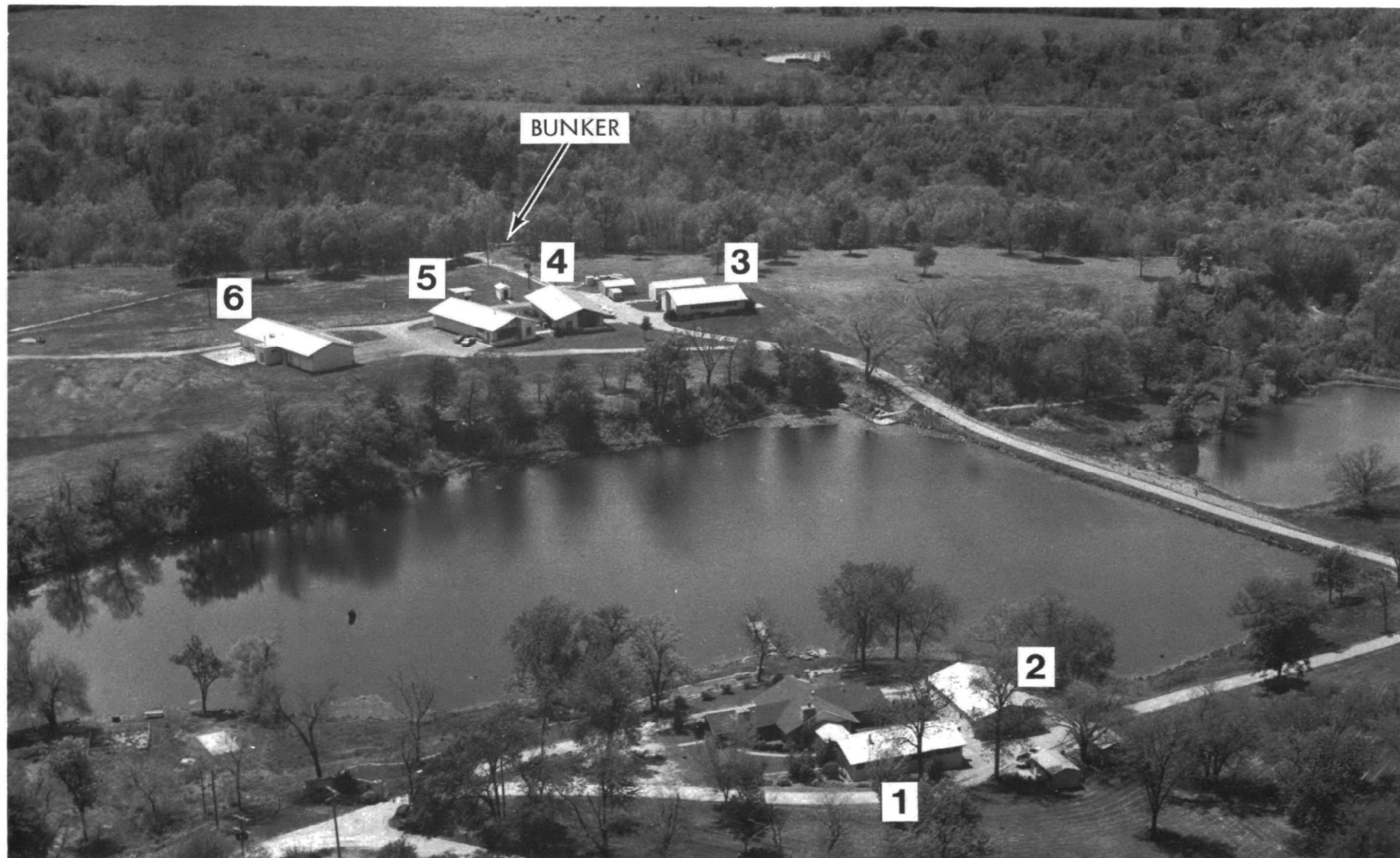
The general criteria one would use in selecting a site include the ambient level of NO₂ and variation thereof, general meteorological and climatological conditions, work facilities for the collaborators (adequate space, facilities, housing, etc.), cooperation of the organization furnishing the site, logistic aspects, and local lodging accommodations.

The levels of NO₂ required are those representative of ambient NO₂ conditions, which are in the range of a few micrograms per cubic meter to 350 µg/m³. These levels could be achieved at one site with a low level of NO₂ by spiking the ambient air with various levels of NO₂ in a manifold sampling system.

MRI's field station (see Figure 9) which is located in a rural area south of Kansas City, meets all the criteria and was selected as the test site. The NO₂, ambient-air sampling station is housed in Building 3 shown in Figure 9. The input to the sampling system is located outside the building near the roadway (see Photograph 3 of Figure 3).

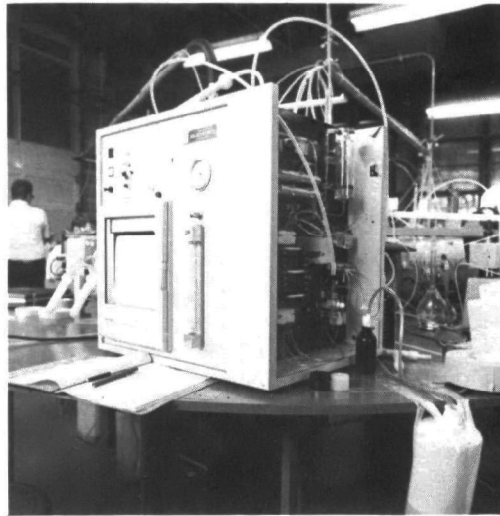
These test facilities are described in conjunction with the sampling system. Photographs of the facilities are given in Figure 10. Photograph 3 shows the circular tables that house the sampling manifolds and the collaborators' sampling trains. Each table--spiked and unspiked--has a multiplicity of AC power receptacles, with each collaborator having its own branch of outlets. Each branch has its own circuit breaker and branch indicator. This arrangement is to protect other collaborators in case one collaborator has a power failure due to faulty equipment.

Photographs 1 and 2 of Figure 10 give close-up views of some of the collaborators' trains positioned in their table areas (see Figure 11). Since each collaborator had only one instrument, Teflon or polypropylene tubing was run through the 2-in. pipe, which spanned the two test tables, to the other manifold. This allowed the instruments to remain in one place during tests and yet sample from within the spiked or unspiked line by singly switching lines.

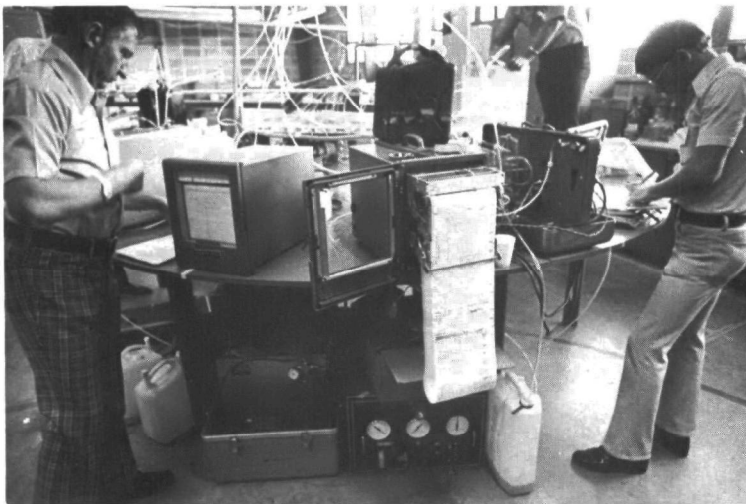


DERAMUS FIELD STATION

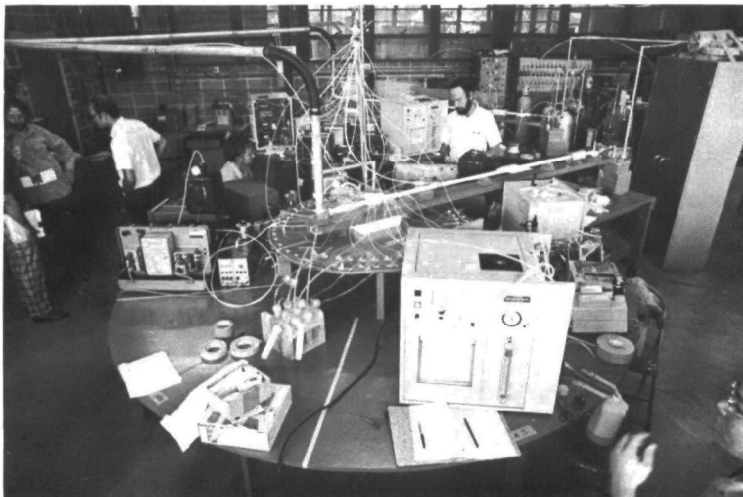
Figure 9. Collaborative test site: MRI's field station.



Photograph 1. A collaborator's instrument in operation

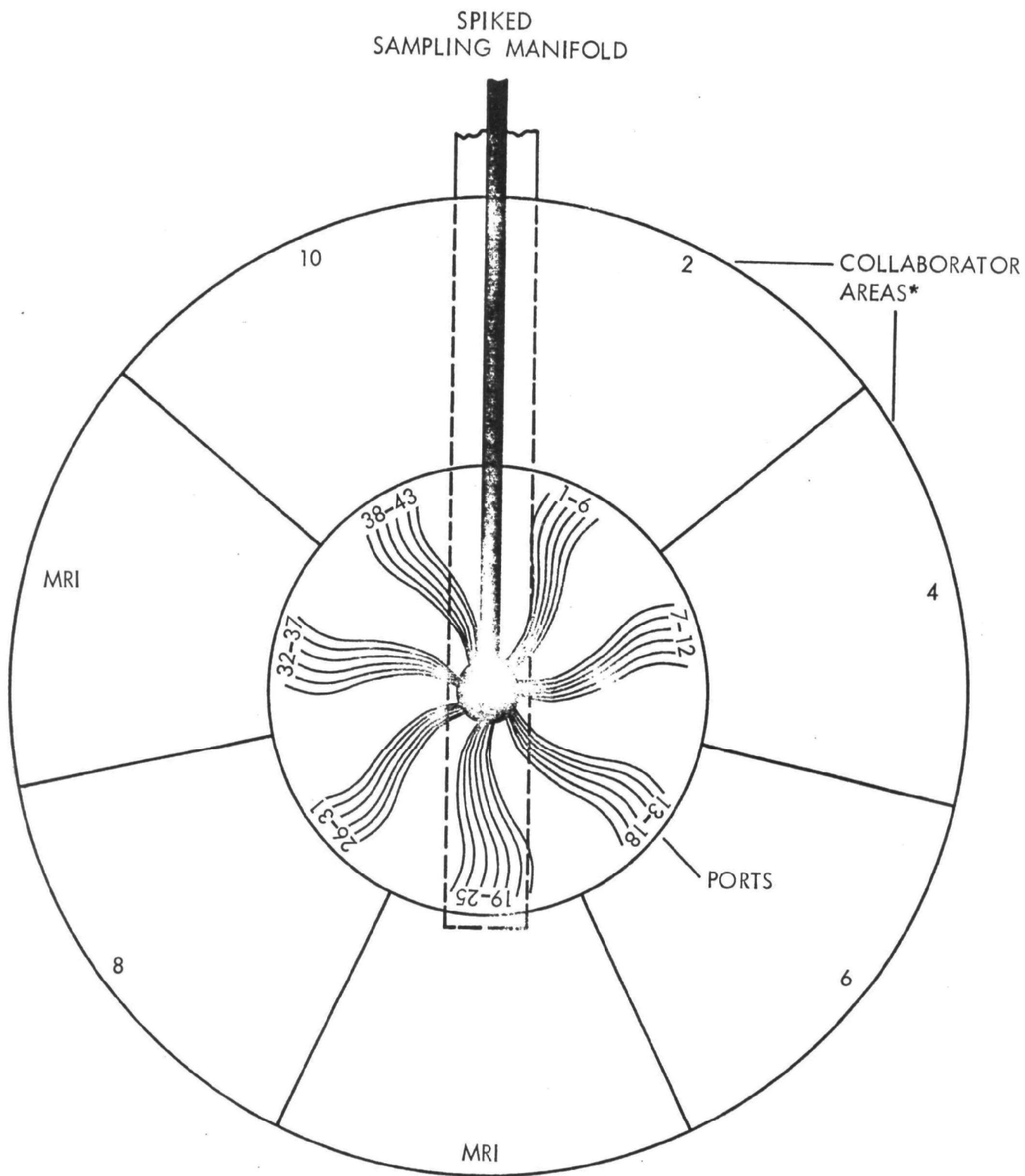


Photograph 2. Collaborator preparing for a test



Photograph 3. Unspiked sampling line and area in foreground

Figure 10. Test facilities and collaborators instruments.



* Unspiked manifold layout similar (see Appendix F).

Figure 11. Collaborators' sampling areas at the test site.

The windows on the north side of the building were boarded to keep electromagnetic radiation from entering the building. With this blockage and a temperature control system in the building, the 25.1°C permeation bath was able to be maintained at that temperature throughout the four 24-hr runs with no detectable deviation from the 25.1°C temperature, except for a few hours when the deviation was 0.1°C.

SELECTION OF COLLABORATORS

A principal activity was to compile a list of potential collaborators and from this list select 10 to perform the testing according to the tentative continuous-colorimetric method. Information was obtained from EPA (names and addresses of 150 organizations) and from MRI's files to compile a list of nearly 200 potential collaborators .

A letter was sent to 162 organizations seeking their desire to participate as a volunteer collaborator on this test and evaluation program. Attached to this letter was a "Collaborator Form" to be completed which surveyed their experience with the four methods, methods they had used, equipment they could make available for the tests, acceptable length of test period, etc. A second letter was sent to those who expressed interest in the continuous-colorimetric method after a test date was selected. A copy of these letters and the collaborator form are given in Appendix D.

A majority of the responses indicated the desire that a test period for a method be no more than 6 days.

Nine organizations* were selected for the continuous-colorimetric collaborative test from those organizations that responded in the affirmative to participate in the test. The selection was based upon the following criteria:

1. Willingness to participate on a volunteer basis .
2. Technical capabilities .
3. Related past experience .
4. Availability .

* One organization provided two collaborators, each of which had his own equipment and worked entirely independent of one another.

5. Ability to furnish sampling equipment, instruments, and materials required to perform the test strictly according to the method ; and

6. Type of organization (industrial, educational, governmental--local, state, federal--etc.).

The information needed to make the selection based on the above criteria was obtained from the collaborator forms that were returned, and from subsequent telephone conversations with the candidate collaborators.

The nine organizations selected as collaborators for the continuous-colorimetric collaborative test were:

Michigan Department of
Natural Resources
Stevens T. Mason Building
Lansing, Michigan 48926
(Mr. Ken Smith)

Kennecott Copper Corporation
P.O. Box 11299
Salt Lake City, Utah 84111
(Mr. Lynn Hutchinson)

Air Pollution Control District
of Jefferson County
400 Reynolds Building
2500 South Third Street
Louisville, Kentucky 40208
(Mr. Harold Davis)
(Mr. Cole McKinney)

Kansas City Air Pollution
Control Laboratory
Two Northeast 32nd Street
Kansas City, Missouri 64116
(Mr. Glenn Smith)

Air Pollution Control District
County of Los Angeles
434 South San Pedro Street
Los Angeles, California 90013
(Mr. John Higuchi)

New Jersey Department of
Environmental Protection
Division of Environmental Quality
John Fitch Plaza
P.O. Box 2807
Trenton, New Jersey 08625
(Mr. Norman J. Lewis)

Nassau County Department of
Health
Division of Laboratories and
Research
209 Main Street
Hemstead, New York 11550
(Mr. Cleveland Dodge)

State of Utah
Department of Social Services
Division of Health
44 Medical Drive
Salt Lake City, Utah 84113
(Mr. Rolf E. Doebbeling)

Wayne County Department of
Health
Air Pollution Control Division
1311 East Jefferson
Detroit, Michigan 48207
(Mr. Larry Saad)

These organizations will be referred to as Collaborators A through J, without specifying which is A, B, etc., to allow the organization data to remain anonymous.

STATISTICAL DESIGN

GENERAL CONSIDERATIONS AND COMMENTS

The purpose of this collaborative test was to determine the precision and bias of the continuous-colorimetric method. A major element of the collaborative test was to have an experimental design that would allow this purpose to be met. Considerations that formed the bases of this design, which is given later in this section in a formal manner, are:

1. Challenge (spike) levels of NO₂,
2. Ambient levels of NO₂,
3. True values of NO₂,
4. Sampling time of a run,
5. Test period of the method,
6. Number of collaborators,
7. Number of samples per run,
8. Interferences,
9. Adsorptivity,
10. Sampling ports, and
11. Instrumentation.

Challenge spike level of NO₂ is an experimental design variate. Four levels of challenge were selected, based upon the normal range of

values found in ambient air on a 24-hr average basis: one low level on the order of $50 \mu\text{g}/\text{m}^3$; two medium levels, one near $100 \mu\text{g}/\text{m}^3$ and the second near $200 \mu\text{g}/\text{m}^3$; and one high level of approximately $300 \mu\text{g}/\text{m}^3$. A challenge level should be steady state, or continuous at a specific level, plus or minus acceptable deviations--less than $\pm 2\%$.

Ambient levels should be lower than the lowest challenge (spike) level (approximately $50 \mu\text{g}/\text{m}^3$). Since the ambient levels are the actual ambient levels of NO_2 at the test site, those levels present during the time of testing may vary from this criteria. (See page 22.) The ambient levels will be mixed with the challenge levels to provide the spiked challenges. There will be just ambient challenges which are identical with the ambient portion of the spiked challenges. The collaborators will sample both spiked and ambient challenges (not simultaneously--see Appendix D).

For a run, the true value of NO_2 sampled by the collaborators will be taken as the NO_2 spiked level generated by the permeation tube assembly plus the average value of the ambient challenges sampled at the same time. Since not all collaborators participate in estimating this "true" value, a potential bias is created that adds the overall error in the analysis.

Ten collaborators were deemed to be sufficient to obtain a cross-section of the population of the type organizations that would be involved in sampling NO_2 , be within acceptable project costs, and provide statistical significance with the results.

Adsorptivity is of concern because of the possibility of error in the NO_2 level received by the collaborators' sampling devices in contrast to the known level of the challenge--from both the standpoints of increasing and decreasing the challenge level from run to run. Teflon material was used from the NO_2 bleed-in through the sampling manifold to minimize if not eliminate the adsorptivity factor. For further assurance, prior to commencing a run, the challenge could be run for a sufficiently long period so that all surfaces exposed would have reached a state of equilibrium with the new concentration. Both aspects were covered; Teflon was used in the construction and sufficiently long challenges were made to the system prior to commencing a run.

The port-to-port effect did not need to be incorporated in the experimental design because results of the evaluation of the NO_2 , ambient-air sampling system indicated that all ports were identical.

The major considerations with regard to instrumentation for the continuous-colorimetric collaborative test were: (a) MRI would only instruct the collaborators that they are to use the sampling equipment

and calibration specified in the method writeup, and (b) MRI's monitoring instrumentation and test instrumentation used in the calculation of the NO_2 , ambient-air system was sufficiently reliable and accurate. In both cases, all requirements were met.

THE DESIGN

Since some spiked readings were being taken throughout the test, but ambient readings were only sometimes obtained, there were two experimental designs used.

One statistical model applies to all the spiked readings, but does not incorporate any ambient observations. In this analysis then, all 10 collaborators are used to estimate precisions.

This analysis of variance model is:

$$X_{ijkl} = \mu C_i + t_j + L_k + e_{l(ijk)} ,$$

where μ = Overall mean,

C_i = i^{th} collaborator, $i = 1, \dots, 10$,

t_j = j^{th} hour, $j = 1, \dots, 20$,

L_k = K^{th} NO_2 level, $K = 1, \dots, 4$, and

$e_{l(ijk)}$ = Measurement error in l^{th} reading in ijk^{th} cell,
 $l = 1$ for every ijk .

Since the NO_2 level may change from hour to hour, there are no replicates in this framework ($l = 1$ always). Also, some cells are missing altogether (because sometimes a collaborator was on the ambient line and did not get a spiked reading). Each collaborator measured the spiked line only (a maximum of) 17 out of the 20 experimental hours. So all effects have to be "adjusted" for this sample imbalance.

Therefore, the general analysis of variance was performed.* (In practice, four such analyses were performed (one per level) because it turned out that the repeatability of the method depended on the NO₂ level.)

The second experimental design model describes the data set of 6 hr/run when both ambient and spiked readings were taken (by different collaborators, of course). Since the hourly variation in ambient NO₂ is significant, a "true" value was constructed for each of the 6 hr (per level). That is, for each hour, the true value was estimated as the spiked NO₂ amount plus the average ambient reading in that hour. An individual response is a bias; i.e., the collaborator's reading minus the true value. Thus, the data framework becomes three responses per collaborator** per level. Thus, the bias estimates are based on five collaborators on the spiked line and the other five collaborators on ambient. Since these groups of five may be separated in their means, a potential error is introduced into the bias determination.

* See Appendix E for a discussion of this general analysis.

** Collaborator G not included.

COLLABORATORS' FIELD SAMPLING

The collaborative test took place at the MRI Deramus Field Station during 29 July to 2 August 1974. The 10 collaborators (see Figure 12), started the test at 0830, 29 July, with an orientation. The NO₂, ambient-air sampling system they used was shown and explained to them. The written instructions that comprise Appendix F were given to and discussed with the collaborators. After this orientation period the collaborators set up their equipment in preparation for the first run. The actual schedule of the four runs that took place is given in Table 1. All 10 collaborators cleared the site by 1900, Friday evening, 2 August.

All collaborators sampled from the spiked line during the A runs. During the B and C runs, the collaborators were divided into two groups with one group sampling on the spiked line while the other group sampled from the unspiked line. At 1250 each day all collaborators then switched sample manifolds--those that had been on spiked went to unspiked and vice versa. Also, the group that was on the spiked line for Run 1B changed to the unspiked line for 2B, so that each group began every other B + C run set on the same manifold.

During the test, MRI personnel observed that all collaborators followed the sampling procedures given in the method write-up. All collaborators made a dynamic calibration and established a static span point at their home laboratories prior to the test for reference at the site. They used a static calibration check during the test period. The calibration checks were made during 0800 to 0930 and 1630 to 1800 each day. Each collaborator also supplied his own chemicals and prepared his own absorbing solution and standards to minimize bias.

Each collaborator recorded all pertinent sampling data on his recorder chart. The calculations of the NO₂ levels from the recorder chart readings were made after returning to their home laboratories.



Front row: Paul Constant,^{1/} Ken Smith, Lynn Hutchinson, Cleveland Dodge,
Rolf Doebbeling, Norman Lewis, Harold Davis.

Back row: John Higuchi, Cole McKinney, Larry Saad, George Scheil,^{1/}
Fred Bergman,^{1/} John LaShelle,^{1/} Glenn Smith, John Margeson^{2/}

^{1/} MRI personnel.

^{2/} EPA Project Monitor.

Figure 12. Photograph of field personnel of the NO₂ collaborative test of the continuous colorimetric procedure, MRI field station, 29 July to 2 August 1974.

Table 1. COLLABORATIVE-TEST SCHEDULE

<u>Level</u>	<u>Run</u>	<u>NO₂ Spike Level ($\mu\text{g}/\text{m}^3$)</u>	<u>Date/Time</u>	
			<u>Started</u>	<u>Completed</u>
1	A	102	7-29-74 at 1800	7-30-74 at 0800
	B	102	7-30-74 at 0930	7-30-74 at 1250
	C	102	7-30-74 at 1250	7-30-74 at 1630
2	A	288	7-30-74 at 1800	7-31-74 at 0800
	B	288	7-31-74 at 0930	7-31-74 at 1250
	C	288	7-31-74 at 1250	7-31-74 at 1630
3	A	187	7-31-74 at 1800	8-1-74 at 0800
	B	187	8-1-74 at 0930	8-1-74 at 1250
	C	187	8-1-74 at 1250	8-1-74 at 1630
4	A	47.1	8-1-74 at 1800	8-2-74 at 0800
	B	47.1	8-2-74 at 0930	8-2-74 at 1250
	C	47.1	8-2-74 at 1250	8-2-74 at 1630

MRI had a laboratory supervisor who was in charge of the NO₂, ambient-air system operation. He was on duty from 0800 to 1800 each day, which was the period of run starts and completions. He was available anytime during the 24-hr runs, if any problems arose, as was the program manager.

There was a technician on duty throughout each run at all times during the test. These people monitored the sampling system operation, recording operational data and general observations. A general logbook was kept as well as the log sheet for operational data. Copies of these log sheets are given in Appendix G.

COLLABORATORS' SAMPLING RESULTS

Each collaborator's sampling instrumentation included an analog recorder on which all his sampling data was recorded. Each collaborator calculated 1-hr averages from his analog sampling recordings by a method of his own choosing. These results were submitted to MRI along with his calibration data. The 1-hr averages of the collaborators are tabularized by NO₂ spiked level* in Tables 2 through 5, with Table 2 comprising Level 1 (102 µg/m³ of NO₂) results, Table 3 comprising Level 2 (288 µg/m³ of NO₂) results, Table 4 comprising Level 3 (187 µg/m³ of NO₂) results, and Table 5 comprising Level 4 (47.1 µg/m³ of NO₂) results. Each table presents the results of the 10 collaborators for a test day. Explanatory notes are given at the bottom of each table.

MRI checked the collaborators' results for any gross overall error, e.g., misplacement of the decimal point. Also the data were culled for statistical outliers. Collaborator G is an "outlier" and the data from Collaborator G shown in Tables 2 and 4 are so noted. Minor deviations were attributed to the reading of the analog charts.

The collaborators' comments on the test are given in Appendix H.

The NO₂ sampling-system data, along with calculated flow rates and spike levels of the system and data on ambient test conditions, are given in Appendix I.

STATISTICAL ANALYSIS OF COLLABORATORS' RESULTS

The analysis of the spiked readings and the analysis of the ambient readings will be discussed separately. A summary discussion will follow.

* The level value of NO₂ is that generated by the permeation tubes.

Table 2. HOURLY AVERAGE RESULTS OF COLLABORATORS FROM THEIR SAMPLING NO₂ AT LEVEL 1 (102 µg/m³)^{a/}

Run	Date	Time	Collaborator									
			<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u> ^{b/}	<u>H</u>	<u>I</u>	<u>J</u>
A	7-29-74	1800-1900	113 ^{c/}	-	-	119	128	132	201	184	116	115
	7-29-74	1900-2000	116	-	175	123	133	132	154	184	120	124
	7-29-74	2000-2100	133	-	186	152	152	141	160	196	133	139
	7-29-74	2100-2200	178	197	235	200	195	188	220	230	169	143
	7-29-74	2200-2300	184	205	237	206	199	197	226	247	177	147
	7-29-74	2300-2400	188	210	250	207	203	207	226	256	178	152
	7-30-74	2400-0100	190	212	259	214	210	207	226	266	184	158
	7-30-74	0100-0200	178	197	250	206	197	197	192	259	175	143
	7-30-74	0200-0300	160	178	231	196	178	188	154	240	156	-
	7-30-74	0300-0400	154	173	220	188	167	169	135	237	147	-
	7-30-74	0400-0500	148	169	212	186	164	169	122	240	143	-
	7-30-74	0500-0600	137	160	194	176	158	160	98	230	135	-
	7-30-74	0600-0700	162	182	218	202	175	179	109	249	150	-
	7-30-74	0700-0800	128	178	216	190	169	179	84	254	143	-
B	7-30-74	0930-1000 ^{c/}	2 ^{d/}	-	-	20 ^{d/}	-	-	150	116	122	141
	7-30-74	1000-1100	0 ^{d/}	9 ^{d/}	26 ^{d/}	10 ^{d/}	-	132	141	97	118	137
	7-30-74	1100-1200	0 ^{d/}	9 ^{d/}	15 ^{d/}	5 ^{d/}	-	132	141	94	113	132
	7-30-74	1200-1300	0 ^{d/}	9 ^{d/}	13 ^{d/}	5 ^{d/}	4 ^{d/}	122	132	97	111	135
C	7-30-74	1300-1400	109	132	-	102	122	9 ^{d/}	47 ^{d/}	14 ^{d/}	11 ^{d/}	4 ^{d/}
	7-30-74	1400-1500	126	165	158	108	132	19 ^{d/}	141 ^{d/}	19 ^{d/}	17 ^{d/}	21 ^{d/}
	7-30-74	1500-1600	113	132	154	101	122	9 ^{d/}	66 ^{d/}	2 ^{d/}	11 ^{d/}	8 ^{d/}
	7-30-74	1600-1630 ^{c/}	113	132	154	99	120	9 ^{d/}	9 ^{d/}	2 ^{d/}	11 ^{d/}	8 ^{d/}

a/ This is the spiked value--the statistically determined average true value of NO₂ (which includes ambient NO₂) is 112 µg/m³. (In compiling biases there is an individual true value per hour).

b/ Data from collaborator "G" is unreliable at this level.

c/ Indicates reading is for ≤ 1/2 hr.

d/ From unspiked samples--all other results are spiked samples.

Table 3. HOURLY AVERAGE RESULTS OF COLLABORATORS FROM THEIR SAMPLING NO₂ AT LEVEL 2 (288 µg/m³)^{a/}

Run	Date	Time	Collaborator									
			A	B	C	D	E	F	G	H	I	J
A	7-30-74	1800-1900	301	329	-	303	318	310	385	288	402	378
	7-30-74	1900-2000	310	338	414	316	333	310	414	293	415	402
	7-30-74	2000-2100	320	348	432	328	340	329	423	310	432	408
	7-30-74	2100-2200	325	357	434	348	350	329	442	319	434	417
	7-30-74	2200-2300	344	376	451	372	363	329	466	358	447	423 ^{b/}
	7-30-74	2300-2400	344	382	470	387	372	357	492	373	466	-
	7-31-74	2400-0100	357	385	481	392 ^{b/}	382	357	526	370	472	-
	7-31-74	0100-0200	321	348	442	344 ^{b/}	342	348	466	324	444	428
	7-31-74	0200-0300	316	350	427	363	338	329	455	327	419	427
	7-31-74	0300-0400	321	352	434	365	348	338	466	329	432	432
	7-31-74	0400-0500	320	342	430	360	338	329	470	332	427	421
	7-31-74	0500-0600	299	320	406	342	314	310	436	300	402	395
	7-31-74	0500-0700	297	320	395	342	316	310	451	305	397	406
	7-31-74	0700-0800	293	353	432	375	350	329	503	339	432	432
B	7-31-74	0930-1000 ^{b/}	-	-	-	299	-	-	9 ^{c/}	5 ^{c/}	-	22 ^{c/}
	7-31-74	1000-1100	301	310	395	309	310	19 ^{c/}	13 ^{b/}	10 ^{c/}	51 ^{c/}	19 ^{c/}
	7-31-74	1100-1200	301	310	397	303	306	9 ^{c/}	2 ^{c/}	2 ^{c/}	38 ^{c/}	13 ^{c/}
	7-31-74	1200-1300	301	310	404	306	310	9 ^{c/}	2 ^{c/}	4 ^{c/}	36 ^{c/}	15 ^{c/}
C	7-31-74	1300-1400	2 ^{c/}	6 ^{c/}	22 ^{c/}	-	8 ^{c/}	310	428	293	-	370
	7-31-74	1400-1500	2 ^{c/}	6 ^{c/}	15 ^{c/}	8 ^{c/}	9 ^{c/}	310	428	299	541	374
	7-31-74	1500-1600	1 ^{c/}	6 ^{c/}	13 ^{c/}	6 ^{c/}	6 ^{c/}	310	436	302	545	385
	7-31-74	1600-1630 ^{b/}	2 ^{c/}	0 ^{c/}	21 ^{c/}	6 ^{c/}	11 ^{c/}	310	442	300	553	395

^{a/} This is the spiked value. The statistically determined average true value of NO₂ challenge (which includes ambient NO₂) is 302 µg/m³. (Incompiling biases there is an individual true value per hour).

^{b/} Indicates reading is for ≤ 1/2 hr.

^{c/} From unspiked samples--all other values are from spiked samples.

Table 4. HOURLY AVERAGE RESULTS OF COLLABORATORS FROM THEIR SAMPLING NO₂ AT LEVEL 3 (187 µg/m³)^{a/}

Run	Date	Time	Collaborator									
			<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u> ^{b/}	<u>H</u>	<u>I</u>	<u>J</u>
A	8-1-74	1800-1900	169	171	267	199	197	207	286	198	207	229
	8-1-74	1900-2000	171	173	269	201	201	207	297	201	203	241
	8-1-74	2000-2100	178	180	278	208	209	216	304	208	209	252
	8-1-74	2100-2200	173	177	278	210	203	216	291	203	205	248
	8-1-74	2200-2300	173	175	272	228	205	207	286	215	207	248
	8-1-74	2300-2400	173	178	310	235	203	207	259	202	203	248
	8-2-74	2400-0100	169	169	258	223	195	207	244	191	194	242
	8-2-74	0100-0200	171	175	263	232	203	207	226	192	197	256
	8-2-74	0200-0300	175	175	267	237	205	216	226	202	203	263
	8-2-74	0300-0400	169	169	261	232	199	207	192	192	197	252
	8-2-74	0400-0500	171	171	258	230	199	207	188	210	197	258
	8-2-74	0500-0600	180	182	263	238	210	207	192	210	203	267
	8-2-74	0600-0700	180	182	263	248	216	216	188	217	207	271
	8-2-74	0700-0800	188	188	271	255	218	216	184	213	210	272 ^{c/}
B	8-2-74	0930-1000 ^{c/}	2 ^{d/}	-	-	29 ^{d/}	-	-	244	218	-	248
	8-2-74	1000-1100	2 ^{d/}	-	26 ^{d/}	27 ^{d/}	19 ^{d/}	207	244	213	207	250
	8-2-74	1100-1200	2 ^{d/}	11 ^{d/}	21 ^{d/}	9 ^{d/}	13 ^{d/}	197	229	203	201	242
	8-2-74	1200-1300	2 ^{d/}	15 ^{d/}	24 ^{d/}	4 ^{d/}	17 ^{d/}	197	241 ^{c/}	201	199	246
C	8-2-74	1300-1400	188	178	231	197	197	19 ^{d/}	4 ^{d/}	12 ^{d/}	11 ^{c, d/}	15 ^{d/}
	8-2-74	1400-1500	184	171	229	191	194	0 ^{d/}	2 ^{d/}	1 ^{d/}	4 ^{d/}	9 ^{d/}
	8-2-74	1500-1600	186	171	231	197	194	0 ^{d/}	4 ^{d/}	0 ^{d/}	4 ^{d/}	6 ^{d/}
	8-2-74	1600-1630 ^{c/}	188	169	231	197	194	9 ^{d/}	-	0 ^{d/}	4 ^{d/}	9 ^{d/}

^{a/} This is the spiked level. The statistically determined average true value of NO₂ challenge (which includes ambient NO₂) is 198 µg/m³. (In computing biases there is an individual true value per hour).

^{b/} Data from Collaborator "G" is unreliable at this level.

^{c/} Indicates reading is for ≤ 1/2 hr.

^{d/} From unspiked samples--all other values are from spiked samples.

Table 5. HOURLY AVERAGE RESULTS OF COLLABORATORS FROM THEIR SAMPLING NO₂ AT LEVEL 4 (47.1 µg/m³)^{a/}

Run	Date	Time	Collaborator									
			A	B	C	D	E	F	G	H	I	J
A	7-31-74	1800-1900	66	64	68	66 ^{b/}	66	75	73	73	71 ^{b/}	84
	7-31-74	1900-2000	75	70	79	-	73	85	83	86	81	94
	7-31-74	2000-2100	77	81	102	89	86	94	94	109	92	105
	7-31-74	2100-2200	100	113	133	122	116	122	130	140	120	141
	7-31-74	2200-2300	77	79	113	94	90	94	96	104	94	105
	7-31-74	2300-2400	79	81	103	99	90	94	94	102	94	107
	8-1-74	2400-0100	90	100	115	110	100	103	107	111	103	122
	8-1-74	0100-0200	86	90	118	108	96	103	103	126	98	120
	8-1-74	0200-0300	92	92	118	107	92	103	96	106	96	100
	8-1-74	0300-0400	73	75	103	89	83	94	83	92	83	96
	8-1-74	0400-0500	73	77	98	88	81	94	81	92	81	96
	8-1-74	0500-0600	73	79	98	89	81	94	84	94	79	90
	8-1-74	0600-0700	79	90	109	100	90	103	98	108	90	109
	8-1-74	0700-0800	86	94	116	107 ^{b/}	96	113	109	125	98	113
B	8-1-74	0930-1000 ^{b/}	73	79	122	35	-	-	47 ^{c/}	44 ^{c/}	45 ^{c/}	43 ^{c/}
	8-1-74	1000-1100	62	70	98	91	73	28 ^{c/}	22 ^{c/}	13 ^{c/}	21 ^{c/}	28 ^{c/}
	8-1-74	1100-1200	58	56	88	40	64	19 ^{c/}	8 ^{c/}	10 ^{c/}	11 ^{c/}	15 ^{c/}
	8-1-74	1200-1300	56	53	84	-	58	9 ^{c/}	4 ^{c/}	5 ^{c/}	9 ^{c/}	11 ^{c/}
C	8-1-74	1300-1400	1 ^{c/}	0 ^{c/}	26 ^{c/}	33 ^{c/}	-	66	62	50	56 ^{b/}	68
	8-1-74	1400-1500	1 ^{c/}	0 ^{c/}	24 ^{c/}	5 ^{c/}	6 ^{c/}	56	60	51	56	68
	8-1-74	1500-1600	1 ^{c/}	0 ^{c/}	19 ^{c/}	25 ^{c/}	6 ^{c/}	56	71	52	60	70
	8-1-74	1600-1630 ^{b/}	1 ^{c/}	0 ^{c/}	19 ^{c/}	13 ^{c/}	8 ^{c/}	66	66	34	64	71

^{a/} This is the spiked value. The statistically determined average true value of challenge (which includes ambient NO₂) is 60 µg/m³. (In computing biases there is an individual true value per hour).

^{b/} Indicates reading is for ≤ 1/2 hr.

^{c/} From unspiked samples--all other values are from spiked samples.

Analysis of All Spiked Readings (Precision Estimates)

Recall that the experimental design model for this set is:

$$X_{ijk\ell} = \mu + C_i + t_j + L_k + e_{\ell(ijk)} ,$$

where μ = Overall mean,

C_i = i^{th} collaborator, $i = 1, \dots, 10$,

t_j = j^{th} hour, $j = 1, \dots, 20$,

L_k = k^{th} NO₂ level, $k = 1, \dots, 4$,

$e_{\ell(ijk)}$ = Measurement error in ℓ^{th} reading in ijk^{th} cell,
 $\ell = 1$ for every ijk ,

$X_{ijk\ell}$ = $ijk\ell^{\text{th}}$ response (spiked reading).

The results of the analysis of variance of the spiked readings are shown in Tables 6 through 8.

Table 6 shows the basic analyses of variance themselves. Note that a separate analysis of variance was done for each level. This was necessary because the variance within a collaborator (described by σ_e) was not the same at all NO₂ levels (see also Table 8).*

All the F-values in Table 6 are significant, i.e., at all levels of NO₂ the collaborator averages are separated and a significant variability in NO₂ exists in time.

Since the C and t effects are significant, it is desirable to quantitatively describe the differences between collaborators. Table 7 displays these differences for each NO₂ level. The average NO₂ value per level is listed in this table in order to give a rough idea of the relative separation of collaborators (even though the average value is not the true value used in the analysis of variance).

Since the collaborator (mean) differences are often quite large, at least some of the collaborators must be biased significantly. Also, the order of the collaborators seem to vary quite a bit from level to level. The Kendall concordance (a coefficient of agreement equal to 1 when order is perfectly preserved) is only 0.52. Therefore it is reasonable to suppose that a significant collaborator-level interaction exists (see Figure 13, e.g., lines are not parallel).

* An assumption (the homoscedastic assumption) of all analysis of variance models is that σ_e is uniform.

Table 6. ANALYSIS OF VARIANCE SPIKED READINGS

<u>Source</u>	<u>df</u>	<u>SS</u>	<u>MS</u>	<u>F</u>
A. Level 1 ^{a/}				
Total	139	4,345,388		
Collaborator, adjusted	8	74,517	9,315	32.28
Time (t), adjusted	19	127,072	6,688	23.14
Error (e)	111	32,039	289	
B. Level 2				
Total	163	22,912,110		
Collaborator, adjusted	9	416,836	46,315	143.79
Time (t), adjusted	19	71,471	3,762	11.68
Error (e)	134	43,165	322	
C. Level 3 ^{a/}				
Total	152	6,930,854		
Collaborator, adjusted	8	117,350	14,669	1,552.28
Time (t), adjusted	19	7,171	377	39.94
Error (e)	124	11,070	89	
D. Level 4				
Total	164	1,391,497		
Collaborator, adjusted	9	11,257	1,251	39.13
Time (t), adjusted	19	45,577	2,399	424.60
Error (e)	135	4,316	32	

^{a/} Collaborator G is deleted as an outlier.

Table 7. COLLABORATOR AVERAGE DIFFERENCES SPIKED READINGS ($\mu\text{g}/\text{m}^3$)

<u>Difference</u> ^{a/}	<u>Level 1</u> <u>(average 154)</u>	<u>Level 2</u> <u>(average 371)</u>	<u>Level 3</u> <u>(average 212)</u>	<u>Level 4</u> <u>(average 90)</u>
D-E	22.3	8.2	20.2	6.9
A-E	1.2	-21.1	-24.7	-7.8
C-E	60.6	88.9	61.9	18.2
G-E	-	110.7	-	8.0
F-E	18.1	-15.4	1.8	9.5
B-E	21.0	5.9	5.6	-4.2
J-E	25.2	70.8	-25.4	17.7
H-E	-6.0	-20.3	48.7	13.7
I-E	64.5	100.9	1.3	3.4
[E =	(131)	(335)	(202)	(83)]

^{a/} This difference is the estimate of five mean difference between collaborators (see Appendix E).

Table 8. COMPONENTS OF VARIANCE SPIKED READINGS ($\mu\text{g}/\text{m}^3$)

<u>Source</u>	<u>Level</u>			
	<u>L1</u>	<u>L2</u>	<u>L3</u>	<u>L4</u>
σ_e	16.99	17.95	9.45	5.65
σ_c	21.24	47.95	27.00	7.81
σ_t	26.67	18.55	5.66	15.39
$\sqrt{\sigma_e^2 + \sigma_c^2}$	27.20	51.20	28.61	9.64

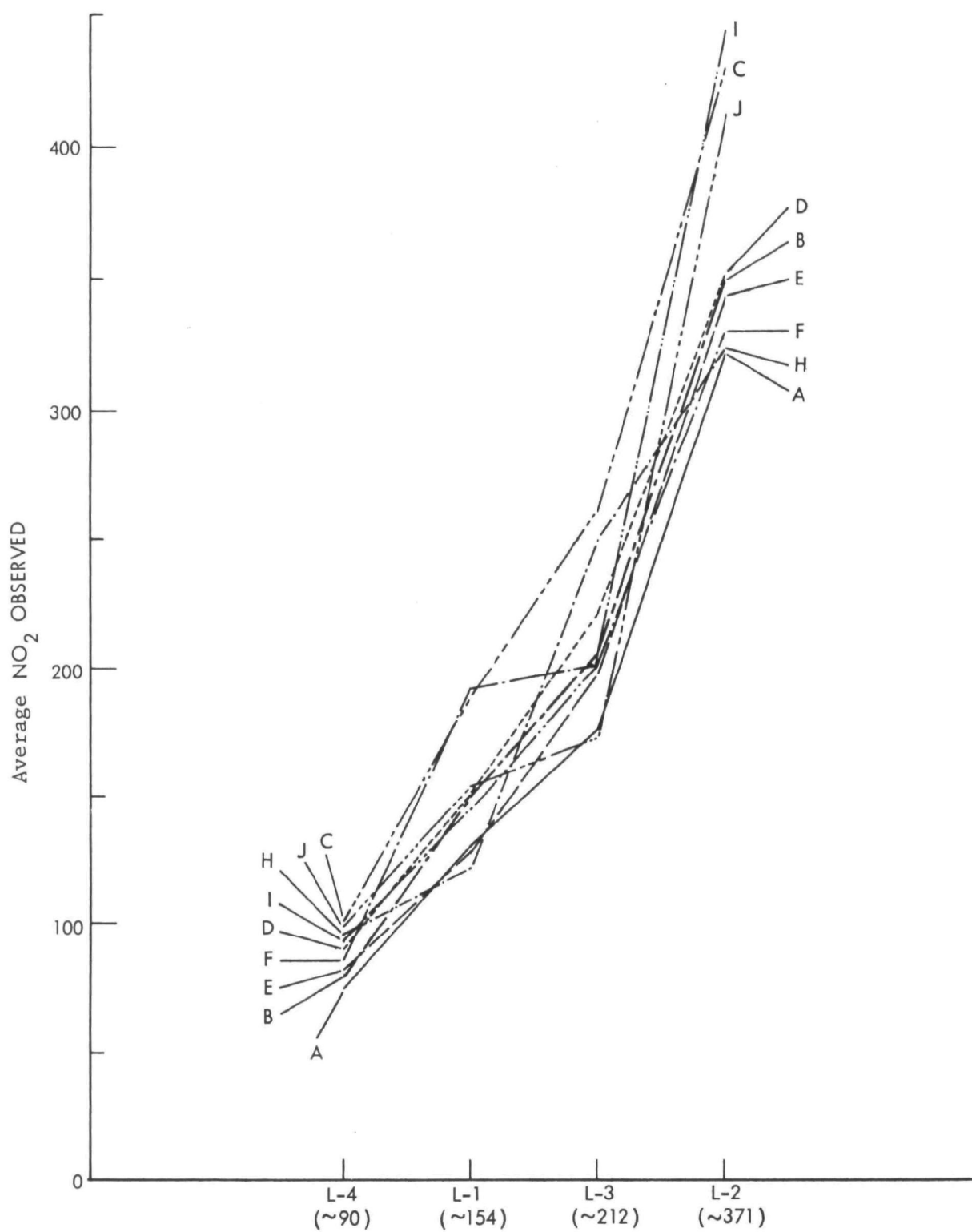


Figure 13 - Collaborator-Level Interaction (w/o collaborator G)

The components of variance are shown in Table 8. Recall that:

σ_e = standard deviation within a collaborator,

σ_c = standard deviation of collaborator effects, and

σ_t = standard deviation of hourly effects.

Although we do not know the exact NO₂ values per level, it is surely true that in ascending order the levels are L4, L1, L3, L2; approximately spanning the range 90 to 370 µg/m³. Therefore, Table 8 indicates that σ_c is proportional to the NO₂ level. The σ_e component varies with the NO₂ level, but not in a simple way. Also, σ_c is larger than σ_e , i.e., the variability between collaborators is greater than the variability within a collaborator.

Since both σ_e and σ_c "depend" on the NO₂ level, it is not very useful to construct average estimates of precision.

As a point of interest, note that σ_t also varies but is not proportional to the NO₂ level; that is, the ambient fluctuations were not consistent from day to day.

Analysis of Spiked-Ambient Readings (Bias Estimates)

The experimental design model for this data set is:

$$X_{ijk} = \mu + C_i + L_j + CL_{ij} + e_{k(ij)} \quad ,$$

where μ = Overall mean,

C_i = i^{th} collaborator, $i = 1, \dots, 9, *$

L_j = j^{th} NO₂ level, $i = 1, \dots, 4,$

CL_{ij} = Collaborator-level interaction,

$e_{k(ij)}$ = k^{th} measurement error in ij^{th} cell,
 $k = 1, \dots, 3$ for every ij , and

X_{ijk} = ijk^{th} bias (collaborator reading - true value).

* Collaborator G not included since he produced less than one-half the designed set of observations.

Recall that a true value for each hour is constructed from the average ambient observation during that hour. Since only half the collaborators were measuring the ambient at a given time, their average value has this source of error in it.

The analysis of variance is shown in Table 9.

All the F-values in Table 9 are highly significant. Therefore, the bias does differ between collaborators, does depend on the NO₂ level, and the individual collaborator's bias curves are not parallel (See Figure 14).

The average true values for the levels are 111.9 µg/m³, 301.6 µg/m³, 197.7 µg/m³, and 60.0 µg/m³ (overall average is 167.8 µg/m³). Thus, the overall average bias is not too great (about + 10%). On the average, the bias is greatest at the highest NO₂ level (+ 15%) and least around 200 µg/m³ (+ 3%). (See Table 10.)

These average results are not sufficiently descriptive of the bias situation, however. Only about four of the collaborators (D, A, F, and E) exhibited even fairly consistently bias per NO₂ level results. Note that the really large biases are all positive (thus the average bias is positive), but in the more or less "normal" results almost half the biases are negative.

Summary Discussion of Statistical Analysis

In general, the relative measurement errors are stable over the range of NO₂ measured (approximately 50 to 400 µg/m³) and not very large (approximately 6% true value). The collaborator-collaborator relative standard error is also fairly stable but larger (approximately 12% true value) so that the method standard deviation $\sqrt{\frac{2}{\sigma_e} + \frac{2}{\sigma_c}}$ is on the average about 13% of the true value.

However, the bias is not stable with respect to NO₂ level, and is not consistent within collaborators, either. Although the overall average bias is only about + 10%, individual collaborators produced biases as great as + 80% (at some levels). Thus, it is fair to say that the continuous-colorimetric method may produce extremely inaccurate readings in an unpredictable fashion (even though the overall average results are fairly accurate).

It might be noted that about half of the collaborators did achieve fairly stable results throughout the experiment. A subjective interpretation of this fact is that the continuous-colorimetric method is difficult to use, but will produce reliable results in some hands.

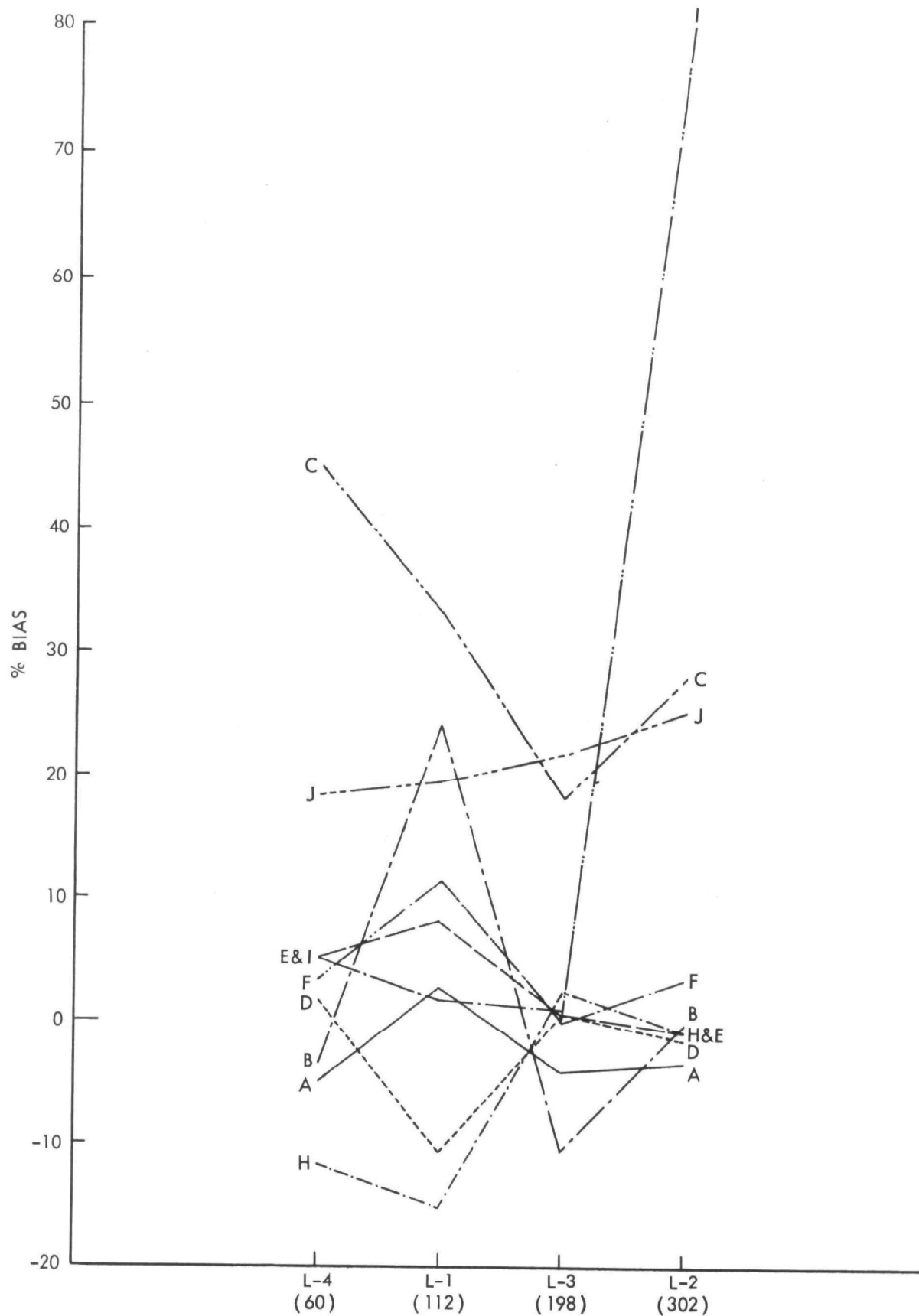


Figure 14 - Collaborator-Level Interaction in % Bias (w/o collaborator G)

Lower Detectable Limit (LDL)

Two measuring of LDL are used in the following discussion: (a) the smallest value of NO_2 that can be reliably identified as existing (i.e., positive) when the method is used by a collaborator (a "pure" LDL), and (b) the smallest reliable NO_2 estimate from a set of collaborators using the method (a "practical" LDL).

Two methods of estimating the LDL were used. The first method uses the ambient readings obtained during the actual experiment, while the second method uses the collaborators' calibration curves.*

The ambient readings furnish estimates of σ_e (standard deviation within a collaborator) and σ_c (standard deviation between collaborators) that allow estimation of the LDL's, although there is no way to incorporate bias with these estimates. Using $\sigma_e = 4.48 \mu\text{g}/\text{m}^3$ and $\sigma_c = 6.19 \mu\text{g}/\text{m}^3$ results in:

$$\text{estimated pure LDL} = 9 \mu\text{g}/\text{m}^3$$

$$\text{estimated practical LDL} = 15 \mu\text{g}/\text{m}^3 .$$

The calibration curves do allow estimation of biases** in addition to components of variance. Using the average σ_e of individual calibration curves results in a pure LDL estimate of $13 \mu\text{g}/\text{m}^3$, of which $2 \mu\text{g}/\text{m}^3$ is bias. Using the whole data set, one arrives at an estimated practical LDL of $19 \mu\text{g}/\text{m}^3$, of which $3 \mu\text{g}/\text{m}^3$ is bias.

The two sets of results agree fairly well. It seems reasonable to state that the pure LDL is probably $\leq 13 \mu\text{g}/\text{m}^3$, and the practical LDL $\leq 19 \mu\text{g}/\text{m}^3$.

* The only calibration data available were from collaborators A, G, B, and E.

** Deviations from the correct values, e.g., a nonzero intercept for a blank value.

CONCLUSIONS

The major conclusions that can be drawn from the results of this collaborative test are:

1. The NO₂, ambient-air sampling system developed by MRI is an effective system for use in collaborative testing of methods such as the continuous-colorimetric procedure.

2. If the tentative continuous-colorimetric procedure as given in Appendix A of this report is followed by people knowledgeable of the sampling and analysis techniques given therein, then such persons will obtain results with an average bias of + 16.1 µg/m³ (6% true value) over the range 90 to 370 µg/m³. On the average, the within laboratory standard deviation (σ_e) is 13.5 µg/m³, and the collaborator standard deviation $\sqrt{\sigma_c^2 + \sigma_e^2}$ is 32.7 (13% true value). These components are dependent, however, upon the NO₂ level.

3. The bias of the method is collaborator dependent, although four of the collaborators produced fairly stable results in this regard.

RECOMMENDATIONS

Based upon the conclusions that have been drawn from the results of this collaborative test, it is recommended that:

1. The same NO₂ sampling system be used in the evaluation of the chemiluminescent method to be tested .
2. The data sets to be obtained from the subsequent method to be evaluated be based on experimental designs, test procedures and sampling system operational procedures as similar as possible to those of the continuous-colorimetric collaborative test so that comparisons of the methods are based on similar criteria .
3. No further analysis be made of the results from the continuous-colorimetric method until the results from the other method are obtained.

APPENDIX A

TENTATIVE METHOD FOR THE DETERMINATION OF NITROGEN DIOXIDE IN THE ATMOSPHERE (CONTINUOUS-COLORIMETRIC PROCEDURE)

TENTATIVE METHOD FOR THE DETERMINATION OF NITROGEN DIOXIDE
IN THE ATMOSPHERE (CONTINUOUS COLORIMETRIC PROCEDURE)^a

JUNE 1974

METHODS STANDARDIZATION BRANCH
QUALITY ASSURANCE AND ENVIRONMENTAL MONITORING LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL RESEARCH CENTER
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^aA tentative method is one which has been carefully drafted from available expert ental information, reviewed editorially within the Methods Standardization Branch and has undergone extensive laboratory evaluation. The method is still under investigation and therefore is subject to revision.

CONTINUOUS COLORIMETRIC METHOD FOR MEASUREMENT OF NITROGEN DIOXIDE IN AMBIENT AIR

1. Principle and Applicability

1.1 The method is based on the reaction of NO_2 in acid media to produce nitrous acid (HONO) with subsequent diazotization and coupling. NO_2 in ambient air is continuously absorbed in a solution of diazotizing-coupling reagents to form an azo-dye which absorbs light, with a maximum absorbance at approximately 540 nm. The transmittance, which is a function of the NO_2 concentration, is measured continuously in a colorimeter and the output read on a recorder or a digital voltmeter.

1.2 The method is applicable to the continuous determination of nitrogen dioxide in ambient air.

2. Range and Sensitivity

2.1 Typical ranges are 0 to 470 $\mu\text{g}/\text{m}^3$ (0 to 0.25 ppm); 0 to 940 $\mu\text{g}/\text{m}^3$ (0 to 0.50 ppm); and 0 to 1880 $\mu\text{g}/\text{m}^3$ (0 to 1.0 ppm); Beer's law is obeyed throughout this range.

2.2 For optimum sensitivity, the wavelength specification of the filter in the colorimeter should correspond to the wavelength of maximum absorbance of the dye. This may not be the case in some instruments. Therefore, the dye should be scanned and the wavelength of maximum absorbance determined. If the filter is not within ± 10 nm of the wavelength maximum obtained by scanning the dye, the filter should be replaced by one that meets this specification.

3. Interferences

3.1 Recent studies⁽¹⁾ have shown that ozone can produce a negative interference, the magnitude of which depends on the O_3 to NO_2 ratio. In the study cited, O_3/NO_2 ratios of 1:1, 2:1 and 3.5:1 produced interferences of 5, 19 and 38%, respectively.

3.2 Alkyl nitrites are positive interferents. The magnitude of the interference depends on the structure of the alkyl nitrite.⁽²⁾

3.3 A 30/1 ratio of SO_2 to NO_2 slowly bleaches the color of the azo-dye in the manual procedure,⁽³⁾ and this effect may be applicable to the continuous procedure.

4. Precision, Accuracy and Stability

4.1 No data are available on precision and accuracy.

4.2 Air bubbles can accumulate in the optical cell and will cause an erratic response. This instability can be minimized by increasing the air and solution flow rates. The ratio of the air to solution flow rate should be maintained at the value recommended by the manufacturer (see Section 7).

4.3 The modified Saltzman absorbing reagent (Section 6.8.1) is stable for one month under laboratory conditions, 22° C. - exposed to light. The Lysikow solution (Section 6.8.2) develops an absorbance of approximately 0.02 after one month under laboratory conditions. The net absorbance (absorbance developed by adding a NO_2^- solution - blank is unchanged after one month).

The stability of both solutions is unchanged after temperature cycling, to simulate ambient conditions, up to 30° C for four hours per day for seven days.

5. Apparatus

5.1 Continuous NO₂ analyzer. Sample air is drawn through a gas/liquid contact column at an accurately determined flow rate concurrent to a controlled flow of absorbing reagent. The sample inlet line prior to the absorber column should be constructed of either glass or Teflon. The absorber column must be carefully designed and properly sized because NO₂ is somewhat difficult to absorb. The colored solution is passed through a colorimeter where the transmittance is measured continuously.

5.1.1 Probe. Glass or Teflon, with inverted polypropylene or glass funnel at the end.

5.1.2 Installation. Instruments should be installed on location and demonstrated, preferably by the manufacturer, to meet or exceed the specifications described in the addendum.

5.2 Calibration. The calibration apparatus and its use is described in Section 8. Additional components follow:

5.2.1 Dilution Air and Flushing Air (or N₂). This can be compressed (house) air or cylinder air. It should be purified by passing through silica gel for drying, and through activated charcoal (6-14 mesh), and molecular sieve (6-16 mesh, type 4A) to remove any NO₂ and hydrocarbons.

5.2.1.1 Purity. Test the purity of the dilution and flushing air by operating the instrument in the zero mode until a stable baseline is obtained. Connect the dilution or flushing air to the air intake of the gas/liquid contact column and operate the instrument in the ambient mode. If the response changes by more than twice the noise level, the air is impure. Correct before proceeding.

5.2.2 Flow rates. One each with ranges of 0-100 cm³/min., 0 to 1 l/min. and 0 to 20 l/min. is required.

5.2.2.1 Calibration. This can be accomplished with a bubble flow meter or a wet test meter. With a stopwatch, determine the rates of air flow (cm³/min) through the flow meter at a minimum of four different ball positions. Plot ball positions versus flow rates.

5.2.3 Thermometer. Graduated in 0.1° intervals over the range 20 to 30° C.

6. Reagents

6.1 Sulfanilamide [4-(H₂N)C₆H₄SO₂NH₂]. Melting point 165-167°C.

6.2 Sulfanilic Acid Monohydrate, [4-(NH₂)C₆H₄SO₃H·H₂O]. ACS reagent grade. Either the monohydrate or anhydrous form can be used, provided the degree of hydration is known. If the degree of hydration is not known, recrystallize from water and dry over night at 120°C.⁽⁴⁾ This will give the anhydrous material.

6.3 N-(1-Naphthyl)-ethylenediamine dihydrochloride (NEDA).

Best grade available.

6.4 Tartaric Acid. ACS Reagent grade.

6.5 Glacial Acetic Acid. ACS Reagent grade.

6.6 2-Naphthol-3,6-disulfonic acid disodium salt.

$[\text{HOOC}_{10}\text{H}_5(\text{SO}_3\text{Na})_2]$ Technical Grade. This compound is also known by its trivial name, R-salt.

6.7 Nitrite-free distilled water. Mix the water with absorbing solution. Absence of any visible pink coloration indicates that the water is of acceptable quality. If the solution turns pink, redistill the water in an all-glass still after adding a crystal of potassium permanganate and barium hydroxide.

6.8 Absorbing Solutions. Either the modified Saltzman⁽⁵⁾ solution or the Lyshkow^(6, 7) modification of the Saltzman solution can be used.

6.8.1 Modified Saltzman absorbing solution. 0.5% sulfanilic acid, 5.0% acetic acid, 0.005% NEDA. For 1 liter of solution prepare as follows: Dissolve 5.52 g of sulfanilic acid monohydrate (or 5.00 g of the anhydrous material) in hot distilled water and allow to cool to room temperature. Add 50 ml of glacial acetic acid followed by 0.050 g of NEDA. Dilute to 1 liter with distilled water.

6.8.2 Lyshkow solution. 0.15% Sulfanilamide, 1.5% Tartaric acid, 0.005% NEDA and 0.005% 2-Naphthol-3,6-disulfonic acid disodium salt. For 1 liter of solution, dissolve 15.0 g of

tartaric acid, 1.50 g sulfanilamide, 0.050 g of 2-naphthol-3,6-disulfonic acid disodium salt, and 0.050 g NEDA in 500 ml of distilled water. Dilute to 1 liter with distilled water.

7. Procedure

Allow the instrument to warm-up in accordance with the manufacturer's instructions and until a stable baseline is obtained. Turn pumps on and adjust the air and absorbing reagent flow rates and their ratio to the recommended values. Verify the air flow rate by measurements with the 1 l/min. flow meter.

Calibrate the instrument as described in Section 8.

8. Calibration

8.1 General Description. A dynamic calibration is carried out by generating synthetic atmospheres from the output of a reliable NO_2 -permeation device and determining the instrument response. Instrument response is then plotted against NO_2 concentration to obtain a calibration curve.

8.2 NO_2 -Permeation Device. Obtain or prepare a reliable NO_2 -permeation device with a permeation rate of approximately 1.0 $\mu\text{gNO}_2/\text{min}$. The following precautions must be observed in preparing NO_2 -permeation devices:

1. The NO_2 used to fill the device must be dry.⁽⁸⁾
2. The filling operation must be carried out in a dry atmosphere to insure that water is not introduced while filling the tube.

3. The H_2O_2 should be pure, assay 99% or greater.
4. All seals in the device should be leak free.
5. The permeation rate should be checked gravimetrically as follows:

a. Allow the device to reach temperature equilibrium in the H_2O_2 -atmosphere generation system (Section 8.3). This will be attained over-night, in most cases.

b. Weigh the device periodically and record the time. (Transport the device from the atmosphere generation system to the balance area in a dessicator.)

c. All weighings should be carried out at the same relative humidity $\pm 10\%$. The time of exposure of the device to the atmosphere during weighing should be constant (± 30 sec.) from weighing to weighing. This technique cancels any weight gain, due to moisture - H_2O_2 reactions at the effusing surface, and gives a reliable measure of the H_2O_2 -weight loss.

d. The time interval between weighings will depend on balance sensitivity. With a sensitivity (standard deviation at the mass being weighed) of 40 μg , weighing at 24-hour intervals will produce reliable weight losses.

e. Plot device weight (in micrograms) on the y-axis versus cumulative time (in minutes) on the x-axis. Obtain sufficient data (at least five well-spaced points) to establish the slope of the line, which is the permeation rate in $\mu\text{g}/\text{min}$. Determine the slope algebraically or by regression analysis.

f. The permeation rate should be constant and in reasonable agreement with the suppliers or other previous value.

8.3 NO_2 -Atmosphere-Generation System. This consists of an NO_2 -permeation device contained in a water-jacketed condenser which is connected to a constant-temperature bath. A homogenous NO_2 in air atmosphere is produced by flushing the NO_2 , effusing from the calibrated NO_2 -permeation device, into a mixing bulb where it is further diluted with dilution air. Figure 1 shows a diagram of this system with suggested specifications for the component parts. The following key specifications must be met to insure the generation of reliable calibration atmospheres:

8.3.1 Temperature control must be maintained to within $\pm 0.1^\circ \text{C}$. of a fixed value.

8.3.2 Flushing and dilution air These must be dry and free of NO_2 (see section 5.2.1).

8.3.3 A Kieldahl connecting bulb with a volume of at least 150 cm^3 is required to obtain adequate mixing of NO_2 and dilution air.

8.3.4 Connections must be of glass or Teflon when contacting NO_2 . Rubber tubing may be used for flushing and dilution air connections. Tygon tubing should not be used. Systems for preparation of calibration atmospheres have been described in detail by O'Keeffe and Ortran,⁽⁹⁾ Scaringelli, et al.,⁽¹⁰⁾ and Scaringelli, Rosenberg and Palma.⁽⁴⁾ Commercial calibration systems using the permeation tube technique are now available.

8.4 NO_2 Atmospheres. Allow the NO_2 atmosphere generation system to equilibrate for at least one hour with flushing and dilution air flowing. Generate a calibration gas equal to $80 \pm 5\%$ of full scale by adjusting the dilution flow rate. Calculate the exact concentration from the following relationship:

$$C = \frac{P \times 10^3}{D + F}$$

where:

C = NO_2 concentration, $\mu\text{g}/\text{m}^3$

P = NO_2 permeation rate, $\mu\text{g}/\text{min}$.

F = Flushing air flow rate, ℓ/min .

D = Dilution air flow rate, ℓ/min .

10^3 = Factor to convert liters to cubic meters.

Sample the atmosphere until a stable response is obtained and record the response. Generate four additional concentrations of approximately 10, (a) 20, 40 and 60% of full scale and determine the response.

8.5 Other reliable dynamic procedures for generating NO_2 can be used. For example, gas phase titration of excess NO with O_3 ,⁽¹¹⁾ and analyzed cylinders of NO_2 in N_2 that are stable.⁽¹²⁾

8.6 Calibration Curve. Plot the concentration of NO_2 in micrograms/cubic meter (x - axis) against instrument response (y - axis), and draw the line of best fit. Some instruments are designed to give a linear and some a non-linear response.

(a) The NO_2 permeation rate and highest workable dilution air flow rate may necessitate a higher value.

8.7 Frequency of Calibration. The calibration should be checked daily by spanning the calibration curve at 80% of full scale. Spanning by generation of a dynamic standard is preferred. However, if field use of the instrument makes this impractical, a static-calibration check can be carried out by adding a solution of nitrite ion, NO_2^- , (as NaNO_2) to the absorbing solution to generate the dye. (Most instruments have a static calibration mode through which solutions can be introduced.) CAUTION: Static and dynamic calibrations may not agree. Therefore, if static spanning is to be used, a static reference point should be established at the time of calibration.

9. Calculations

9.1 NO_2 Concentration. This is read directly from the calibration curve. A one-hour or longer average concentration is reported. Electronic or electro-mechanical integration, equal area averaging, a planimeter, paper weighing techniques, or the average of a digital output can be used to obtain the average concentration.

9.2 The NO_2 concentration can be converted to ppm as follows:

$$\text{ppm NO}_2 = \mu\text{g NO}_2/\text{m}^3 \times 5.32 \times 10^{-4}$$

9.3 Air Volume. The volume of air sampled is not corrected to S.T.P., because of the uncertainty associated with average temperature and pressure values.

10. References

1. Clark, T. A., et al., Environmental Protection Agency, Research Triangle Park, N.C. 27711. "Instrumentation for the Measurement of Nitrogen Dioxide." Presented at the ASTM-EPA Symposium on "Instrumentation for Monitoring Air Quality, 8-14 to 8/16/73, in Boulder, Colorado.
2. Thomas, M. D., et al., "Automatic Apparatus for Determination of Nitric Oxide and Nitrogen Dioxide in the Atmosphere," Anal. Chem., 28, 1810-1816 (1956).
3. Saltzman, B. E., "Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere," Anal. Chem., 26, 1949-1955 (1954).
4. Scaringelli, F. P., Rosenberg, E., and Rehme, K. A., "Comparison of Permeation Devices and Nitrite Ion as Standards for the Colorimetric Determination of Nitrogen Dioxide," Environ. Sci. Tech., 4, 924-929 (1970).
5. Saltzman, B. E., "Modified Nitrogen Dioxide Reagent for Recording Air Analyzers," Anal. Chem., 32, 135-136 (1960).
6. Lyszkow, H. A., "A Rapid and Sensitive Colorimetric Reagent for Nitrogen Dioxide in Air," J.A.P.C.A., 15, 481-484 (1965).
7. U.S. Patent 3, 375, 079.

8. National Bureau of Standards Technical Note No. 585. This can be obtained from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. Price - 70 cents.
9. O'Keeffe, A. E., and Ortman, G. C., "Primary Standards for Trace Gas Analysis," Anal. Chem., 38, 760 (1966).
10. Scaringelli, F. P., O'Keeffe, A. E., Rosenberg, E., and Bell, J. P., "Preparation of Known Concentrations of Gases and Vapors with Permeation Devices Calibrated Gravimetrically." Anal. Chem., 42, 871 (1970).
11. Federal Register, 36, 22392-22396 (November 25, 1971).
12. Hiroshi, J. E. et al., "A Straightforward Dynamic Calibration Procedure for Use With NO_x Instruments." Presented at the A P C A Convention, Denver, Colorado, June 9-13, 1974. Preprint No. 74-13.

ADDENDUM

A. Performance Specifications for Continuous Colorimetric Atmospheric Analyzers.

Range	Multiple
Noise	0.005 ppm
Lower Detectable Limit	0.01 ppm
Zero Drift	
12 Hour	± 0.02 ppm
24 Hour	± 0.02 ppm
Span Drift - 24 hour	0.02 ppm
Lag Time	20 minutes
Rise Time, 95%	15 minutes
Fall Time, 95%	15 minutes

B. Definitions of Performance Specifications

Range - Minimum and maximum concentrations which the system shall be capable of measuring.

Noise - Spontaneous, short duration deviations in the instrument output about the mean output, which are not caused by input concentration changes.

Lower Detectable Limit - The minimum pollutant concentration which produces a signal of twice the noise level.

Zero Drift - The change in instrument output over a stated time period of unadjusted continuous operation, when the input concentration of pollutant is zero.

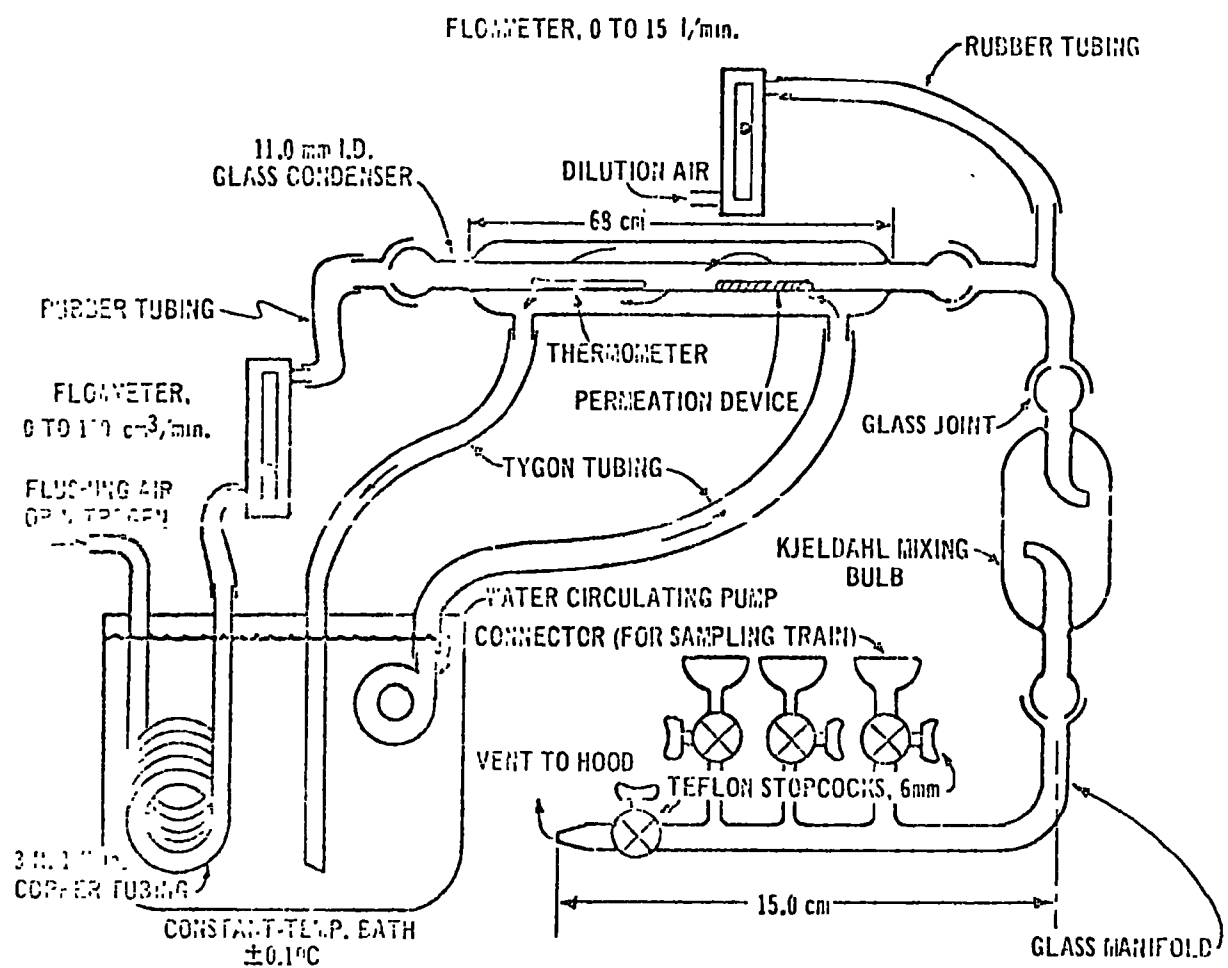


Figure 1. Typical NO_2 atmosphere generation system.

APPENDIX B

DATA ON THE PERMEATION TUBES USED AS THE SOURCE OF THE SPIKED LEVELS OF NO₂

There were four branches to the NO₂ permeation tube assembly. Each branch contained a set of permeation tubes as follows:

<u>Branch</u>	<u>Permeation Tube</u>		<u>± 1S</u> <u>(µg/min)</u>	<u>Branch NO₂^{a/}</u> <u>(µg/min)</u>
	<u>Number</u>	<u>Rate of NO₂</u> <u>(µg/min)</u>		
1	35-8	1.434	0.001	-
1	35-16	1.597	0.002	-
1	29-3	1.345	0.002	-
1	28-10	1.160	0.002	-
1				5.536
2	34-3	1.195	0.002	-
2	34-13	1.275	0.002	-
2	34-6	1.548	0.001	-
2	34-1	1.226	0.003	-
2	34-10	1.138	0.001	-
2				6.382
3	35-13	1.990	0.0003	-
3	29-4	1.210	0.001	-
3				3.200
4	29-2	1.210	0.001	-
4	34-12	1.770	0.002	-
4				2.980

Permeation rates for the above tubes were determined by the National Bureau of Standards and validated by the Methods Standardization Branch (MSB) of EPA at 25.1°C before they were given to MRI for use on the collaborative test.

The combinations of branches used for the four runs of the continuous-colorimetric collaborative test are:

<u>Level</u>	<u>Date</u>	<u>Branches Used</u>
1	July 29-30	2
2	July 30-31	1, 2, 3, and 4
3	July 1-August 1	1, 3, and 4
4	August 1-2	4

a/ The sum of the NO₂ generated by each permeation tube in the branch.

APPENDIX C

CALIBRATION OF THE VENTURI AND DRY-GAS METER

The venturi and dry-gas meter were calibrated using a 1.0-ft³/rev., wet-test meter, as shown in Figure 9 of the text. The wet-test meter is connected between the splitter and the dry-gas meter. A bubbler is used before the wet-test meter to saturate the air with water. The air flow then proceeds through the venturi to the NO₂ bleed-in as it does in normal operation (see Figure 3 of the text).

Since the saturated air coming from the wet-test meter is not dried before going into the dry-gas meter, no connection for water vapor pressure is necessary and only the normal corrections for temperature and pressure are used. The flowrate of the wet-test meter (to stp) is:

$$\text{Flow}_{\text{stp}} = \text{Flow (meter reading)} \times \frac{P}{760} \times \frac{294}{T}$$

where T = temperature of wet-test meter + 273, and

$P = P_{\text{atm}} + \text{pressure of test meter manometer.}$

The venturi flowrate is dependent on both temperature and pressure. Therefore Flow_{stp} is corrected to venturi conditions

$$\text{Flow}_{\text{venturi}} = \text{Flow}_{\text{stp}} \times \frac{760}{P_2} \times \frac{T_2}{294}$$

where T_2 = temperature of gas stream + 273, and

$P_2 = P_{\text{atm}} + P_{\text{(gas stream)}}$.

The dry-gas meter is temperature compensated, so only pressure corrections are made for its readings and a temperature base of 21°C is used for calibration. Thus the true flowrate of the dry-gas meter (F_m) is

$$F_m = \text{Flow}_{\text{stp}} \times \frac{760}{P_3}$$

where $P_3 = P_{\text{atm}} + P_{\text{(gas stream)}}$.

The correction factor f to convert f_m , measured dry-gas meter flowrate, to true flowrate is then

$$f = \frac{f_m}{f_m} \quad .$$

The venturi and dry-gas meter were calibrated at three flowrates; 50, 55, and 60 ℓ/min . Normal system flowrates are 55 to 60 ℓ/min . The calibration factor for the dry-gas meter is constant at the calibration flows ($\pm 0.2\%$). The average value of flow from seven determinations is used in calculating true flowrates of the system. The plot of venturi ΔP versus flowrate follows a straight line over the range used in calibration. From the slope and intercept of the line flowrates were calculated.

APPENDIX D

WRITTEN COMMUNICATIONS WITH POTENTIAL COLLABORATORS

1 July 1974

Dear :

This confirms our selection of your organization as one of the 10 collaborators for the EPA-Sponsored Nitrogen Dioxide Collaborative Test Using The Continuous Colorimetric Method, and presents information about this test.

A copy of the "Tentative Method for the Determination of Nitrogen Dioxide In The Atmosphere (Continuous Colorimetric Procedure)," is enclosed for your study and retention. This write up is the same as the one I sent you 10 days ago with the exception of the revision (see Section 8.5 of the enclosed write up) that pertains to the use of reliable dynamic procedures other than the nitrogen dioxide permeation device for generating nitrogen dioxide can be used.

The test schedule is given in Table I. The starting date is Monday, 29 July 1974. We will meet in the Lobby of the Ramada Inn (see Figure 1, upper right-hand portion) which is located at 87th Street and Highway I-435. From there we will go to the field site which is several miles from the motel. At the site there will be an orientation program of the facilities prior to your preparing your instruments for sampling.

The schedule of Table I is based on the assumptions that all equipment of the collaborators will be on-site early Monday morning, and that all goes well during the week.

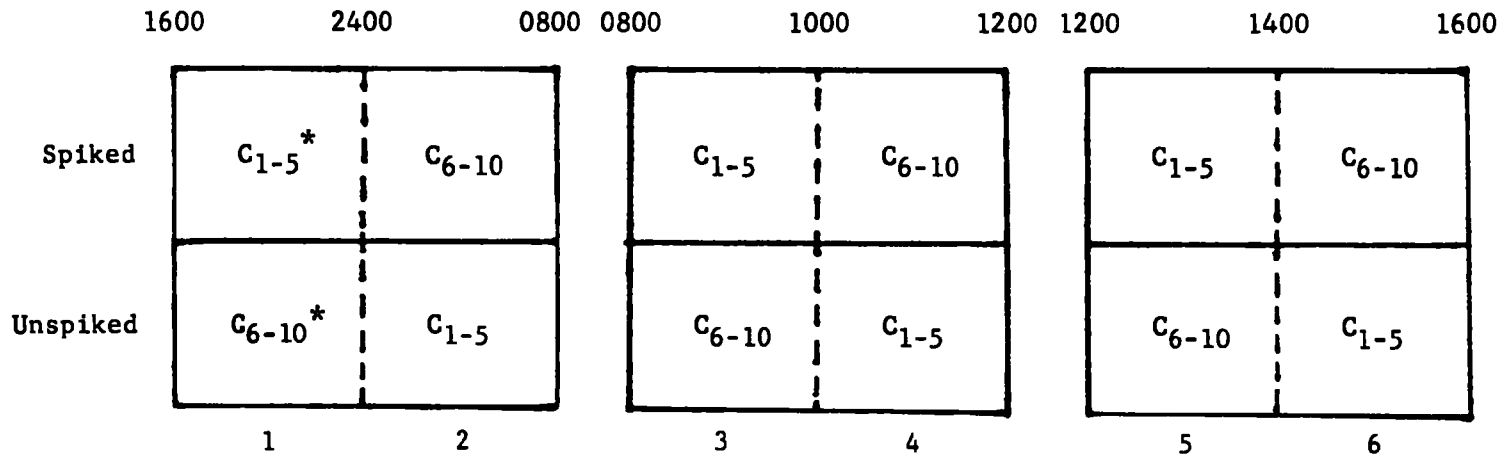
The sampling by each collaborator must be performed according to the attached write-up. You should calibrate your instrument both dynamically and statically (as a reference) at your home laboratory, and then use static calibrations in the field. Of course, if you choose to bring your dynamic system with you, then a static calibration at home is not required.

The sampling system that will be used in this collaborative test is shown in diagram form in Figure 2, an enclosure to this letter. Each collaborator will attach his instrument to ports of the spiked and unspiked manifolds according to a specific experimental design pattern, which is given in generality on the following page:

XXXXXXXXXXXX

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1 July 1974



* The particular partition of collaborators into two groups of five will be done randomly; for convenience, the groups are always labeled C₁₋₅ and C₆₋₁₀ in the diagram.

Enclosed is a Teflon adaptor. One of these adaptors constitutes a port of the sampling manifolds. It is the type of port to which you will attach your instrument. The larger-diameter end is the one to which an instrument is to be attached. This adaptor is being sent to you, as an enclosure, so that you will know what size tubing will be required for the connection of your instrument to the sampling manifolds. You will need at least 30 feet of this tubing.

The switching of your instrument between the spiked and unspiked lines will be done manually. During the night portion (1600-0800), MRI man on duty will do the switching. During the day, each collaborator will switch his device.

Each collaborator will be reimbursed for travel, subsistence, and lodging for the employee it sends to Kansas City to perform the field work as a collaborator, as well as miscellaneous expenses such as costs for shipping the field equipment you will use on site for the sampling. Please keep receipts such as airline tickets and equipment shipment invoices. Mr. Fred Damon, MRI Administrative Officer, will be contacting you to make contractual arrangements. If you have any questions you may contact him at (816) 561-0202.

Reservations will be made by MRI for each collaborator at the Ramada Inn. These lodging charges will be billed directly to MRI, therefore, you will need not consider this expense. Also, if you are not driving to Kansas City, but rather arrive by plane, MRI will provide local transportation.

XxxxxXxxXxxxxXx

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1 July 1974

Upon your arrival at the Kansas City International Airport call Econo-Car-Rent-A-Car Company at 464-5656 and you will be provided a car. As is the case of the motel, these changes will be billed directly to MRI.

If you are not driving and bringing your equipment with you, I suggest that you ship it a couple of weeks before the 29th of July so that it will be at MRI before 27 July. For your convenience, you could send it to yourself, % Mr. Paul C. Constant, Jr., Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, COD or prepaid.

To help us with preparations at this end, I would like the following information if you have not already given it to us:

1. The type and size (I.D.) of the connecting tubing you will bring with you to connect your instrument to the sampling manifolds.
2. The name of the person(s) from your organization who will be coming to Kansas City.
3. The mode of transportation the person will use to come to Kansas City (in case of airline, the airline and flight number), and the time of his arrival.
4. How your equipment will be sent to Kansas City and when it is expected to arrive.

Very truly yours,

Paul C. Constant, Jr., Head
Environmental Measurements Section

PCC:cdn

Enclosures:

1. "Tentative Method for the Determination of Nitrogen Dioxide In the Atmosphere."
2. Table I -- Test Schedule
3. Figure 1 -- Map: Ramada Inn to Field Station
4. Map -- Kansas City International Airport to Ramada Inn
5. Map -- Deramus Field Station
6. Figure 2 -- Nitrogen Dioxide Ambient-Air Sampling System Concept
7. Teflon Adaptor

APPENDIX E

GENERAL ANALYSIS OF VARIANCE

This appendix presents a brief description of the analysis of variance of the general linear statistical model. Due to the missing values inherent in the execution of the NO₂ collaborative Tests 3 and 4, this general analysis of variance was necessary in order to make the F-tests and estimate the components of variance. The first two NO₂ collaborative tests produced data sets that were standard balanced frameworks (factorials). Of course, the factorials for Methods 1 and 2 were special cases of the general linear model, and all NO₂ data sets could have been analyzed by the general analysis of variance. However, computing algorithms for particular cases exist that greatly reduce the labor involved, i.e., for many special cases of the general linear model it is not necessary to perform the analysis of variance "the long way."

Factorial experimental designs are, in fact, so convenient to analyze that the analysis of variance associated with them is often presented without reference to the general analysis of variance. In other words, certain particular cases of the general analysis of variance are so common that they have their own nomenclature. This means that the appearance of the statistical analyses for the NO₂ collaborative tests changes somewhat between Methods 1, 2 and Methods 3, 4. Therefore this appendix is offered to help the reader understand the statistical analyses performed for all NO₂ collaborative tests.

The general analysis of variance rationale will be presented first,* and the "special case" effects pointed out second.

The general linear statistical model supposes that a "response" (y) is predictable from knowledge of the levels of some "treatments" (T,B)** but that a random error (e) is associated with observing the response. That is, the model is of the form:

$$Y_{ijk} = \mu + T_i + B_j + e_{k(ij)}^{***} ,$$

* This subject is treated more compactly with the aid of matrix notation. However, the presentation here will avoid the use of matrices for the sake of simplicity.

** Two treatments are sufficient to illustrate the concepts involved; obviously, the discussion could be generalized to K treatments.

*** Including interaction terms would only complicate the discussion.

where μ = overall mean;

T_i = i^{th} level of T; $i = 1, \dots, I$;

B_j = j^{th} level of B; $j = 1, \dots, J$;

$e_k(ij)$ = "measurement" error associated with ijk^{th} response;
 $k = 1 \dots K$ for every ij ; and

Y_{ijk} = ijk^{th} response.

It is assumed that the e 's have independent normal distributions with mean zero and variance σ_e^2 , i.e., the "measurement" error is unbiased and of the same size everywhere. Note that since e is a random variable, Y is also a random variable. Therefore functions of the sample Y_{ijk} 's have probability distributions.

Suppose that the object of collecting data is to make "proper" estimates of the $I + J + 1$ parameters μ , $\{T_i\}$, $\{\beta_j\}$. By proper we mean estimates that satisfy some sensible criteria. The criteria used in this case is that of least squares, i.e., the parameters are estimated such that $\sum_{ijk} e^2_{ijk}$ is minimized. In other words, the parameters are assigned so that the measurement error (residual variation) is minimized. Formally minimizing $\sum_{ijk} e^2_{ijk}$ (via setting the partial derivative equal

to zero) produces a set of $I + J + 1$ simultaneous equations (in μ , $T_1 \dots T_I$, $\beta_1 \dots \beta_J$). The solution to this set of "normal equations" therefore furnishes the prediction equation for Y_{ijk} . Also, the size of the error variability can be estimated now, i.e., the (sample) variance of the Y_{ijk} 's is now partially "explained" by μ , $\{T_i\}$, $\{\beta_j\}$. Whatever is left over is "unexplained" variability. So setting up and solving the normal equations furnishes: (1) an estimate of the model parameter and (2) an estimate of unexplained variability, σ_e^2 .

Now suppose that some hypothesis is of interest, e.g., $H_0: T_1 = T_2 = \dots = T_I$. This hypothesis, in effect, dictates a "reduced" model $Y_{ijk} = \mu + T + \beta_j = e_{(ij)k}$, i.e., under the null hypothesis there are not I individual T parameters but instead only one common T parameter. Obviously, the reduced model has to explain less of the variability in Y than the other ("alternative") model did. So going through the same procedure of constructing and solving a set of normal equations for the reduced model produces another estimate of σ_e^2 ($\sigma_e^{2'}$, say), and $\sigma_e^{2'} \geq \sigma_e^2$. Now if $\sigma_e^{2'}$ is $\approx \sigma_e^2$, then the hypothesis is reasonable because the model works about as well when the T_i 's are constrained to equality as when they are not. (The actual test statistic involved

is an F-ratio but it is not pertinent to consider how to derive the F-ratio here.) Now, suppose $H_0: T_1 = \dots T_I$ had been tested and it is now desirable to test $H_0: \beta_1 = \dots \beta_J$; this is possible of course but in general it requires another set of normal equations and their solutions; namely, the σ_e^2 estimate (σ_e^2 say) from the model $Y_{ijk} = \mu + T_i + \beta_j + e_{(ij)k}$. Usually these two hypotheses are the interesting ones but an infinitude of others (e.g., $\beta_3 = \pi$, $\beta_1 = 2.6 \beta_2$, even $T_3 = \beta_2 - \beta_1$, etc.) could be tested.

Summing up, then, in the general lineal model a set of normal equations is generated (according to the least squares criteria) and solved, and the solution "explains" a proportion of the variability in the response. The unexplained proportion is represented by σ_e^2 (the "residual" variance). A hypotheses, usually of equality, dictates a reduced model and thus another σ_e^2 , and the comparison of σ_e^2 and σ_e^2 decides whether or not the hypothesis is reasonable.

Except there is a catch. The system of normal equations is over determined, i.e., the system of $I + J + 1$ normal equations discussed previously contains only $(I-1) + (J-1) + 1 = I + J - 1$ independent equations. Thus there are infinite number of solutions to any set of normal equations. All solutions, of course, necessarily explain the same fraction of the data, i.e., result in the same value of estimated σ_e^2 . Therefore, any solution suffices to test hypotheses of the form $H_0: T_1 = \dots + T_I$, etc.

In other words, any solution to the normal equations allows estimation of σ_e^2 and the decision $H_0: T_1 = \dots = T_I$? But suppose H_0 is rejected, i.e., not all T's are equal. Now it is certainly desirable to have the T estimates "mean something" physically, e.g., although setting $T_6 = \text{any value}$ would test H_0 , it would make the parameter estimates in the prediction equation weird.

Now consider the situation from a slightly different viewpoint. The normal equation are of dimension $I + J + 1$ in the parameters $\mu \{T_i\}$, $\{\beta_j\}$, but only $I + J - 1$ independent estimates can be extracted from them. In statistical jargon, there are only $I + J - 1$ independent "estimable" functions. A statistical theorem says that the only linear combinations of the T_i that are estimable are contrasts of the T_i 's.* Using this theorem it can be shown that, for example, setting $T_I = 0$ and solving the normal equations for T_1, \dots, T_{I-1} results in the $T_{i,i} < I$ solutions being estimates of $T_i - T_I$, i.e., after setting $T_I = 0$ in the normal equations and solving for T_3 (say), the numerical value of T_3 is a proper estimate of the quantity $T_3 - T_I$. In fact, setting $T_I = 0$ (and $\beta_J = 0$, I am ignoring the other treatment

* Other functions of the parameters are also estimable, but in general to have physical meaning one wants to stick to one variable (the T's or β 's in our example) at a time.

for simplicity) is a convenient constraint and is the usual procedure for solving normal equations. When the general analysis of variance is necessary as in the 3rd and 4th NO₂ collaborative tests, then, the results are estimates of from $T_i - T_I$, for example, the $C_1 - C_{10}$ estimates for collaborator differences, etc.

So far we have considered the original statistical model to generate an $I + J + 1$ system of normal equations that require two constraints, i.e., have only $I + J - 1$ independent equations. Another way to approach the situation is to change the model itself so that the normal equations have a unique solution; i.e., put the constraints in beforehand, so to speak. This approach is called "reparametrization." There are, as one would expect, an infinite number of ways to reparametrize a model, but one method is standard because it is convenient and does not confuse the physical interpretation of the new model. Consider the original model $Y_{ijk} = \mu + T_i + \beta_j + e_k(ij)$, but rewrite the equation as:

$$Y_{ijk} = (\mu + \bar{T}_\cdot + \bar{\beta}_\cdot) + (T_i - \bar{T}_\cdot) + (\beta_j - \bar{\beta}_\cdot) + e_k(ij), \text{ or}$$

$$Y_{ijk} = \mu^* + T_i^* + \beta_j^* + e_k(ij),$$

where now $\sum_i T_i^* = 0$ and $\sum_j \beta_j^* = 0$.

This is a valid reparametrization, i.e., the normal equations have a unique solution for μ^* , $\{T_i^*\}$, $\{\beta_j^*\}$, and the new parameters are meaningful since T_i^* estimates the difference between T_i and its mean. The reparametrization, in effect, uses $\sum T_i^* = 0$ and $\sum \beta_j^* = 0$ as the two constraints. Unfortunately, where this reparametrization is used the results, by custom, are not presented as T_i^* but merely as T_i 's and the reader is supposed to remember that " $\sum T_i$ " = 0. Therefore it is natural to suspect that something has changed when the results of the reparametrized model are presented as compared to the results from the original model using $T_I = 0$ and $\beta_j = 0$.

It is easier to solve normal equations by setting $T_I = 0$ (and $\beta_j = 0$) than it is to reparametrize, i.e., when executing the general analysis of variance the easiest estimates to get are the $T_i^{\wedge} - T_I$'s. But in special cases like balanced factorials the normal equations are trivially easy to solve under the above reparametrization. In fact, the solution is so trivial that the normal equations are not even written down, but the reparametrization is in effect, i.e., the constraints $\sum T_i^* = 0$, $\sum \beta_j^* = 0$ are used.

Perhaps a numerical example will clarify the situation. Consider the following data set:

	T ₁	T ₂	T ₃	
β ₁	Y ₁₁₁ = 1 Y ₁₁₂ = 2	4 6	8 10	31
β ₂	2 3	5 6	9 9	34
β ₃	1 3	3 5	8 11	31
	12	29	55	96

This data set is balanced (a 3 x 3 factorial with 2 observations per cell), but we will not take advantage of any shortcuts in order to illustrate all the concepts involved. The complete set of normal equations is:

$$18 \mu + 6 T_1 + 6 T_2 + 6 T_3 + 6 \beta_1 + 6 \beta_2 + 6 \beta_3 = 96.$$

$$6 \mu + 6 T_1 + 2 \beta_1 + 2 \beta_2 + 2 \beta_3 = 12.$$

$$6 \mu + 6 T_2 + 2 \beta_1 + 2 \beta_2 + 2 \beta_3 = 29.$$

$$6 \mu + 6 T_3 + 2 \beta_1 + 2 \beta_2 + 2 \beta_3 = 55.$$

$$6 \mu + 2 T_1 + 2 T_2 + 2 T_3 + 6 \beta_1 = 31.$$

$$6 \mu + 2 T_1 + 2 T_2 + 2 T_3 + 6 \beta_2 = 34.$$

$$6 \mu + 2 T_1 + 2 T_2 + 2 T_3 + 6 \beta_3 = 31.$$

We need to solve these normal equations, and then we need the new set under H_0 , where H_0 is (say) $H_0: T_1 = T_2 = T_3$. Looking at the normal equations, though, we see that if $\sum T_i = 0$ and $\sum \beta_j = 0$, the solutions are obvious. For example, the first equation yields $\hat{\mu} = 96/18$, the second equation yields $\hat{\mu} + \hat{T}_1 = 12/6$, i.e., $\hat{T}_1 = 12/6 - 96/18$, etc. Thus, for this balanced data set, the normal equations can be solved by inspection under the constraints $\sum T_i = 0$, $\sum \beta_j = 0$, i.e., with reparametrization. Also, under the null hypothesis $H_0: T_1 = T_2 = T_3$ (say), the reduced normal equations are also solvable by inspection, and in fact yield the same β_j estimates. In statistical jargon, the "adjusted" β reduction equals the "unadjusted" β reduction, consequently in balanced designs like this the AOV table shows a row for the β_{ss} , i.e., since β_{ss} is the same adjusted and unadjusted, it is just called the β_{ss} .

So we see that the reparametization (i.e., the constraints $T_i^* = 0$, $\beta_j^* = 0$) allows an easy solution to all pertinent normal equations. (In fact, it is so easy that methods books for such analyses omit the subject of normal equations altogether.)

But now suppose the observation Y_{112} was missing.* Then the normal equations would be: (1) $\mu + 5 T_1 + 6 T_2 + 6 T_3 + 5 \beta_1 + 6 \beta_2 + 6 \beta_3 = 94$; (2) $5 \mu + 5 T_1 + \beta_1 + 2 \beta_2 + 2 \beta_3 = 10$, etc. Obviously, the constraints $\sum T_i = 0$, $\sum \beta_j = 0$ are not particularly helpful in solving these normal equations. The constraints $T_3 = 0$, $\beta_3 = 0$ are handier. So these constraints would be used, and as a result the numerical solution for T_1 (say) would be an estimator of $T_1 - T_3$, etc. Also, the reduced set of normal equations (under H_0 : $T_1 = T_2 = T_3$) remains to be solved, i.e., there are adjusted and unadjusted sums of squares to compute.

In summary any statistical model of the form $Y_{ijk} = \mu + T_i + \beta_j + e_{k(ij)}$, $i = 1, \dots, I_j$, $j = 1, \dots, J$ produces: (1) a residual variation σ_e^2 for the model and a residual variation $\sigma_e^{2'}$ for the model constrained by hypotheses of the form H_0 : $T_1 = \dots = T_I$, (2) a statistical test for H_0 , and (3) $I - 1$ (independent) estimates of differences among the $\{T_i\}$, $J - 1$ independent estimates of differences among the $\{\beta_j\}$. In particular, which $I - 1$ estimates are produced depends upon whether or not the design is balanced. In general, the $I - 1$ $\widehat{T_1 - T_I}$ estimates are the easiest to obtain, but in a balanced design the T_i^* 's subject to the constraint $\sum_i T_i^* = 0$ are the easiest to obtain, i.e., the new T_i^* 's ($T_i^* = T_i - T$) are easier to estimate than differences among the original T_i 's.

Unfortunately for the sake of clarity, balanced designs are such an important special class of linear models that, to some extent, they have their own nomenclature.

In particular, in balanced designs the parameter estimates are estimates of differences between treatment levels and their mean, but this is not shown in the AOV table. Also, adjusted and unadjusted estimates are equal so the words adjusted and unadjusted are not used.

This appendix intends only to resolve the apparent differences in the form of the results for the first two collaborative tests. Actually, even in the general case the analysis of variance does not require solution of both the null and alternative normal equations, i.e., by subtraction among sums of squares one can test H_0 : $T_1 = \dots = T_I$ by solving only one system of normal equations. Also, the analysis of variance produces components of variance estimates that are not discussed here, interaction effects can be included, etc.

* "Fudging" rules of thumb exist for such slight distortions of balance, but this is not germane to the discussion.

APPENDIX F

INSTRUCTIONS FOR COLLABORATORS NO₂ COLLABORATIVE TEST:

CONTINUOUS-COLORIMETRIC PROCEDURE

General Information

1. Calibration, sampling, analysis, etc., should be done explicitly as stated in the June 1974 write-up furnished you on the "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere," (Continuous-Colorimetric Method).

2. Each collaborator will have an area for his analyzer on one or the other table. Use of connecting tubing to the opposite table will enable alternate sampling of the spiked and unspiked manifolds by each collaborator.

3. For each run, each collaborator will connect his analyzer to either the unspiked manifold or the spiked manifold, according to the instructions given before the run. Heavier tubing, for those collaborators whose instruments require higher flow rates is available in several areas of both the spiked and unspiked side. Please ask the MRI person in charge concerning use of the heavier tubing.

4. Collaborators are urged to make ample explanatory notes on their analyzer charts to coordinate information and aid in data reduction. All pertinent data should appear on the charts.

5. Each collaborator should work independently of other collaborators.

6. On the spiked table, a separate power circuit (120 v 60-cycle, four-outlet strip) is to be used by each collaborator for his analyzer. On the unspiked side one strip will be shared by two collaborators where necessary. These strips are under the table tops near the periphery of the tops.

Test Instructions

1. Preparation by collaborators will precede sampling runs.

2. Analyzer calibration will be included in preparation time, not to be done during the run.

3. Upon notification of "start testing" from the MRI person on site, collaborators will mark the appropriate place on their analyzer charts. It is expected that the analyzer will be operating and the connecting tubing in proper hook-up arrangement prior to the start signal.

4. Note all pertinent data on the analyzer charts as the run progresses.

5. Upon notification by the MRI person in charge, indicate the end of the run by marking on the analyzer chart.

General Schedule

There will be two runs per each of four 24-hr periods. The duration of one run will be approximately 14 hr; the other will be 7 hr. For the 14-hr runs, all collaborators will sample from the spiked manifold. For the 7-hr runs, each collaborator will sample from each manifold--spiked and unspiked--for approximately 3-1/2 hr.

The hours 0800-1630 on Monday, 29 July are for collaborator preparation. From then on testing will be according to the following schedule:

<u>Time</u>	<u>Activity</u>	<u>Spiked Line</u>	<u>Unspiked Line</u>
1630-1800	Calibrate	-	-
1800-0800	Sample	1 through 10	-
0800-0930	Calibrate	-	-
0930-1250	Sample	4, 6, 7, 8, 10	1, 2, 3, 5, 9
1250-1310	Switch lines	-	-
1310-1630	Sample	1, 2, 3, 5, 9	4, 6, 7, 8, 10

The numbers given in the spiked and unspiked columns are the collaborators' I.D. numbers. (See attached table for your number.)

**COLLABORATOR ANALYZER LOCATION AREAS
AND PRINCIPLE PORT ASSIGNMENTS**

<u>Collaborator</u>		<u>Spiked Table</u>		<u>Unspiked Table</u>	
<u>I.D. No.</u>	<u>Name</u>	<u>Area</u>	<u>Ports</u>	<u>Area</u>	<u>Ports</u>
1	Ken Smith	--	--	1	32-37
2	Lynn Hutchinson	2	1-6	--	--
3	Harold Davis	--	--	3	26-31
4	Glenn Smith	4	7-12	--	--
5	John Higuchi	--	--	5	7-12
6	Norman Lewis	6	13-18	--	--
7	Cleveland Dodge	--	--	7	1-6
8	Rolf Doebbeling	8	26-31	--	--
9	Cole McKinney	--	--	9	38-43
10	Larry Saad	10	38-43	--	--

NOTE: Assignments of secondary ports (on the opposite table from the analyzer location) will be made prior to the start of each test.

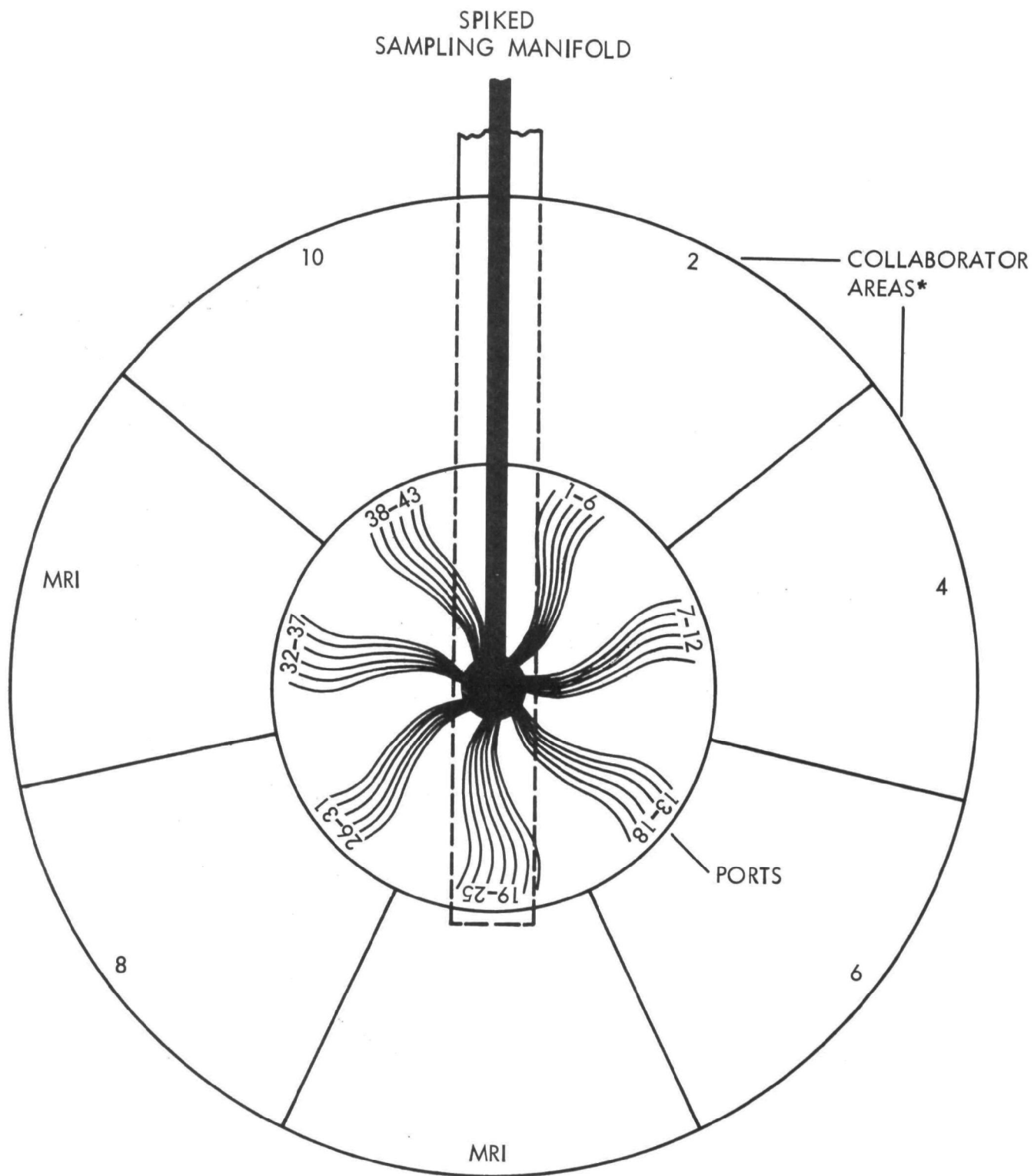


Diagram illustrating the layout of a circular MRI scanner, showing the distribution of Collaborator Areas and Ports.

The diagram is a circular cross-section divided into sectors by radial lines. The sectors are labeled with numbers: 1, 3, 5, 7, 9, and 13. The sectors 1, 3, 5, 7, and 9 are labeled "COLLABORATOR AREAS*". The sectors 13 and 25 are labeled "PORTS".

A central vertical line represents the "MRI" magnet. A dashed vertical line indicates the "COLLABORATOR AREAS*". A central circular area contains a complex pattern of lines representing the "PORTS".

APPENDIX G

NO₂ AMBIENT-AIR SAMPLING SYSTEM OPERATION DATA: TEST LOG SHEETS WITH
FIELD OPERATIONAL DATA

LOG SHEET

Run 1

Side 2

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
TIME	1515	193	300	413	521	630	740	850	960	1070	1180	1290	1400	1510	1620	1730	1840	1950	2060	2170	2280	2390	2500	2610	2720
NO ₂ ANALYZER - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
VAC PRESSURE	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
O ₂ PRESSURE	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
UNSPIKED - NO	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
NO ₂	3	3	4	8	11	11	13	13	14	18	2	7	1	10	11	14	4	2	2	2	2	2.5	2.5	2.5	2.5
SPIKED - NO	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
NO ₂	17	17	18	23	25	24	25	27	23	23	21	21	21	21	23	20	18	16	16	16	16	17	17	16	16
VENTURI MANOMETER - HI	502	502	506	505	504	506	509	511	513	513	513	513	513	513	508	511	509	505	505	504	508	500	500	499	499
LO	235	232	231	232	232	229	228	226	223	223	224	224	223	223	230	227	224	234	231	237	236	236	238	240	240
VENTURI ΔP	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7
INDOOR TEMP.	22	23	23	23	23	23	23	23	23	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22
GAS FLOW TEMP.	21.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5
GAS FLOW MANOMETER - HI	508	510	510	510	510	510	510	511	511	511	511	511	511	511	511	511	511	509	509	509	508	507	507	506	506
LO	391	391	391	391	391	391	391	391	391	391	391	391	391	391	391	391	391	391	391	391	391	391	391	391	391
GAS FLOW PRESSURE	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11
EXHAUST - U MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
S MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CHECK SAMPLE TRAINS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
INITIALS	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL	JRL

SPINED

LOG SHEET

Side 1

CLEAR

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DATE	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24	1/24
TIME	1800	1900	2000	2100	2200	2300	2400	0100	0200	0300	0400	0500	0600	0700	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	
OUTDOOR TEMP.	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54
WET BULB	53	52	51	50	49	48	47	46	45	44	43	42	41	40	39	38	37	36	35	34	33	32	31	30	29
DRY BULB	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54	54
REL. HUMIDITY	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%	26%
BAR. PRESSURE	738	738	738	738	738	738	738	738	738	738	738	738	738	738	738	738	738	738	738	738	738	738	738	738	738
WIND SPEED	18	24	05	00	00	00	00	00	00	00	00	00	00	00	00	00	00	00	00	00	00	00	00	00	00
WIND DIRECTION	NW	NW	NW	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
POWER LIGHTS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
LEAKS PERMEATION ASSEMBLY	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
BATH TEMP.	25.1		25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1
ROTAMETERS - 1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101
3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
N ₂ PRESSURE	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K
RECORDER 1 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
RECORDER 2 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

LOG SHEET *RUN 2*

Side 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DATE	7/30	7/30	7/30	7/30	7/30	7/30	7/30	7/31	7/31	7/31	7/31	7/31	7/31	7/31	7/31	7/31	7/31	7/31	7/31	7/31	7/31	7/31	7/31	7/31	7/31
TIME	1800	1900	2000	2100	2200	2300	2400	0100	0200	0300	0400	0500	0600	0700	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	
OUTDOOR TEMP.	90	88	89	81	79	75	73	72	72	72	71	71	70	68	70	77	81	85	90	94	95	92	94	94	
WET BULB	64	63	62	61	65	59	58	53	53	53	52	51	51	57	59	64	66	68	69	70	69	70	71	70	
DRY BULB	90	88	89	81	79	75	73	72	72	72	71	71	70	68	70	77	81	85	90	94	95	92	94	94	
REL. HUMIDITY	22%	20%	19%	30%	46%	37%	59%	42%	42%	42%	45%	44%	58%	58%	58%	48%	42%	40%	32%	29%	29%	32%	26%	36%	
BAR. PRESSURE	738	738	738	738	739	739	739	739	739	739	739	739	739	739	739	739	739	739	739	739	739	739	738	738	
WIND SPEED	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0	1	0	0	1	1 1/2	1.5	0.9	0.5	1.0	1.8	1.4	1.6	1.7	.4	.7	
WIND DIRECTION	W	W	W	W	W	W	W	W	W	SE	W	W	SE	SE	SE	SE	SE	S	SE	SE	SW	SW	NE	NE	
POWER LIGHTS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
LEAKS PERMEATION ASSEMBLY	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
BATH TEMP.	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.2	25.2	25.2	25.2	25.2	25.2	25.1	25.1	
ROTAMETERS - 1	98	99	98	98	99	99	99	99	99	99	99	99	99	99	98	97	97	97	96	97	96	96	97	97	
2	100	100	100	100	100	100	100	100	100	100	100	100	100	100	99	98	98	98	97	98	97	97	99	99	
3	99	99	98	99	99	99	99	99	99	99	99	99	99	99	98	97	97	97	96	97	97	98	97	97	
4	100	100	99	100	100	100	100	100	100	100	100	100	100	100	99	98	98	98	97	98	98	98	99	99	
N ₂ PRESSURE	1.7K	1.7K	1.6K	1.6K	1.6K	1.6K	1.6K	1.55K	1.53K	1.55K	1.55K	1.55K	1.55K	1.55K	1.49K	1.47K	1.45K	1.44K	1.44K	1.39K	1.37K	1.36K	1.35K	1.35K	
RECORDER 1 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
RECORDER 2 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	

LOG SHEET

Side 2

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
TIME	1500	1600	1700	1800	1900	2000	2100	2200	2300	2400	2500	2600	2700	2800	2900	3000	3100	3200	3300	3400	3500	3600	3700	3800	3900
NO ₂ ANALYZER - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
VAC PRESSURE	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
O ₂ PRESSURE	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
UNSPIKED - NO	1	1	1	1	1	1	4	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
NO ₂	3	3	5	5	7	11	13	2	5	7	7	6	4	6	6	4.5	4	3	3	3	2	2	3	3	3
SPIKED - NO	1	1	1	1	1	1	1	4	2	1	1	1	1	1	1	1	1.5	1	1	1	1	1	1	1	1
NO ₂	39	40	41	42	42	48	43	46	44	46	46	51	37	39	42	40	39	38	38	39	38	39	39	39	26
VENTURI MANOMETER - HI	497	500	502	503	503	503	507	504	510	511	511	512	512	511	509	508	509	505	504	501	500	501	495	497	
LO	239	236	239	233	233	233	229	227	226	225	225	224	221	215	228	230	231	235	238	239	240	242	240	240	
VENTURI ΔP	258	254	258	253	253	253	257	255	254	256	256	255	252	246	250	250	251	252	252	252	252	252	252	252	252
INDOOR TEMP.	23.5	24	24	23	24	23	24	23	23	22.5	22	22	22	22	22.5	23	23	23.5	23.5	24	24.5	24.5	24	24	
GAS FLOW TEMP.	23.5	23.5	23.5	23	23	23	22.5	22.5	22	22	22	22	22	22	22.5	23.0	23.2	23.5	23.8	23.5	24	24	23.5	23	
GAS FLOW MANOMETER - HI	506	506	508	508	508	508	509	510	510	511	511	511	510	511	511	510	511	509	509	507	506	509	505	505	
LO	391	391	390	390	390	390	389	388	388	388	388	388	388	388	388	389	388	390	390	393	393	390	392	391	
GAS FLOW PRESSURE	115	115	117	115	115	115	115	115	115	115	115	115	115	115	115	115	115	115	115	115	115	115	115	115	
EXHAUST - U MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
S MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CHECK SAMPLE TRAINS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
INITIALS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS	DS
GAS METER FLOW 2 REV. (sec.)	58.3	57.8	57.6	56.9	57.4	56.8	56.3	56.2	56.2	56.2	56.2	56.2	56.2	56.2	56.2	56.2	56.2	56.2	56.2	56.2	56.2	56.2	56.2	56.2	56.2

LOG SHEET *P tubes* Run#3 1-3-4

Side 2

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
TIME	1800	1900	2000	2100	2200	2300	2400	0100	0200	0300	0400	0500	0600	0700	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800
NO ₂ ANALYZER - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
VAC PRESSURE	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
O ₂ PRESSURE	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
UNSPIKED - NO	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
NO ₂	3	3	4	4	3	3	2	3	3	4	3	3	4	4	4	4	4	3.5	3.5	4	2	2	2	3	
SPIKED - NO	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
NO ₂	25	25	26	25	25	25	20	24	25	25	24	25	26	26	26	25	25	25	25	24	25	24	24	10	
VENTURI MANOMETER - HI	498	499	503	503	504	503	505	505	507	507	507	507	507	507	506	511	507	505	504	505	506	507	505	507	
LO	238	237	233	233	232	233	231	231	230	230	230	230	230	230	232	231	230	231	231	231	231	234	235	233	
VENTURI ΔP	260	262	270	270	272	270	274	271	271	271	272	271	271	271	274	274	270	270	270	270	270	270	270	270	
INDOOR TEMP.	24	24	24	24	24	24	24	25	23	24	23	23	23	23	23	23.5	22.5	21.5	21	21	24	24	24	24	
GAS FLOW TEMP.	23.5	23.5	23.5	23.5	23	23	22.5	24.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	23	23	23	23.5	23.5	23.5	23.5	23.5	
GAS FLOW MANOMETER - HI	506	506	507	507	508	508	508	509	509	509	509	509	509	509	508	509	509	508	508	508	509	508	508	507	
LO	390	390	389	389	388	388	388	387	387	387	387	387	387	387	389	389	390	387	387	387	389	389	389	390	
GAS FLOW PRESSURE	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	
EXHAUST - U MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
S MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CHECK SAMPLE TRAINS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
INITIALS	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE

LOG SHEET Run # 3

Side 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DATE	7/31	7/31	7/31	7/31	7/31	7/31	7/31	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1
TIME	1800	1900	2000	2100	2200	2300	2400	0100	0200	0300	0400	0500	0600	0700	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	
OUTDOOR TEMP.	90	88	85	83	80	80	77	78	77	77	74	74	74	73	74	77	77	77	80	82	86	86	87	91	83
WET BULB	70	68	68	67	65	65	67	67	66	65	66	66	64	65	66	67	67	68	70	70	67	69	69	69	67
DRY BULB	90	88	85	83	80	80	77	78	77	77	74	74	74	73	74	77	77	77	80	82	86	86	87	91	83
REL. HUMIDITY	35%	35%	41%	40%	44%	44%	47%	57%	56%	52%	54%	65%	56%	65%	65%	59	59%	54%	51%	44%	41%	42%	32	44	
BAR. PRESSURE	737	737	737	737	737	738	738	737.5	737.5	737.5	737.5	737.5	737.5	737.5	738	738	738	738	738	737	737	737	737	737	737
WIND SPEED	3.2	2.2	2.0	2.0	2.4	2.2	2.4	3.0	1.7	2.4	1.5	0	1	1	2.4	0.9	0	0.9	2.4	1.6	1.9	0.6	0.2	-	
WIND DIRECTION	E	E	E	E	E	E	E	E	E	E	E	-	E	E	E	S	-	SE	SE	SE	SE	SE	SE	SE	0
POWER LIGHTS	✓	✓	✓	✓	✓	✓	✓	✓	-	✓	-	-	✓	✓	✓	-	-	✓	✓	✓	✓	✓	✓	✓	✓
LEAKS PERMEATION ASSEMBLY	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
BATH TEMP.	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1
ROTAMETERS - 1	97	97	97	98	98	97	97	97	97	97	97	97	97	97	97	97	97	96	95	-	96	96	95	99	
2	N/A																								
3	97	97	97	98	98	97	97	97	97	97	97	97	97	97	97	96	96	95	95	-	95	95	95	99	
4	98	98	98	99	99	99	99	99	99	99	99	99	99	99	98	97	98	97	95	-	96	96	96	100	
N ₂ PRESSURE	1.3K	1.3K	1.3K	1.3K	1.3K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K	1.2K
RECORDER 1 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	-	✓	-	-	-	-	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
RECORDER 2 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

*SPECIAL
CUTTING

Rain

Run 4

LOG SHEET

Side 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DATE	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1	8/1
TIME	1800	1900	2000	2100	2200	2300	2400	0100	0200	0300	0400	0500	0600	0700	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800
OUTDOOR TEMP.	76	77	76	74	72	71	66	70	69	68	66	68	68	69	69	72	73	72	71	70	68	67	67	67	67
WET BULB	68	69	68	68	66	65	64	65	65	65	65	64	64	64	66	67	66	67	68	68	67	67	67	67	67
DRY BULB	76	79	76	74	72	71	66	70	69	68	66	68	68	69	69	72	73	72	71	70	68	67	67	67	67
REL. HUMIDITY	66%	57%	66%	74%	73%	72%	90%	17%	89%	85%	85%	87%	87%	85%	83	77%	69%	71%	71%	71%	71%	71%	71%	71%	71%
BAR. PRESSURE	736	736	735	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736
WIND SPEED	2.8	0.0	0.0	0.0	0.6	0.0	0.0	0	0	0	0	0	0	0	0	0	1.6	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
WIND DIRECTION	ESE	-	-	-	NE	-	-	-	-	-	-	-	-	-	-	-	NW	SW	SW	SW	SW	SW	SW	SW	SW
POWER LIGHTS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
LEAKS PERMEATION ASSEMBLY	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
BATH TEMP.	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1
ROTAMETERS - 1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	101	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
N ₂ PRESSURE	950	925	900	900	875	860	850	850	850	850	850	850	850	850	850	850	850	850	850	850	850	850	850	850	850
RECORDER 1 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
RECORDER 2 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

LOG SHEET

Side 2

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
TIME	1800	1900	2000	2100	2200	2300	2400	0100	0200	0300	0400	0500	0600	0700	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800
NO ₂ ANALYZER - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
VAC PRESSURE	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
O ₂ PRESSURE	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
UNSPIKED - NO	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
NO ₂	3	4	6	6	6	6	6	8	5	7	5	4	5	6	7	8	4	7	2	2	2	2	2	2	2
SPIKED - NO	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
NO ₂	10	10	11	12	16	12	12	13	15	11	14	11	11	11	13	15	11	11	11	9	8	5	5	5	5
VENTURI MANOMETER - HI	505	505	505	505	505	507	508	511	513	513	513	513	512	512	512	509	508	507	511	511	511	505	504	506	506
LO	230	230	230	230	230	228	229	226	229	226	226	226	223	223	223	227	229	229	227	227	232	233	233	233	233
VENTURI ΔP	275	275	275	275	275	275	279	275	275	275	275	275	275	275	275	275	275	275	275	275	275	275	275	275	275
INDOOR TEMP.	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23
GAS FLOW TEMP.	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23
GAS FLOW MANOMETER - HI	508	508	508	508	508	508	508	509	510	510	510	510	510	510	510	509	508	510	510	510	508	508	508	508	508
LO	338	338	338	338	338	338	338	347	344	344	344	344	344	344	344	343	342	344	344	344	342	342	342	342	342
GAS FLOW PRESSURE	125	125	125	125	125	125	125	125	125	125	125	125	125	125	125	125	125	125	125	125	125	125	125	125	125
EXHAUST - U MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
S MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CHECK SAMPLE TRAINS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
INITIALS	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL

APPENDIX H

COLLABORATORS COMMENTS

Collaborator A

1. Solution flow fell off towards the end, resulting in several no record areas. Bubbles were entering the flow cell causing fake high or low readings.

2. Recording of known permeation rate remained constant throughout the test, as did wet standards.

3. Base-line drift was erratic changing at random. This changing did not seem to affect response or calibration while in an operational mode.

4. When I returned, re-calibration of the instrument indicated drastic changes in instrument response. I will not report this re-calibration since something, as yet not defined, has definitely altered.

Collaborator J

Our instrument was dynamically calibrated prior to the tests. The sensitivity of the instrument was set for 1% full scale responded equivalent to 0.0025 ppm NO₂. Static calibrations were run during the testing for indicating references only. No adjustments were made to change the span sensitivity during the test period.

Base-line calibrations were run during the testing, and reset when needed. The standard value used for the base line was 5% of full scale. No correction was incorporated in the data for apparent drift during a test run.

Collaborator I

The value for each run was obtained by taking readings every 15 min and averaging the result. The flowrate was varied in order to accommodate the higher concentrations.

Collaborator E

The use of a planimeter for the number of measurements required was impractical. However, the reeuction to hourly averages allowed a fairly accurate determination of mean responses by estimating the square wave which would give the same area as the actual response. The square wave was determined by the horizontal line drawn through the actual response curve at the point where it was estimated that the area below the line and above the actual curve was equal to the area above the line and below the actual curve.

Collaborator G

Because a NO₂ permeation tube was not available at the time, the Beckman (K-1008) was calibrated indirectly using a Bendix calibrator (8851) in conjunction with a Bendix NO - NO₂ - NO_x (8101B) Chemiluminescent analyzer.

Our first step consisted of calibrating the NO and NO_x mode of the Bendix analyzer with the Bendix calibrator and a 99.0 ppm NO gas as a source.

Next, some of the NO gas was converted to NO₂ by mixing it with ozone generated by the Bendix calibrator.

The amount of NO₂ produced was determined by subtracting the final NO concentration from the initial NO concentration; assuming that the difference has been converted to NO₂. The sample stream was then introduced into the Beckman analyzer and an attempt to adjust the infinity control to the concentration indicated by the Bendix analyzer was made.

There are some potential inaccuracies in this method of calibration; it does not allow for error within the equipment itself nor does it take into account NO₂ contamination of the calibration gas. (Because the gas is certified as to purity, this error should be insignificant.)

Initially it was discovered that the Beckman analyzer was reading 20.5% higher than the Bendix analyzer; and all attempts to adjust the Beckman machine to a value that corresponded with the Bendix were futile.

At the time it was believed that there was not enough electronic adjustment on the Beckman analyzer to set an NO₂ value corresponding to the Bendix analyzer; however, at the MRI testing site, it was discovered that the solution pump had developed a leak, which resulted in displacing solution with air. In addition, it was determined that, the lowering of the solution flow from 20 ml/20 min to 15 ml/20 min resulted in a sharp increase of color development in the reagent and in an apparent high NO₂ concentration.

The Beckman analyzer has since been recalibrated using the corrected solution flow (20 ml/20 min) and this time the readout of NO₂ concentrations from the Beckman and Bendix machines corresponded closely. This can be verified from the attached calibration curve.

The data from 6:00 p.m. Monday to 8:00 a.m. Tuesday and from 6:00 p.m. Wednesday to 8:00 a.m. Thursday should be deleted because of the excessive optical drift experienced by the equipment during these periods. All other data up until Thursday morning (at which time the solution pump was repaired) should be either deleted or reduced by 20.5%. Data collected from Thursday morning through Friday afternoon should be correct and no correction factor needs to be applied.

All data has been averaged in 1/2-hr periods. No correction factor has been applied to the 1/2-hr averages. The 7 hr runs have been broken down into 1/2 hr, 3-1/2 hr and 7 hr averages. The 20.5% correction factor has been applied to the 3-1/2 hr and 7 hr averages.

The 14 hr runs have been broken down into 1/2 hr and 14 hr averages and the 20.5% correction factor has been applied to the 14 hr averages.

APPENDIX I

FIELD DATA

The first nine columns of Tables I-1 through I-4 list various readings used in calculating flowrates and spike levels, which are given in Columns 10-14. The last six columns list various ambient air conditions at the test site. The venturi and meter flowrates (Columns 10-11) are calculated from the calibration equations in Appendix C. Due to the temperature compensations of the dry-gas meter and the above-ambient pressure of the gas stream at these instruments, the flowrates are calculated at 21°C and 760 mm Hg. The readings of the two devices are then averaged (Column 12) and the average flowrate is corrected to the temperature and pressure at the sampling ports (Column 13). Some of the methods being evaluated with this system are not corrected for temperature and pressure. However, if the spike levels are not calculated at the temperature and pressure existing at the manifold ports, a significant degree of uncertainty enters into any subsequent use of the spike level. The spike level (Column 14) is determined from the permeation rates of the permeation tubes used in each test.

Table I-1 LEVEL 1 TEST DATA

NO ₂ Sampling System Data									Calculated Flow Rates and Spike Levels					Ambient Conditions						
Date Time	Room Temp. (°C)	Bar. Press. (mm Hg)	Flow Press. (mm Hg)	Flow Temp. - Meter (°C)	Flow Rate Meter (L/min)	Venturi Pressure Reading (mm H ₂ O)	N ₂ Carrier Flowrate (cc/min)	Permeation Tube Temp. (°C)	Flowrate		Average Flowrate		Spike Level Ambient ^a / (µg/m ³)	NO Back- ground (µg/m ³)	NO ₂ Back- ground (µg/m ³)	Out- door Temp (°C)	Wind Speed (m/sec)	Wind Direc- tion	Relative Humidity (%)	
									Venturi to 21° + 760 mm Hg (L/min)	Meter to 21° + 760 mm Hg (L/min)	to 21° + 760 mm Hg (L/min)	Ambient ^a / (L/min)								
7-29-74																				
1800	22.0	738	8	22.5	59.4	267	200	25.1	59.0	59.6	59.3	61.4	104	0	20	29	5	NW	26	
1900	23.0	738	9	22.5	60.2	277	200	25.1	60.3	60.4	60.4	62.5	102	0	20	29	6	NW	26	
2000	23.0	738	9	22.5	60.1	275	200	25.1	60.1	60.3	60.2	62.3	102	0	30	26	2	NW	34	
2100	23.0	738	9	22.5	59.1	273	200	25.1	59.8	59.3	59.6	61.7	103	0	60	23	0	--	36	
2200	23.0	738	9	22.5	59.8	271	200	25.1	59.6	60.0	59.8	61.9	103	0	90	21	0	--	47	
2300	23.0	738	9	22.5	60.1	279	200	25.1	60.6	60.3	60.4	62.6	102	0	90	21	0	--	44	
2400	23.0	738	9	22.5	60.5	281	200	25.1	60.8	60.7	60.8	62.9	101	0	110	21	0	--	47	
7-30-74																				
0100	23.0	739	9	22.5	61.0	285	200	25.1	61.4	61.3	61.3	63.4	100	10	110	20	0	--	50	
0200	23.0	739	9	22.0	61.8	290	200	25.1	62.1	62.1	62.1	64.1	99	0	80	19	0	--	58	
0300	22.0	739	9	21.5	61.8	290	200	25.1	62.2	62.1	62.2	64.0	99	0	60	19	0	--	58	
0400	22.0	739	9	21.5	61.8	290	200	25.1	62.2	62.1	62.2	64.0	99	0	60	17	0	--	60	
0500	22.0	739	9	21.0	61.6	290	200	25.1	62.3	61.9	62.1	63.9	100	0	50	17	0	--	59	
0600	22.0	739	9	21.0	61.8	290	200	25.1	62.3	62.1	62.2	64.0	99	0	40	17	0	--	64	
0700	22.5	739	9	21.5	61.8	290	200	25.1	62.2	62.1	62.2	64.0	99	10	80	17	0	--	64	
0800	22.5	740	9	23.5	60.9	279	200	25.1	60.5	61.3	60.9	63.1	101	20	90	19	0	--	62	
0900	24.5	740	9	23.5	60.7	284	200	25.0	61.1	61.1	61.1	63.3	101	10	80	24	0	--	41	
1000	24.0	740	9	23.5	60.7	280	200	25.0	60.6	61.1	60.9	63.0	101	0	30	28	0	--	27	
1100	25.0	740	8	23.5	59.7	271	200	25.0	59.5	60.0	59.7	61.9	103	0	10	29	0	--	26	
1200	25.0	740	8	23.5	59.4	271	200	25.0	59.5	59.7	59.6	61.7	103	0	10	31	0	--	24	
1300	25.0	741	8	23.5	59.4	267	200	25.0	59.1	59.8	59.4	61.5	103	0	10	32	0	--	20	
1400	24.0	741	8	24.0	58.6	272	200	25.0	59.6	59.0	59.3	61.4	104	0	10	32	0	--	20	
1500	24.5	739	8	24.2	58.5	264	200	25.2	58.4	58.7	58.6	60.9	104	0	15	34	5	NW	20	
1600	24.5	739	8	24.2	58.3	262	200	25.2	58.2	58.5	58.3	60.7	105	0	15	34	5	NW	18	
1700	24.5	738	8	24.2	57.9	259	200	25.2	57.7	58.0	57.9	60.3	106	0	15	32	4	NW	20	
Average														2	49					

^a/ Temperature and pressure at sampling ports

Table I-2 LEVEL 2 TEST DATA

Date Time	NO ₂ Sampling System Data								Calculated Flowrates and Spike Levels				Ambient Conditions							
	Room Temp (°C)	Bar Press (mm Hg)	Flow Press (mm Hg)	Flow Temp - Meter (°C)	Flow- rate Meter (L/min)	Venturi Pressure Reading (mm H ₂ O)	N ₂ Carrier Flowrate (cc/min)	Permeation Tube Temp (°C)	Flowrates		Average Flowrate		Spike Level Ambient ^{a/} (µg/m ³)	NO Back- ground ^{b/} (µg/m ³)	NO ₂ Back- ground ^{b/} (µg/m ³)	Out- door Temp (°C)	Wind Speed (m/sec)	Wind Direc- tion	Relative Humidity (%)	
									Venturi to 21" + 760 mm Hg (L/min)	Meter to 21" + 760 mm Hg (L/min)	to 21" + 760 mm Hg (L/min)	Ambient ^{a/} (L/min)								
7-30-76																				
1800	23.5	738	8	23.5	58.3	258	800	25.1	57.7	58.5	58.1	60.3	296	0	20	32	3	NW	22	
1900	24.0	738	8	23.5	58.8	264	800	25.1	58.5	59.0	58.7	61.0	293	0	20	32	0	-	20	
2000	24.0	738	8	23.5	59.0	268	800	25.1	58.9	59.2	59.0	61.3	291	0	40	32	0	-	19	
2100	23.0	738	8	23.0	59.7	270	800	25.1	59.3	59.9	59.6	61.8	289	0	40	27	0	-	30	
2200	24.0	739	8	23.0	59.2	270	800	25.1	59.4	59.4	59.4	61.5	291	0	50	26	0	-	46	
2300	23.0	739	8	23.0	59.8	270	800	25.1	59.4	60.0	59.7	61.8	289	0	90	24	0	-	37	
2400	24.0	739	9	22.5	60.4	278	800	25.1	60.5	60.7	60.6	62.7	285	30	110	23	0	-	39	
7-31-76																				
0100	23.0	739	9	22.5	60.5	282	800	25.1	61.0	60.8	60.9	63.0	294	0	60	22	0	-	42	
0200	23.0	739	9	22.0	60.7	284	800	25.1	61.3	61.0	61.2	63.1	283	0	40	22	1	-	42	
0300	22.5	739	9	22.0	61.2	286	800	25.1	61.6	61.5	61.6	63.5	281	0	50	22	3	SE	42	
0400	22.0	739	9	22.0	60.9	286	800	25.1	61.6	61.2	61.4	63.3	282	0	50	22	0	-	45	
0500	22.0	739	9	22.0	60.5	288	800	25.1	61.8	60.8	61.3	63.3	282	0	40	21	0	-	44	
0600	22.0	739	9	22.0	61.3	288	800	25.1	61.8	61.6	61.7	63.7	281	0	30	20	3	SE	58	
0700	22.0	739	9	22.0	61.0	286	800	25.1	61.6	61.3	61.5	63.4	282	0	40	20	4	SE	58	
0800	22.5	739	9	22.5	60.7	281	800	25.1	60.9	61.0	60.9	63.0	284	0	40	21	4	SE	58	
0900	23.0	739	9	23.0	60.2	278	800	25.1	60.4	60.5	60.5	62.6	285	0	35	25	3	SE	48	
1000	23.0	739	9	23.2	60.4	278	800	25.2	60.4	60.7	60.5	62.7	285	0	30	27	2	SE	42	
1100	23.5	739	8	23.5	59.6	270	800	25.2	59.3	59.8	59.5	61.8	289	0	20	29	3	S	40	
1200	23.5	739	8	23.8	59.3	266	800	25.2	58.7	59.5	59.1	61.4	291	0	20	32	5	SE	32	
1300	24.0	739	8	23.5	58.8	262	800	25.2	58.3	59.0	58.7	60.8	294	0	20	34	4	SE	29	
1400	24.5	739	8	24.0	58.5	260	800	25.2	58.0	58.7	58.3	60.6	295	0	10	35	4	SW	29	
1500	24.5	739	8	24.0	58.2	259	800	25.2	57.8	58.4	58.1	60.4	296	0	10	33	5	SW	32	
1600	24.0	738	8	23.5	57.8	255	800	25.1	57.4	57.9	57.7	59.9	298	0	20	34	2	NE	26	
1700	24.0	738	8	23.5	58.1	259	800	25.1	57.9	58.3	58.1	60.3	296	0	20	32	2	NE	36	
														1	38					

a/ Temperature and pressure at sampling ports.

b/ Initial spike level incorrect--changed to proper level at 1820

Table 1-3 LEVEL 3 TEST DATA

NO ₂ Sampling System Data										Calculated Flowrates and Spike Levels					Ambient Conditions					
Date Time	Room Temp (°C)	Bar Press (mm Hg)	Flow Press (mm Hg)	Flow Temp - Meter (°C)	Flow- rate Meter (L/min)	Venturi Pressure Reading (mm H ₂ O)	N ₂ Carrier Flowrate (cc/min)	Permeation Tube Temp (°C)	Flowrate		Average Flowrate		Spike Level Ambient ^{a/} (µg/m ³)	NO Back- ground (µg/m ³)	NO ₂ Back- ground (µg/m ³)	Out- door Temp (°C)	Wind Speed (m/sec)	Wind Direc- tion	Relative Humidity (%)	
									+ 760 mm Hg (L/min)	Meter to 21° + 760 mm Hg (L/min)	to 21° + 760 mm Hg (L/min)	Ambient ^{a/} (L/min)								
7-31-74																				
1800	24.0	737	8	23.5	58.2	260	600	25.1	57.9	58.3	58.1	60.4	192	0	20	32	8	E	36	
1900	24.0	737	8	23.5	59.1	262	600	25.1	58.1	59.2	58.7	61.0	190	0	20	31	6	E	35	
2000	24.0	737	8	23.5	59.1	270	600	25.1	59.1	59.2	59.1	61.5	189	0	30	29	5	E	41	
2100	24.0	737	8	23.5	59.2	270	600	25.1	59.1	59.3	59.2	61.6	188	0	30	28	5	E	40	
2200	24.0	737	9	23.0	59.8	272	600	25.1	59.5	60.0	59.7	62.0	187	0	20	27	6	E	44	
2300	24.0	738	9	23.0	59.4	270	600	25.1	59.4	59.6	59.5	61.7	188	0	20	27	6	E	44	
2400	24.0	738	9	22.5	59.6	274	600	25.1	59.9	59.8	59.9	62.0	187	0	10	25	6	E	67	
8-1-74																				
0100	23.0	738	9	22.5	59.8	274	600	25.1	59.9	60.0	60.0	62.1	187	0	20	26	7	E	57	
0200	23.0	738	9	22.5	60.1	277	600	25.1	60.3	60.3	60.3	62.4	186	0	20	25	5	E	56	
0300	24.0	738	9	22.5	60.5	277	600	25.1	60.3	60.7	60.5	62.6	185	0	30	25	6	E	52	
0400	23.0	748	9	22.5	60.1	277	600	25.1	60.3	60.3	60.3	62.4	186	0	20	24	4	E	59	
0500	23.0	738	9	22.5	60.7	277	600	25.1	60.3	60.9	60.6	62.8	185	0	20	23	0	-	65	
0600	23.0	738	9	22.5	60.2	277	600	25.1	60.3	60.4	60.4	62.5	186	0	30	23	3	E	58	
0700	23.0	738	9	22.5	60.7	277	600	25.1	60.3	60.9	60.6	62.8	185	0	30	23	3	E	65	
0800	23.0	738	8	22.5	59.6	274	600	25.0	59.9	59.8	59.8	61.9	187	0	30	23	6	E	65	
0900	23.5	738	9	22.5	59.5	280	600	25.1	60.7	59.7	60.2	62.3	186	0	30	25	3	S	59	
1000	22.5	738	8	23.0	59.7	277	600	25.1	60.1	59.9	60.0	62.2	187	0	30	25	0	-	59	
1100	23.5	738	9	23.0	59.8	274	600	25.1	59.8	60.0	59.9	62.1	187	0	25	27	3	SE	54	
1200	24.0	738	9	23.0	60.8	281	600	25.1	60.7	61.0	60.9	63.1	184	0	25	28	2	SE	51	
1300	24.0	737	9	23.2	59.9	275	600	25.1	59.8	60.1	60.0	62.3	186	0	30	30	4	SE	44	
1400	24.0	737	9	23.5	60.0	275	600	25.1	59.8	60.2	60.0	62.4	186	0	10	30	5	SE	41	
1500	24.0	737	8	23.5	59.5	273	600	25.1	59.5	59.6	59.5	61.9	187	0	10	31	2	SE	42	
1600	24.0	737	8	23.5	59.1	270	600	25.1	59.1	59.2	59.1	61.5	189	0	10	33	1	SE	32	
1700	24.0	737	8	23.5	59.3	274	600	25.1	59.6	59.4	59.5	61.9	188	0	20	28	0	-	44	
Average														0	22					

^{a/} Temperature and pressure at sampling ports

Table I-4 LEVEL 4 TEST DATA

NO ₂ Sampling System Data									Calculated Flowrates and Spike Levels						O ₂ Back-ground (µg/m ³)	O ₂ Back-ground (µg/m ³)	Out-door Temp (°C)	Wind Speed (m/sec)	Wind Direction	Relative Humidity (%)
Date Time	Room Temp (°C)	Bar Press (mm Hg)	Flow Press (mm Hg)	Flow Temp - Meter (°C)	Flow-Rate Meter (L/min)	Venturi Pressure Reading (mm H ₂ O)	N ₂ Carrier Flowrate (cc/min)	Permeation Tube Temp (°C)	Flowrate		Average Flowrate		Spike Level Ambient ^a / (µg/m ³)							
									Venturi to 21* + 760 mm Hg (L/min)	Meter to 21* + 760 mm Hg (L/min)	to 21* + 760 mm Hg (L/min)	Ambient ^a / (°/min)								
<u>8-1-74</u>																				
1800	23.0	736	9	23.0	60.0	275	200	25.1	59.8	60.1	59.9	62.3	47.7	0	20	24	7	ESE	66	
1900	23.0	736	9	23.0	60.1	275	200	25.1	59.8	60.2	60.0	62.4	47.6	0	30	26	0	-	57	
2000	23.0	735	9	23.0	60.4	275	200	25.1	59.7	60.4	60.1	62.5	47.5	0	40	24	0	-	56	
2100	23.0	736	9	23.0	60.5	275	200	25.1	59.8	60.6	60.2	62.6	47.5	0	40	23	0	-	74	
2200	23.0	736	9	23.0	60.7	275	200	25.1	59.8	60.8	60.3	62.7	47.4	0	40	22	2	NE	73	
2300	23.0	736	9	22.5	60.9	281	200	25.1	60.6	61.0	60.8	63.1	47.1	0	40	22	0	-	72	
2400	23.0	736	9	22.0	61.2	279	200	25.1	60.5	61.3	60.9	63.1	47.1	0	40	19	0	-	90	
<u>8-2-74</u>																				
0100	23.0	736	9	22.0	61.8	285	200	25.1	61.2	61.9	61.5	63.8	46.6	0	60	21	0	-	77	
0200	23.0	736	9	22.0	61.6	291	200	25.1	61.9	61.7	61.8	64.0	46.4	0	40	21	0	-	81	
0300	23.0	736	9	22.0	61.3	291	200	25.1	61.9	61.4	61.7	63.9	46.5	0	50	20	0	-	85	
0400	22.5	736	9	22.0	61.8	291	200	25.1	61.9	61.9	61.9	64.1	46.3	0	40	20	0	-	85	
0500	22.0	736	9	22.0	61.8	291	200	25.1	61.9	61.9	61.9	64.1	46.3	0	30	20	0	-	80	
0600	23.0	736	9	22.0	61.6	289	200	25.1	61.7	61.7	61.7	63.9	46.5	0	40	20	0	-	80	
0700	22.0	736	9	22.0	61.8	289	200	25.1	61.7	61.9	61.8	64.0	46.4	0	40	21	0	-	85	
0800	22.0	736	9	22.5	61.4	282	200	25.0	60.8	61.5	61.1	63.4	46.8	0	50	21	0	-	83	
0900	22.0	736	9	22.5	61.2	279	200	25.1	60.4	61.3	60.8	63.1	47.0	10	60	22	0	-	77	
1000	23.0	736	9	22.5	60.7	278	200	25.1	60.3	60.8	60.5	62.8	47.3	0	30	23	4	NW	69	
1100	24.0	736	9	23.0	61.3	285	200	25.1	61.0	61.4	61.2	63.6	46.7	0	25	28	4	SW	45	
1200	23.5	735	9	23.5	60.5	279	200	25.1	60.1	60.5	60.3	62.9	47.2	0	15	28	4	SW	45	
1300	23.5	735	9	23.5	60.1	276	200	25.1	59.7	60.1	59.9	62.5	47.5	0	15	29	5	SW	45	
1400	23.5	735	9	23.5	59.7	273	200	25.1	59.4	59.7	59.5	62.1	47.8	0	15	29	4	SW	45	
1500	23.5	735	9	23.5	59.9	271	200	25.1	59.1	59.9	59.5	62.1	47.9	0	10	28	3	SW	100	
1600	23.5	735	9	23.5	60.2	276	200	25.1	59.7	60.2	60.0	62.5	47.5	0	20	28	3	SW	52	

^a/ Temperature and pressure at sampling ports

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