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Interlaboratory Cooperative Study of the Precision and Accuracy of the Measurement of NITROGEN DIOXIDE CONTENT IN THE ATMOSPHERE using ASTM Method D1607

DS 55

AMERICAN SOCIETY FOR TESTING AND MATERIALS

Interlaboratory Cooperative Study | NITROGEN DIOXIDE IN THE ATMOSPHERE | 05-055000-17 | ASTM DS 55

FINAL REPORT

on

INTERLABORATORY COOPERATIVE STUDY OF THE PRECISION AND ACCURACY OF THE MEASUREMENT OF NITROGEN DIOXIDE CONTENT IN THE ATMOSPHERE USING ASTM METHOD D 1607

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Battelle Memorial Institute

ASTM DATA SERIES PUBLICATION DS 55

List price $5.00
05-055000-17

AMERICAN SOCIETY FOR TESTING AND MATERIALS
1916 Race Street, Philadelphia, Pa. 19103

Library of Congress Catalog Card Number: 73-94362

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Printed in West Point, Pa.
March 1974

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INTERLABORATORY COOPERATIVE STUDY OF THE PRECISION AND ACCURACY OF THE MEASUREMENT OF NITROGEN DIOXIDE CONTENT IN THE ATMOSPHERE USING ASTM METHOD D 1607

by

J. F. Foster and G. H. Beatty

INTRODUCTION

This report presents the results obtained from an experimental study of the accuracy and precision of the measurement of atmospheric levels of nitrogen dioxide using the Griess-Saltzman reaction according to ASTM Method D 1607[1]*. The evaluation of D 1607 was performed as part of the first phase of Project Threshold, a comprehensive program to validate ASTM methods of measuring various atmospheric contaminants, including also sulfur dioxide, lead, dustfall, total sulfation, and particulate matter in Phase 1.

Project Threshold, a multiphase program, is sponsored by American Society of Testing Materials and the experimental program of Phase 1 was organized with Battelle's Columbus Laboratories as the Coordinating Laboratory.

In this experimental program measurements of nitrogen dioxide in ambient air and in ambient air spiked with known quantities of nitrogen dioxide were made at three different geographic locations. The following sections describe the experimental program and present the results of the study.

SUMMARY OF RESULTS AND CONCLUSIONS

An interlaboratory study involving a total of eight cooperating laboratories was conducted to determine the accuracy and precision of ASTM Method D 1607 for measuring nitrogen dioxide in the atmosphere. The laboratories performed a total of 704 measurements of nitrogen dioxide over the concentration

---

* References at end of report.

range of about 10 to 400 $\mu g/m^3$ (0.005 to 0.2 ppm) in ambient air and spiked-ambient air at Los Angeles, California, Bloomington, Indiana, and Manhattan, New York.

Statistical analyses of the nitrogen dioxide measurements yield the following results:

- The average standard deviation, s_b, for variations among single measurements taken by different laboratories (reproducibility) is related to the mean concentration of nitrogen dioxide, m, as follows:

$$s_b = 0.517 + 1.27 \sqrt{m} ,$$

where, s_b, and, m, are given in $\mu g/m^3$. This relation yields standard deviations of 4 and 23 $\mu g/m^3$, respectively, at concentrations of 9 and 324 $\mu g/m^3$, the lower and upper nitrogen dioxide concentrations which were studied.

- The average standard deviation, s_w, for variations among repeated measurements within laboratories (repeatability) is related to mean concentration, m, as follows:

$$s_w = 0.524 \sqrt{m} ,$$

where, s_w, and, m, are given in $\mu g/m^3$. This relation yields standard deviations of 1 $\mu g/m$ and 10 $\mu g/m^3$, respectively, at concentrations of 8 and 397 $\mu g/m^3$, the lower and upper nitrogen dioxide concentrations which were studied.

- The bias of the measurements of the nitrogen dioxide recovered from spiked-ambient samples was +11, -11, and +35 percent at Los Angeles, Bloomington, and Manhattan, respectively. The bias does not appear to be dependent on concentration, but at Manhattan where a significant positive bias was observed, it may be related to an interference in the ambient air. As a measure of the overall bias of the method (including the Manhattan value) the recovery of nitrogen dioxide from spiked samples exceeded the spiked amount which was added by an average of 18 percent of the spiked amount.

- The tendency of simultaneous measurements made by the laboratories during successive time intervals to increase or decrease together was measured by correlation coefficients. A total of 140 correlations including all laboratories, all sites, and all spiked and unspiked samples showed that 115 (82 percent) yield correlation coefficients that are statistically significant at the ninety-five percent level. In general, the results of this analysis which provide a measure of the comparability of the data obtained by the various laboratories show that although systematic differences occurred the same pattern in the change of nitrogen dioxide concentration was observed by all laboratories using the Test Method.

- An estimated minimum concentration of nitrogen dioxide that can be detected based on statistical considerations is 3 $\mu g/m^3$.

EXPERIMENTAL PROGRAM

ASTM Test Method D 1607

The Standard Method of Test for Nitrogen Dioxide in the Atmosphere, ASTM Designation D 1607, is reproduced in the Appendix to this report. The method is applicable to measurement of ambient concentrations in the range of about 10 to 10,000 $\mu g/m^3$ (0.005 to 5 ppm) of nitrogen dioxide. A sample of the ambient atmosphere is drawn through an absorbing solution in a fritted-glass bubbler. The nitrogen dioxide in the air reacts with the reagent solution to form a stable pink azo-dye, whose concentration is measured with a spectrophotometer. The azo-dye concentration is related to the concentration of nitrogen dioxide by calibration with solutions containing known quantities of nitrite ion.

The Test Method incorporates certain optional steps to accommodate variations in test conditions. The following paragraphs summarize the options which were specified and the procedural steps which were emphasized in the instructions to the participating laboratories before the performance of the site tests.

> The fritted bubbler shown in the ASTM Standard Method was used exclusively for sampling nitrogen dioxide. Calibration of the bubblers was performed as specified by the Test Method.
>
> Dichromate solution was used to clean the fritted bubblers. A cleaning solution of nitric acid in alcohol had been proposed by some laboratories, but was not permitted because of the possibility of interference from residual nitrate.
>
> Acetone was added to the absorbing reagent before use to retard fading of the color developed during the analysis. Cooperating laboratories had the option of adding acetone initially to each batch of absorbing reagent, or to the bubbler before each test. Both procedures were used.

Each laboratory used a sampling line of 10 feet of TFE fluorocarbon tubing having a nominal 8 millimeters inside diameter. The tubing was attached to an assigned outlet of the multiple sampling port in the duct carrying a sample stream of the outdoor ambient atmosphere. The sampling line and flow systems were provided with a by-pass or other arrangement to permit flow through the sampling line only, without passing through the bubbler.

Color was read by a spectrophotometer as specified, using water as a reference. Unexposed reagent was used for blank correction.

Calibration curves were prepared from $NaNO_2$ solutions as specified. A copy of the complete calibration curve prepared by each laboratory was submitted to the Coordinating Laboratory as part of the data from the experiments.

A dry bubbler was used for each new measurement instead of the optional drained, wet bubbler with correction. An oven was used on-site to promote drying, as necessary.

The nominal flow rate for sampling was uniformly 0.4 liter per minute.

Both a calibrated dry test meter and the glass rotameter which is specified by the Test Method, were recommended for the measurement of sample volume. The rotameter and dry test meter provide a duplicate measure of sampling rate and volume and permit detection of instrument malfunctions or other sampling problems. The majority of the laboratories used both instruments, although two used only the rotameter for maintaining and measuring constant sample flow during timed sampling periods.

Apparatus

Each participating laboratory supplied the components of two sampling trains which were assembled and operated to draw two concurrent samples in the manner specified by the Test Method. In general, the train was made up of (1) a Teflon tube that was attached to the fitting provided in the manifold of the duct carrying the sample stream of ambient air, (2) a flow meter, (3) the fritted glass bubbler containing nitrogen dioxide absorbing

solution, (4) desiccant/absorbent to protect measuring and pumping apparatus downstream, (5) measuring apparatus for pressure, temperature, and sample volume, and (6) pump and valves to adjust and control sample flow.

Figure 1 is a block diagram of the arrangement of the test apparatus used by one of the eight participating laboratories, and Figure 2 is a schematic diagram which shows the components and the dimensions of the connections used by another laboratory. Comparisons among all the apparatuses showed that there were some differences in arrangement, order, and dimensions, but that all followed the specific instructions included in the Test Method. Otherwise, each setup was permitted to have the individuality dictated by the experience and preference of the operator, because similar variations may occur when the Test Method is applied at any future time. It was appropriate in this study that statistical evaluations should include variations in apparatus that might occur when a competent analyst performs the Test Method with an adequate understanding of the principles of the measurement and the capabilities and limitations of his apparatus.

Figures 3 and 4 are additional illustrations of the nitrogen dioxide sampling system used by two of the participating laboratories.

Sample Generating System

A special sample generating system, which was used at all three test sites, was constructed to draw a stream of outside air to a convenient inside sampling location. The air intake was positioned at least 10 feet above roof level and an induced draft fan was used to draw into the system a continuous sample stream from the ambient atmosphere.

Figure 5 shows a diagram of the sample generating system which consisted of two sampling lines, one carrying ambient air and the other carrying ambient air spiked with a known quantity of nitrogen dioxide. The ambient air sample stream was carried in 3-inch aluminum pipe at a rate of about 150 scfm (50 feet per second) to minimize interactions with the pipe walls and among atmospheric constituents upstream from the sampling manifold. The sampling manifold was an aluminum fitting with sixteen individual sampling ports having outlets for attaching the sampling lines to the nitrogen dioxide sampling trains. A photo of the sampling manifold is presented in Figure 6.

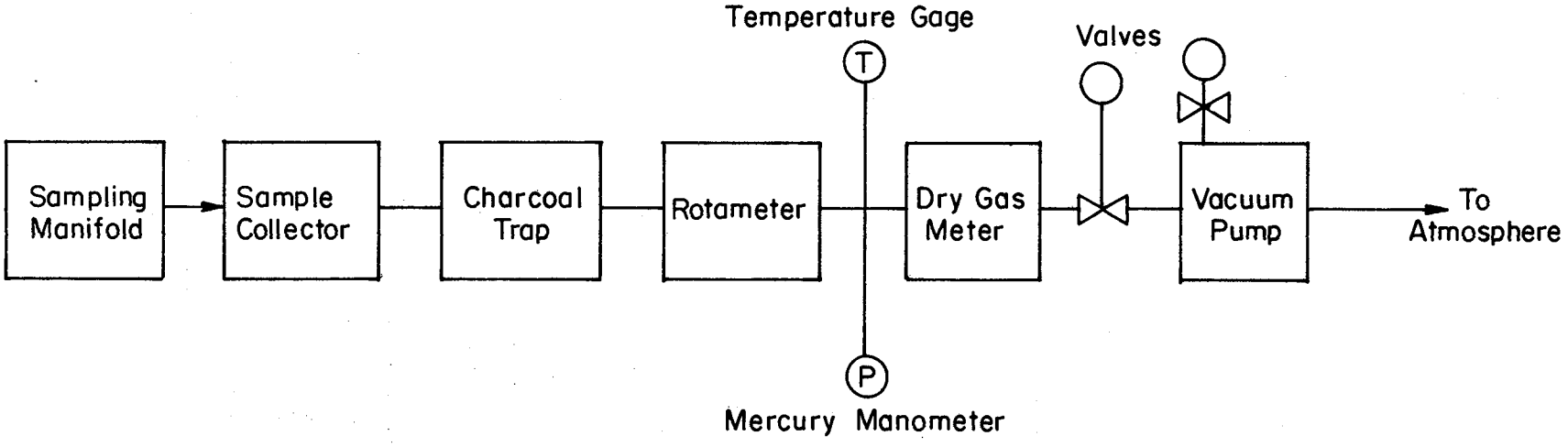
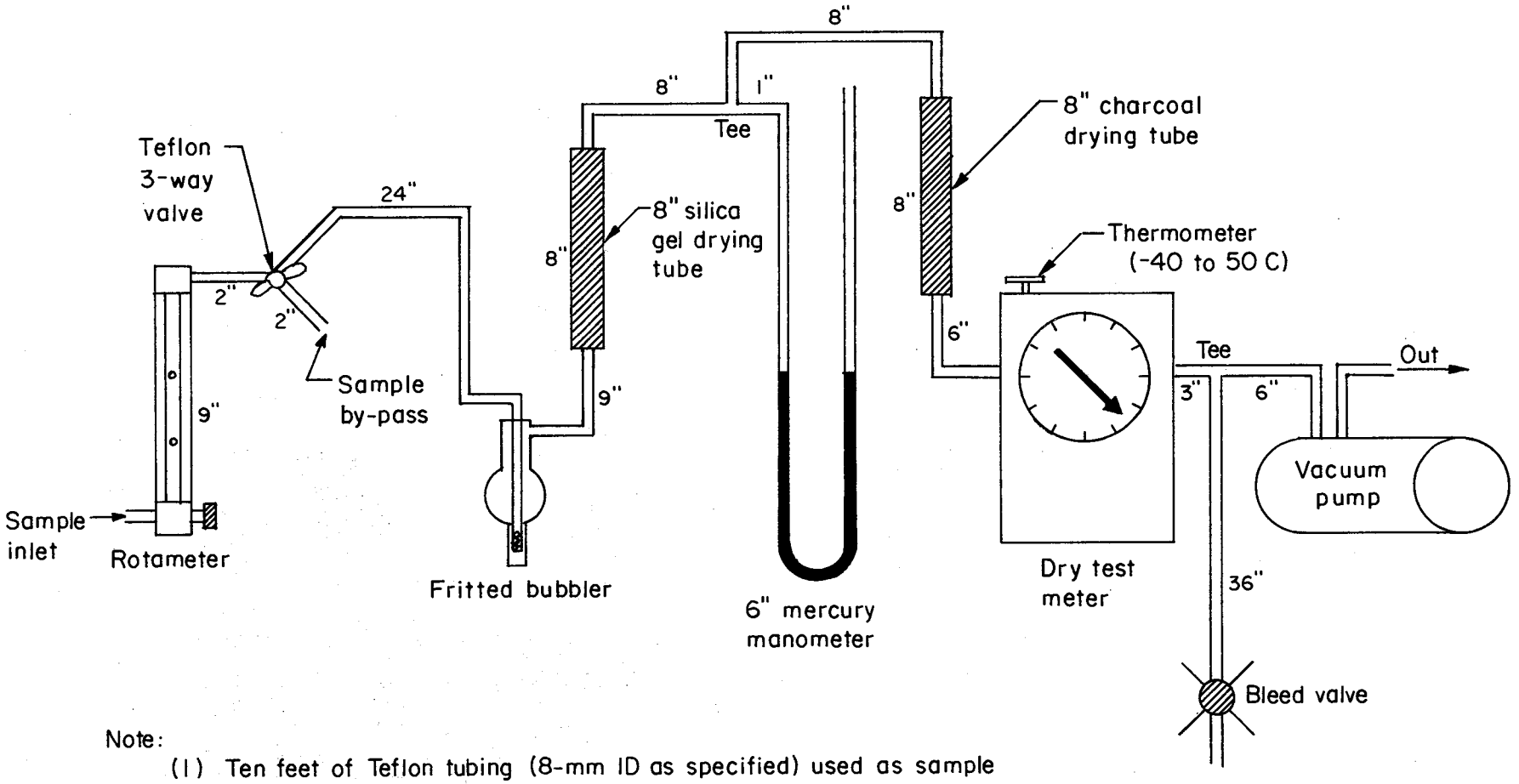


FIGURE 1. SCHEMATIC ARRANGEMENT OF SAMPLING APPARATUS FOR ASTM METHOD D 1607



Note:

(1) Ten feet of Teflon tubing (8-mm ID as specified) used as sample probe prior to fritted bubbler.
Remaining tubing is gum amber vacuum tubing

(2) Rotameter to 3-way valve is a butt joint connection

FIGURE 2. SAMPLING APPARATUS FOR ASTM D 1607

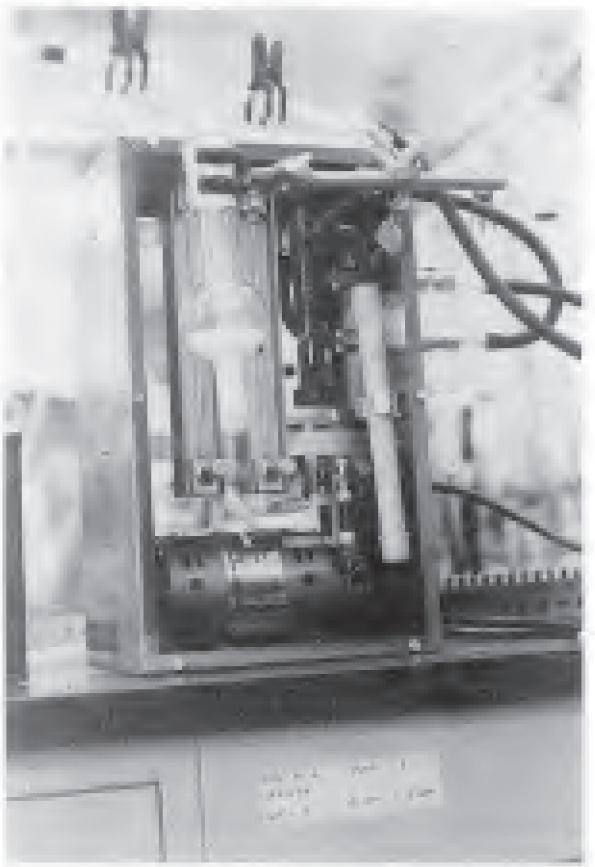


FIGURE 3. ABSORPTION TRAIN FOR ASTM D 1607

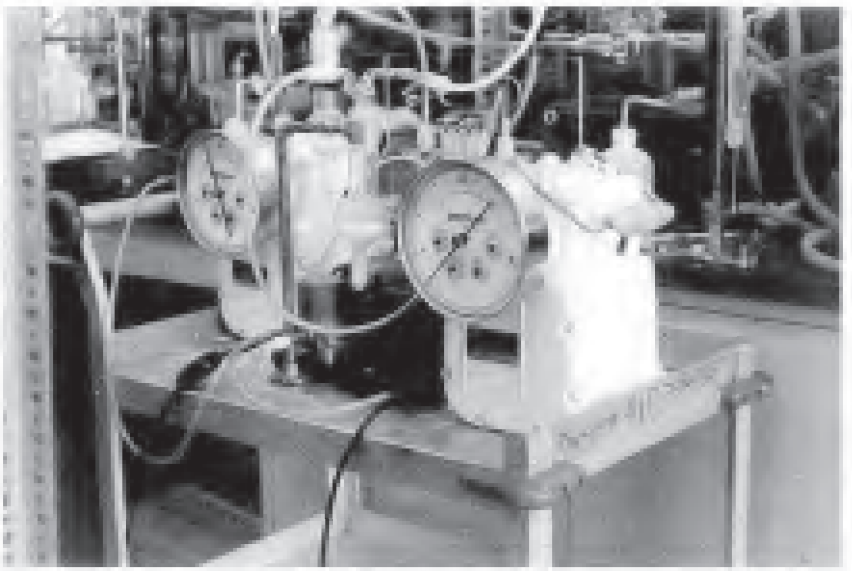


FIGURE 4. PARALLEL ABSORPTION TRAINS FOR CONCURRENT SAMPLING BY ASTM D 1607

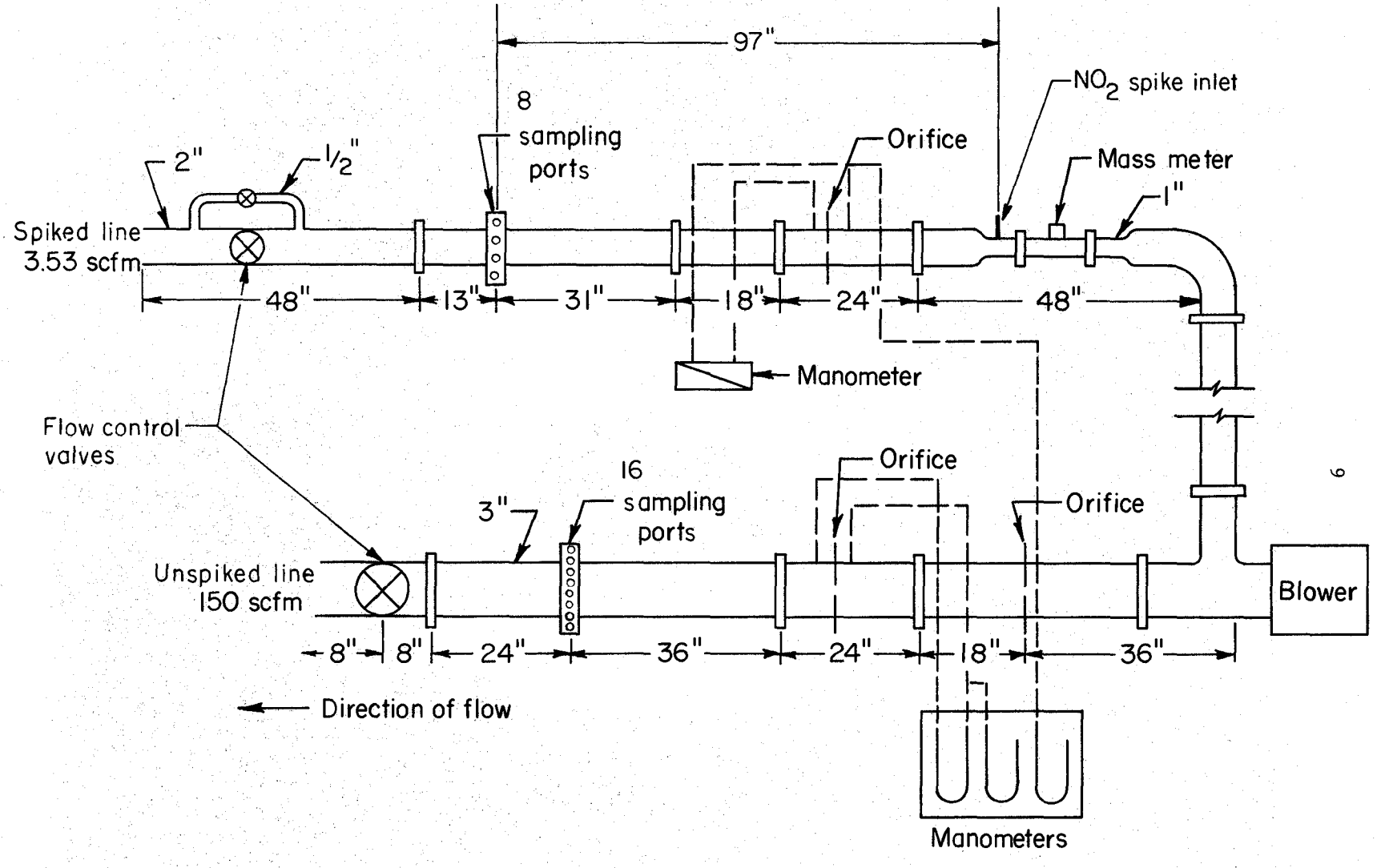


FIGURE 5. SAMPLING SYSTEM USED FOR EVALUATION OF ASTM METHOD D 1607 FOR DETERMINING NITROGEN DIOXIDE IN THE ATMOSPHERE

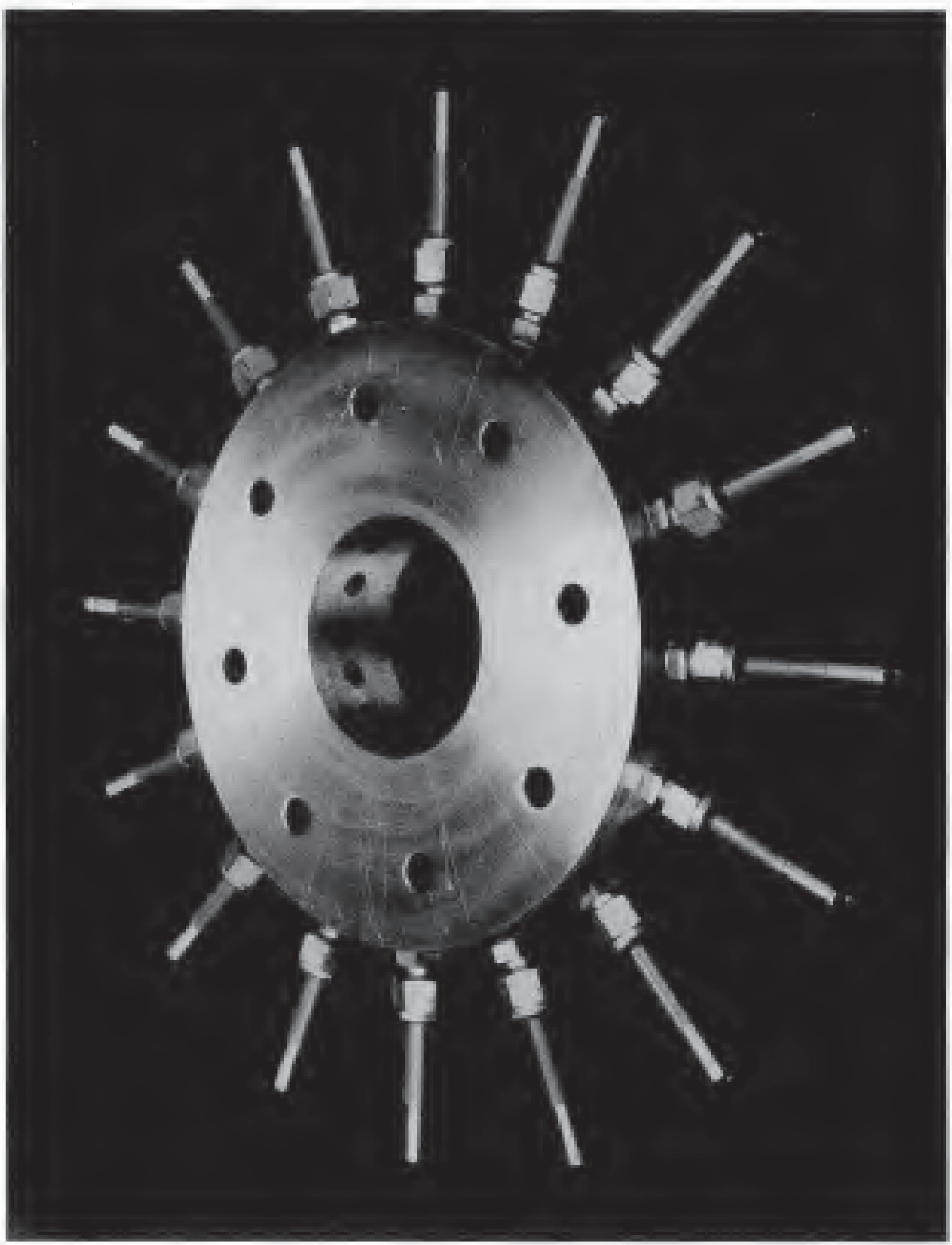


FIGURE 6. SIXTEEN-POSITION SAMPLING MANIFOLD USED IN UNSPIKED SAMPLE LINE

A 2-inch aluminum branch line of the sample generating system carried a spiked-ambient-air stream at a carefully controlled and measured flow rate of 3.5 scfm (100 liters per minute). Nitrogen dioxide was added to the branch stream at a calibrated rate in a small stream of dry, cylinder air through a single 1/8-inch tap. Thus, the concentration of nitrogen dioxide above ambient level could be calculated from the the known flow rates of added nitrogen dioxide and ambient air in the branch line, and was measured as the difference between the nitrogen dioxide levels detected in simultaneous samples taken from the ambient and spiked sampling lines. A sampling manifold with eight outlets, similar to the fitting shown in Figure 6, was incorporated in the spiked-ambient sampling line.

Both lines were equipped with orifices and Model AHL5 Hastings flow meters to control and measure the air flow.

Spiking Procedure

The addition of nitrogen dioxide at a known rate was the procedure used to evaluate the accuracy of the Test Method. The application of this technique involves the simultaneous analysis of an ambient air sample and an ambient air sample to which the known quantity of nitrogen dioxide has been added. The system used to generate the known nitrogen dioxide spike is shown in Figure 7. A permeation tube maintained at a constant temperature within ± 0.05 C, corresponding to ± 0.4 percent output variation, was used as the nitrogen dioxide supply. Dry air from a cylinder was used as a carrier gas to introduce the nitrogen dioxide into the spiked sampling line. Orifice flow meters with an accuracy of ± 1 percent were used in the spike generation system.

The spike concentrations used at Los Angeles, Bloomington, and Manhattan were 66.9, 32.4 to 32.7, and 95.5 to 95.7 $\mu g/m^3$, respectively.

Sampling Procedure

The sampling manifolds were provided with sixteen ports on the ambient stream and eight ports on the spiked stream to accommodate maximum sampling activity and to permit auxiliary samples for purposes other than the statistical

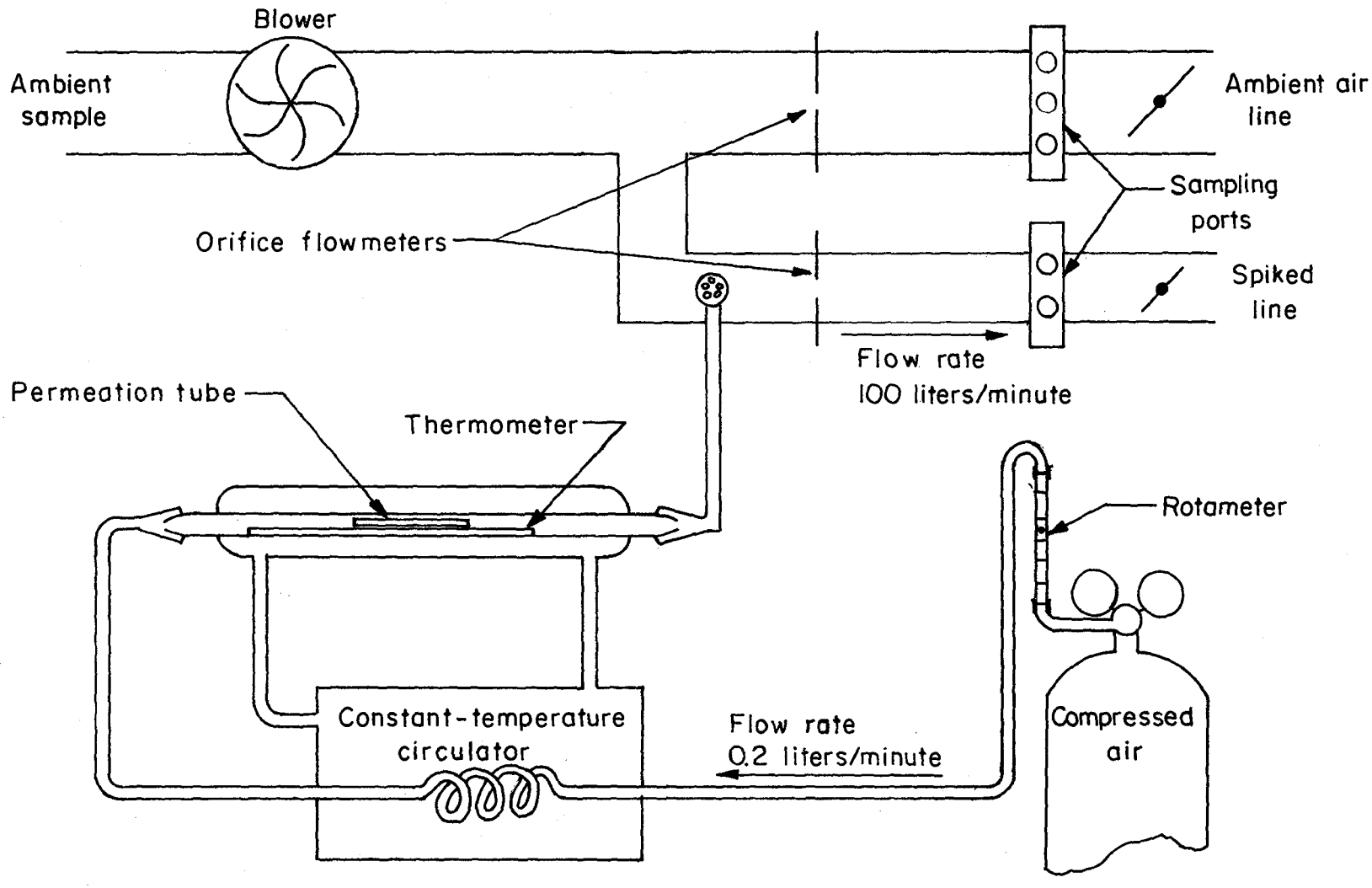


FIGURE 7. NITROGEN DIOXIDE SPIKE GENERATION SYSTEM

study. The statistical pattern, which is described in a following section, required changing each sampling line to a different numbered port for each sampling period to evaluate any differences in individual ports. The logistical problem of shifting each of 16 sampling lines to a specified one of the 24 ports by eight operators working in a coordinated activity before each sampling period appeared difficult, when the problem was examined during the planning phase. Therefore, it was decided to have two groups of four laboratories sampling with eight lines during alternate half-hour periods. This procedure was followed for all tests at Los Angeles, and the first half-day of tests at Bloomington. Thereafter, for the remainder of the Bloomington test and the entire Manhattan tests, the procedure was changed so that all participating laboratories sampled simultaneously for one hour, rather than sampling for one-half hour in two alternating groups. The change in sampling procedure was made for the following reasons.

(1) The ambient nitrogen dioxide concentrations were low at Bloomington, and a longer sampling time was desirable to collect a larger sample of nitrogen dioxide.

(2) More concurrent sampling data were obtained for direct statistical comparisons. It is not necessary to make the questionable assumption that concentration of consecutive samples was the same, in order to pool data for statistical analysis.

(3) A method was devised for coding each sampling line with its change pattern for all tests, so that any operator near the sampling ports could make the necessary changes for his line and others within reach.

Test Sites

Site No. 1, Los Angeles, California

The sampling system was located in Room 357 of the Science Building on the campus of the University of Southern California. This was a third-floor laboratory equipped with laboratory benches to support the sampling apparatus,

and for use in the analyses. The sampling system was suspended from the ceiling or supported on demountable racks, as necessary. The sampling manifolds were positioned in adjacent aisles between benches at a height above head level to permit access to apparatus on either side of the aisles. Sampling lines were passed overhead to either the unspiked or spiked line as required by the specified statistical pattern for sampling from the various ports. Changes of the 16 sample lines to different ports between samples were completed in a few minutes.

Thirty-two samples were taken for analysis by each of eight participating laboratories during four half-day sampling periods on August 16, 17, and 18, 1971. The ambient level of nitrogen dioxide ranged from about 40 to 200 $\mu g/m^3$ during the test period.

Site No. 2, Bloomington, Indiana

The Bloomington test site was a vacant greenhouse of Indiana University Department of Botany located on an isolated experimental plot of land at the edge of Bloomington. The installation of the sampling system at the site is shown in Figures 8 and 9. Figure 8 shows the ambient air intake line extending above the greenhouse roof. Figure 9 shows the spiked and unspiked sample lines and manifolds and several of the nitrogen dioxide sampling trains. Experimental arrangements similar to those shown in these figures were also used at the Los Angeles and Manhattan sites.

Thirty-two samples were taken by each of the seven participating laboratories during four half-day sampling periods on October 25 and 26, 1971. The ambient level of nitrogen dioxide at the Bloomington site ranged from about 10 to 100 $\mu g/m^3$

Site No. 3, Manhattan, New York City

The sampling system was assembled in a student science laboratory on the sixth floor of The Cooper Union Building at 51 Astor Place in lower

FIGURE 8. NITROGEN-DIOXIDE SAMPLING-SYSTEM INTAKE LINE AT BLOOMINGTON TEST SITE

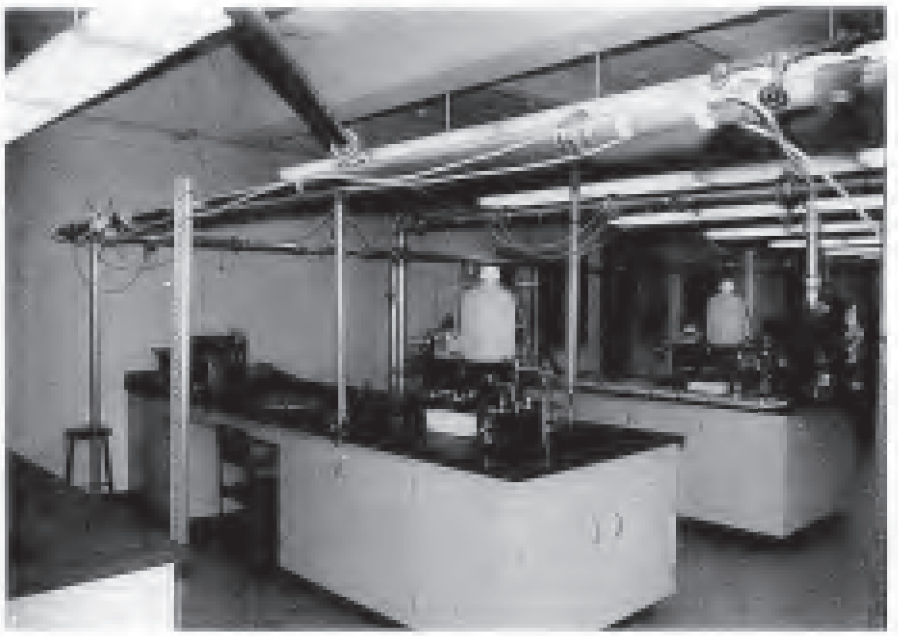


FIGURE 9. NITROGEN-DIOXIDE SAMPLING-SYSTEM ARRANGEMENT AT LOS ANGELES TEST SITE

Manhattan. The configuration and arrangement was similar to that previously described. The intake duct for ambient air passed through a sixth (top) floor window, up and over the parapet of the roof, horizontally across a roof setback, and then vertically up the wall to a height at least ten feet above the building structure. The inlet was set back to some extent from all the streets bounding the building.

Each of the seven participating laboratories obtained 32 samples for analysis in the two-day sampling period on January 10 and 11, 1973. Ambient levels of nitrogen dioxide ranged from about 100 to 200 $\mu g/m^3$ during the test period.

Participating Laboratories

The participating laboratories were:

California Department of Health
George D. Clayton and Associates
Arthur D. Little, Inc.
Midwest Research Institute
Public Service Electric and Gas Company (New Jersey)
Research Triangle Institute
Walden Research Corporation
Western Electric Company.

Throughout this report the identity of the participants is concealed by using a set of code letters. Numerical subscripts with the code letters designate the site at which samples were collected. In general, any particular letter designates a different laboratory at each site.

STATISTICAL DESIGN OF EXPERIMENTAL PROGRAM

In the planning stage careful consideration was given to the choice of the statistical design for the experimental program, as it was realized from the beginning that the proper design would be required to obtain meaningful results. The factors which were considered and the objectives which were established in the development of the statistical design of the experimental program are summarized below.

(1) The determination of the precision with which a given laboratory, using the Test Method, can measure the amount of nitrogen dioxide in the atmosphere, if all extraneous variables are held constant.

(2) Measurement of laboratory-to-laboratory variability in determining atmospheric levels of nitrogen dioxide using the Test Method. This variability may arise from several sources, including differences in equipment, differences in operating techniques, and differences among sampling outlet positions assigned to various laboratories.

(3) Laboratory-to-laboratory variability in precision of the measurements.

(4) The effect of the concentration of nitrogen dioxide on accuracy and precision of the measurements.

(5) The bias of the Test Method when applied to measurement of nitrogen dioxide in typical atmospheric samples.

It was also recognized that the ambient concentration of nitrogen dioxide would be different at each of the three test sites and that at each site the concentration would vary with time during the performance of the tests. At the metropolitan sites, Los Angeles and Manhattan, higher nitrogen dioxide concentrations were expected while at Bloomington, a more rural area, lower concentrations were expected. The changes of nitrogen dioxide concentration with time were expected to occur due to diurnal variations in automotive traffic patterns and other emission sources and in climatological and meteorological conditions. The study of site- and time-related variations of ambient nitrogen dioxide concentration was not an object of this study. However, these variations must be recognized so that the statistical analysis of the data is performed in such a manner as to isolate the components of variance of primary interest, i.e., those related to the Test Method.

Recommended ASTM practices for conducting an interlaboratory study[2] were considered in developing the experimental test program.

The basic building block which was used in the statistical design of the nitrogen dioxide experiments is the four-by-four Latin Square. Blocks 1 through 24 of the design are composed of 12 Latin Squares which were intended to provide data for measuring the reproducibility and the accuracy of the test method. Each Latin Square also provides data which can be subjected to an analysis of variance to test for laboratory, block, or outlet differences. The linking of these various Latin Squares was provided through the use of a balanced incomplete block design, which was superimposed on the design structure as a whole. Linking was achieved by pairing two laboratories into a team. The linking Latin Squares feature was built into the experimental design to provide a means of analyzing the data should sampling outlet position become a significant variable. Blocks 25 through 32 were also of the Latin Square design. Data from these test blocks were intended to provide a measure of the repeatability of the Test Method.

The same statistical design was intended for use at all three sampling sites but, as it turned out, modifications were introduced at each site. For various practical reasons, the field experiments were not conducted in strict accordance with the statistical design described above. In fact, the actual pattern of experimentation was different at each sampling site. This was not wholly unexpected, because it was anticipated that experience at one site might result in modifications to the experimental program at the next site.

The final sampling pattern, after randomization, of nitrogen dioxide experiments at the Los Angeles site is shown in Table 1. During the randomization process, the ability to analyze the difference S-U in Blocks 1 through 24 by a series of Latin Squares was inadvertently lost, although the resulting design still permitted analysis of the Latin Squares for unspiked and spiked samples separately.

Only seven laboratories participated in the experiments at Bloomington. Consequently, data were not obtained for several cells of the Latin Squares of the sampling pattern. Another important difference between these experiments and those at Los Angeles was that beginning with Block 9 eight more outlets were provided permitting all seven laboratories to run tests simultaneously. This enabled the sampling time to be increased to an hour. The final sampling pattern of experimental runs at Bloomington is shown in Table 2.

TABLE 1. SAMPLING PATTERN OF NITROGEN DIOXIDE EXPERIMENTS AT LOS ANGELES SITE

		Sampling Outlet Position[a]							
Hour	Block	U1	U2	U3	U4	S1	S2	S3	S4
1	1	B_1	D_1	H_1	C_1	B_1	D_1	H_1	C_1
	2	F_1	A_1	G_1	E_1	E_1	G_1	F_1	A_1
2	3	H_1	B_1	C_1	D_1	D_1	C_1	H_1	B_1
	4	G_1	F_1	E_1	A_1	A_1	F_1	G_1	E_1
3	5	C_1	H_1	D_1	B_1	B_1	D_1	C_1	H_1
	6	E_1	G_1	A_1	F_1	G_1	E_1	A_1	F_1
4	7	D_1	C_1	B_1	H_1	C_1	H_1	B_1	D_1
	8	A_1	E_1	F_1	G_1	F_1	A_1	E_1	G_1
5	9	H_1	B_1	A_1	G_1	G_1	B_1	H_1	A_1
	10	D_1	F_1	C_1	E_1	C_1	D_1	E_1	F_1
6	11	B_1	H_1	G_1	A_1	B_1	H_1	A_1	G_1
	12	E_1	C_1	F_1	D_1	F_1	E_1	D_1	C_1
7	13	A_1	G_1	H_1	B_1	H_1	A_1	G_1	B_1
	14	C_1	D_1	E_1	F_1	E_1	C_1	F_1	D_1
8	15	G_1	A_1	B_1	H_1	A_1	G_1	B_1	H_1
	16	F_1	E_1	D_1	C_1	D_1	F_1	C_1	E_1
9	17	A_1	C_1	D_1	G_1	G_1	A_1	D_1	C_1
	18	F_1	B_1	E_1	H_1	H_1	E_1	B_1	F_1
10	19	D_1	G_1	A_1	C_1	A_1	C_1	G_1	D_1
	20	B_1	H_1	F_1	E_1	E_1	F_1	H_1	B_1
11	21	G_1	D_1	C_1	A_1	C_1	D_1	A_1	G_1
	22	E_1	F_1	H_1	B_1	B_1	H_1	F_1	E_1
12	23	C_1	A_1	G_1	D_1	D_1	G_1	C_1	A_1
	24	H_1	E_1	B_1	F_1	F_1	B_1	E_1	H_1
13	25	B_1	B_1	C_1	C_1	A_1	H_1	A_1	H_1
	26	E_1	E_1	G_1	G_1	D_1	F_1	D_1	F_1
14	27	C_1	C_1	B_1	B_1	H_1	A_1	H_1	A_1
	28	F_1	F_1	D_1	D_1	G_1	E_1	G_1	E_1
15	29	H_1	H_1	A_1	A_1	C_1	B_1	C_1	B_1
	30	G_1	G_1	F_1	F_1	E_1	D_1	E_1	D_1
16	31	A_1	A_1	H_1	H_1	B_1	C_1	B_1	C_1
	32	D_1	D_1	E_1	E_1	F_1	G_1	F_1	G_1

(a) Letter entries are laboratory code designations.

Ui = unspiked sample collected from the i^{th} outlet.

Si = spiked sample collected from the i^{th} outlet.

TABLE 2. SAMPLING PATTERN OF NITROGEN DIOXIDE EXPERIMENTS AT BLOOMINGTON SITE

		Sampling Outlet Position(a)			Sampling Outlet Position(a)	
Hour	Block	U1 U2 U3 U4	S1 S2 S3 S4	Block	U5 U6 U7 U8	S5 S6 S7 S8
1	1	B_2 D_2 - C_2	B_2 D_2 - C_2			
	2	F_2 A_2 G_2 E_2	F_2 A_2 G_2 E_2			
2	3	- B_2 C_2 D_2	- B_2 C_2 D_2			
	4	G_2 F_2 E_2 A_2	G_2 F_2 E_2 A_2			
3	5	C_2 - D_2 B_2	C_2 - D_2 B_2			
	6	E_2 G_2 A_2 F_2	E_2 G_2 A_2 F_2			
4	7	D_2 C_2 B_2 -	D_2 C_2 B_2 -			
	8	A_2 E_2 F_2 G_2	A_2 E_2 F_2 G_2			
5	9	- B_2 A_2 G_2	- B_2 A_2 G_2	10	D_2 F_2 C_2 E_2	D_2 F_2 C_2 E_2
6	11	B_2 - G_2 A_2	B_2 - G_2 A_2	12	E_2 C_2 F_2 D_2	E_2 C_2 F_2 D_2
7	13	A_2 G_2 - B_2	A_2 G_2 - B_2	14	C_2 D_2 E_2 F_2	C_2 D_2 E_2 F_2
8	15	G_2 A_2 B_2 -	G_2 A_2 B_2 -	16	F_2 E_2 D_2 C_2	F_2 E_2 D_2 C_2
9	17	A_2 C_2 D_2 G_2	A_2 C_2 D_2 G_2	18	F_2 B_2 E_2 -	F_2 B_2 E_2 -
10	19	D_2 G_2 A_2 C_2	D_2 G_2 A_2 C_2	20	B_2 - F_2 E_2	B_2 - F_2 E_2
11	21	G_2 D_2 C_2 A_2	G_2 D_2 C_2 A_2	22	E_2 F_2 - B_2	E_2 F_2 - B_2
12	23	C_2 A_2 G_2 D_2	C_2 A_2 G_2 D_2	24	- E_2 B_2 F_2	- E_2 B_2 F_2
13	25	B_2 B_2 C_2 C_2	A_2 - A_2 -	26	E_2 E_2 G_2 G_2	D_2 F_2 D_2 F_2
14	27	C_2 C_2 B_2 B_2	- A_2 - A_2	28	F_2 F_2 D_2 D_2	G_2 E_2 G_2 E_2
15	29	- - A_2 A_2	C_2 B_2 C_2 B_2	30	G_2 G_2 F_2 F_2	E_2 D_2 E_2 D_2
16	31	A_2 A_2 - -	B_2 C_2 B_2 C_2	32	D_2 D_2 E_2 E_2	F_2 G_2 F_2 G_2

(a) Letter entries are laboratory code designations.

Ui = unspiked sample collected from the i^{th} outlet.

Si = spiked sample collected from the i^{th} outlet.

Only seven laboratories participated in the Manhattan test, consequently many of the Latin Squares in the sampling pattern have empty data cells. In all blocks a total of 14 outlets was employed simultaneously, and a sampling time of one hour was used for all blocks. The final sampling pattern of experimental runs at Manhattan is shown in Table 3.

STATISTICAL ANALYSIS OF NITROGEN DIOXIDE MEASUREMENTS

Statistical Measures

The experimental program was designed to provide a measure of the following statistical parameters.

Reproducibility

The participating laboratories concurrently sampled atmospheres which were generated so that equal concentrations of nitrogen dioxide were expected in each sample. Differences among the concentrations found in simultaneous samples represent a measure of variability between laboratories. The average standard deviation of all such samples over all laboratories serves as a measure of precision which is called "between-laboratory variability" or "reproducibility".

Repeatability

In accordance with the experimental design each laboratory generated some duplicate pairs of samples by sampling ambient atmospheres simultaneously at two different ports of the sampling manifold. Ideally, equal concentrations of nitrogen dioxide would be found in pairs of duplicate samples. A difference between a pair of measurements thus is a measure of variability. The standard deviation of all such differences over all laboratories is a useful measure of precision which is called "within-laboratory variability" or "repeatability".

TABLE 3. SAMPLING PATTERN OF NITROGEN DIOXIDE EXPERIMENTS AT MANHATTAN SITE

		Sampling Outlet Position[a]					Sampling Outlet Position[a]			
Hour	Block	U1	U2	U3	U4	S1 S2 S3 S4	Block	U5	U6	U7	U8	S5 S6 S7 S8
1	1	E_3	A_3	-	G_3	E_3 A_3 - G_3	2	C_3	F_3	D_3	B_3	C_3 F_3 D_3 B_3
2	3	-	E_3	G_3	A_3	- E_3 G_3 A_3	4	D_3	C_3	B_3	F_3	D_3 C_3 B_3 F_3
3	5	G_3	-	A_3	E_3	G_3 - A_3 E_3	6	B_3	D_3	F_3	C_3	B_3 D_3 F_3 C_3
4	7	A_3	G_3	E_3	-	A_3 G_3 E_3 -	8	F_3	B_3	C_3	D_3	F_3 B_3 C_3 D_3
5	9	-	E_3	F_3	D_3	- E_3 F_3 D_3	10	A_3	C_3	G_3	B_3	A_3 C_3 G_3 B_3
6	11	E_3	-	D_3	F_3	E_3 - D_3 F_3	12	B_3	G_3	C_3	A_3	B_3 G_3 C_3 A_3
7	13	F_3	D_3	-	E_3	F_3 D_3 - E_3	14	G_3	A_3	B_3	C_3	G_3 A_3 B_3 C_3
8	15	D_3	F_3	E_3	-	D_3 F_3 E_3 -	16	C_3	B_3	A_3	G_3	C_3 B_3 A_3 G_3
9	17	F_3	G_3	A_3	D_3	F_3 G_3 A_3 D_3	18	C_3	E_3	B_3	-	C_3 E_3 B_3 -
10	19	A_3	D_3	F_3	G_3	A_3 D_3 F_3 G_3	20	E_3	-	C_3	B_3	E_3 - C_3 B_3
11	21	D_3	A_3	G_3	F_3	D_3 A_3 G_3 F_3	22	B_3	C_3	-	E_3	B_3 C_3 - E_3
12	23	G_3	F_3	D_3	A_3	G_3 F_3 D_3 A_3	24	-	B_3	E_3	C_3	- B_3 E_3 C_3
13	25	E_3	E_3	G_3	G_3	F_3 F_3 - -	26	B_3	B_3	D_3	D_3	A_3 A_3 C_3 C_3
14	27	G_3	G_3	E_3	E_3	- - F_3 F_3	28	C_3	C_3	A_3	A_3	D_3 B_3 D_3 B_3
15	29	-	-	F_3	F_3	G_3 G_3 E_3 E_3	30	D_3	D_3	C_3	C_3	B_3 A_3 B_3 A_3
16	31	F_3	F_3	-	-	E_3 E_3 G_3 G_3	32	A_3	A_3	B_3	B_3	C_3 D_3 C_3 D_3

(a) Letter entries are laboratory code designations.

Ui = unspiked sample collected from the i^{th} outlet.

Si = spiked sample collected from the i^{th} outlet.

Accuracy

In a portion of the experiments, the laboratories performed analyses of an ambient sample and a duplicate ambient sample to which a known nitrogen dioxide spike was added. The difference between nitrogen dioxide analyses for each such pair of samples serves as a measure of the concentration of nitrogen dioxide added to the sample. The differences between the experimentally determined and the "true" spike concentration is a measure of accuracy. The average of many independent differences is called "bias".

Comparability

A measure of relative laboratory performance, which in this report is called "comparability", is defined as the extent to which measurements of the nitrogen dioxide concentrations by different laboratories agree in regard to the differences between different concentrations. As nitrogen dioxide concentrations vary from sampling period to sampling period, the same pattern of increasing or decreasing concentrations should be shown by all laboratories although systematic differences may exist. The correlation between corresponding measurements by laboratories is used as a measure of comparability.

Additional discussions of several of the preceding statistical measures have been presented by Mandel[3] and in ASTM publications[4,5].

Analysis of Reproducibility

Experimental Data

A total of 528 measurements of nitrogen dioxide were performed at the three tests sites in accordance with Blocks 1 through 24 of the experimental design: 192 runs were completed at Los Angeles by 8 laboratories; 168 runs were completed at Bloomington by 7 laboratories; and 168 runs were completed at Manhattan by 7 laboratories.

The results of the nitrogen dioxide measurements at the Los Angeles, Bloomington, and Manhattan sites are presented in Tables 4, 5, and 6, respectively. These data are presented in chronological order, corresponding to the statistical designs that governed their collection. The first three columns specify the hour, block, and laboratory according to the sampling patterns presented in Tables 1, 2, and 3. The next two columns contain the measurements of the nitrogen dioxide concentration in the unspiked and spiked samples, respectively, in units of $\mu g/m^3$. These measurements are also identified by outlet position. Column 6 presents the differences, for each hour, block, and laboratory combination, between the measured nitrogen dioxide concentration in the spiked sample and the measured concentration of nitrogen dioxide in the unspiked sample. Column 7 shows the spiking rate that was used to provide a known increase in the concentration of nitrogen dioxide in the sampled atmosphere. The last column shows the percentage difference between the measured concentration of spike and the true concentration of spike, relative to the true concentration.

Evaluation of Reproducibility

The nitrogen dioxide measurements based on one-hour sampling periods in Tables 4 through 6 were analyzed to provide descriptive statistics for these time periods, as shown in Tables 7 through 12. These statistics, computed for both unspiked and spiked samples, include the number of measurements per sampling period, n, the block mean, m, the block standard deviation, s, an estimated standard deviation, $\hat{s}$, the range, w, the ratio of range to estimated standard deviation , $w/\hat{s}$, and the coefficient of variation, CV, in percent.

The 104 pairs of values of the block means, m, and standard deviations, s, given in Tables 7 through 12, representing both unspiked and spiked samples from all three sampling sites, are plotted as points of a scatter diagram in Figure 10.

TABLE 4. DATA FROM NITROGEN DIOXIDE EXPERIMENTS (BLOCKS 1-24) AT LOS ANGELES SITE ARRANGED BY BLOCK AND OUTLET POSITION

Hour	Block	Lab	Unspiked Samples, $\mu g/m^3$ (U)	Spiked Samples, $\mu g/m^3$ (S)	Estimated Spiking Rate, $\mu g/m^3$ (S-U)	True Spiking Rate, $\mu g/m^3$ (R)	Difference, percent of (R)
1	1	B_1	U1 = 45.9(a)	S2 = 68.8(a)	(a)	66.9	(a)
		D_1	U2 = 80.4	S3 = 153.1	72.7		9
		H_1	U3 = 96.3	S1 = 188.0	91.7		37
		C_1	U4 = 87.0	S4 = 174.0	87.0		30
	2	F_1	U1 = 34.1	S3 = 115.1	81.0	66.9	21
		A_1	U2 = 74.7	S4 = 150.6	75.9		13
		G_1	U3 = 62.9	S2 = 133.4	70.5		5
		E_1	U4 = 48.4	S1 = 127.7	79.3		19
2	3	H_1	U1 = 59.8	S3 = 150.0	90.2	66.9	35
		B_1	U2 = 51.4	S4 = 132.7	81.3		22
		C_1	U3 = 47.0	S2 = 130.0	83.0		24
		D_1	U4 = 49.8	S1 = 120.6	70.8		6
	4	G_1	U1 = 57.2	S3 = 131.4	74.2	66.9	11
		F_1	U2 = 50.5	S2 = 122.6	72.1		8
		E_1	U3 = 40.8	S4 = 112.5	71.7		7
		A_1	U4 = 70.1	S1 = 136.3	66.2		- 1
3	5	C_1	U1 = 41.0	S3 = 95.0	54.0	66.9	- 19
		H_1	U2 = 46.4	S4 = 141.0	94.6		41
		D_1	U3 = 47.8	S2 = 109.1	61.3		- 8
		B_1	U4 = 49.3	S1 = 108.4	59.1		- 12
	6	E_1	U1 = 39.9	S2 = 109.7	69.8	66.9	4
		G_1	U2 = 62.9	S1 = 125.7	62.8		- 6
		A_1	U3 = 53.5	S3 = 118.3	64.8		- 3
		F_1	U4 = 54.1	S4 = 133.4	79.3		19
4	7	D_1	U1 = 49.8	S4 = 120.6	70.8	66.9	6
		C_1	U2 = 48.0	S1 = 128.0	80.0		20
		B_1	U3 = 62.2	S3 = 137.0	74.8		12
		H_1	U4 = 56.5	S2 = 140.0	83.5		25
	8	A_1	U1 = 51.0	S2 = 128.6	77.6	66.9	16
		E_1	U2 = 51.5	S3 = 131.7	80.2		20
		F_1	U3 = 61.6	S1 = 144.5	82.9		24
		G_1	U4 = 85.7	S4 = 171.5	85.8		28

(a) These determinations were excluded from the statistical analysis because of the questionable quality of absorbent solution used in sampling.

TABLE 4. DATA FROM NITROGEN DIOXIDE EXPERIMENTS (BLOCKS 1-24) AT LOS ANGELES SITE ARRANGED BY BLOCK AND OUTLET POSITION

(continued)

Hour	Block	Lab	Unspiked Samples, $\mu g/m^3$ (U)	Spiked Samples, $\mu g/m^3$ (S)	Estimated Spiking Rate, $\mu g/m^3$ (S-U)	True Spiking Rate, $\mu g/m^3$ (R)	Difference, percent of (R)
5	9	H_1	U1 = 185.0	S3 = 270.0	85.0	66.9	27
		B_1	U2 = 63.7 (b)	S2 = 69.0 (b)	(b)		(b)
		A_1	U3 = 163.9	S4 = 212.7	48.8		- 27
		G_1	U4 = 163.8	S1 = 158.1 (c)	(c)		(c)
	10	D_1	U1 = 155.0	S2 = 210.5	55.5	66.9	- 17
		F_1	U2 = 188.9	S4 = 253.3	64.4		- 4
		C_1	U3 = 169.0	S1 = 259.0	90.0		35
		E_1	U4 = 137.8	S3 = 232.1	94.3		41
6	11	B_1	U1 = 190.2	S1 = 248.7	58.5	66.9	- 13
		H_1	U2 = 195.0	S2 = 295.0	100.0		49
		G_1	U3 = 205.7	S4 = 381.0 (c)	(c)		(c)
		A_1	U4 = 247.7	S3 = 293.3	45.6		- 32
	12	E_1	U1 = 194.8	S2 = 288.6	93.8	66.9	40
		C_1	U2 = 205.5	S4 = 284.0	78.5		17
		F_1	U3 = 209.6	S1 = 274.6	65.0		- 3
		D_1	U4 = 191.4	S3 = 262.1	70.7		6
7	13	A_1	U1 = 203.6	S2 = 259.7	56.1	66.9	- 16
		G_1	U2 = 182.9	S3 = 203.8 (c)	(c)		(c)
		H_1	U3 = 168.0	S1 = 272.0	104.0		55
		B_1	U4 = 178.9	S4 = 257.1	78.2		17
	14	C_1	U1 = 189.0	S2 = 273.0	84.0	66.9	26
		D_1	U2 = 174.1	S4 = 275.5	101.4		52
		E_1	U3 = 167.0	S1 = 246.7	79.7		19
		F_1	U4 = 216.2	S3 = 285.3	69.1		3
8	15	G_1	U1 = 230.5	S2 = 261.0 (c)	(c)	66.9	(c)
		A_1	U2 = 250.6	S1 = 296.3	45.7		- 32
		B_1	U3 = 191.7	S3 = 259.1	67.4		0.5
		H_1	U4 = 229.0	S4 = 309.0	80.0		20
	16	F_1	U1 = 189.5	S2 = 261.8	72.3	66.9	8
		E_1	U2 = 140.3	S4 = 254.5	114.2		71
		D_1	U3 = 160.7	S1 = 231.5	70.8		6
		C_1	U4 = 215.0	S3 = 199.0 (d)	(d)		(d)

(b) Outlying data, excluded from statistical analysis on the basis of the studentized range test

(c) Malfunctioning gas meter in sampling train, data excluded from analysis.

(d) Incorrect laboratory reading, excluded from statistical analysis.

TABLE 4. DATA FROM NITROGEN DIOXIDE EXPERIMENTS (BLOCKS 1-24) AT LOS ANGELES SITE ARRANGED BY BLOCK AND OUTLET POSITION

(continued)

Hour	Block	Lab	Unspiked Samples, $\mu g/m^3$ (U)	Spiked Samples, $\mu g/m^3$ (S)	Estimated Spiking Rate, $\mu g/m^3$ (S-U)	True Spiking Rate, $\mu g/m^3$ (R)	Difference, percent of (R)
9	17	A_1	U1 = 38.3(e)	S2 = 186.7	(e)	66.9	(e)
		C_1	U2 = 87.0	S4 = 187.0	100.0		49
		D_1	U3 = 95.7	S3 = 174.1	78.4		17
		G_1	U4 = 110.5	S1 = 175.3	64.8		- 3
	18	F_1	U1 = 69.4	S4 = 146.9	77.5	66.9	16
		B_1	U2 = 43.9	S3 = 110.5	66.6		- 0.5
		E_1	U3 = 59.4	S2 = 130.3	70.9		6
		H_1	U4 = 67.9	S1 = 164.0	96.1		44
10	19	D_1	U1 = 51.7	S4 = 124.4	72.7	66.9	9
		G_1	U2 = 68.6	S3 = 142.9	74.3		11
		A_1	U3 = 63.9	S1 = 131.5	67.6		1
		C_1	U4 = 58.0	S2 = 95.0	37.0		- 45
	20	B_1	U1 = 61.1	S4 = 126.4	65.3	66.9	- 2
		H_1	U2 = 59.1	S3 = 143.0	83.9		25
		F_1	U3 = 71.7	S2 = 146.0	74.3		11
		E_1	U4 = 55.0	S1 = 129.2	74.2		11
11	21	G_1	U1 = 76.2	S4 = 137.2	61.0	66.9	- 9
		D_1	U2 = 53.6	S2 = 116.7	63.1		- 6
		C_1	U3 = 70.0	S1 = 109.0	39.0		- 42
		A_1	U4 = 73.4	S3 = 139.2	65.8		- 2
	22	E_1	U1 = 62.2	S4 = 134.4	72.2	66.9	8
		F_1	U2 = 84.4	S3 = 162.9	78.5		17
		H_1	U3 = 68.1	S2 = 170.0	101.9		52
		B_1	U4 = 77.3	S1 = 148.4	71.1		6
12	23	C_1	U1 = 66.0	S3 = 114.0	48.0	66.9	- 28
		A_1	U2 = 67.6	S4 = 119.6	52.0		- 22
		G_1	U3 = 74.3	S2 = 139.0	64.7		- 3
		D_1	U4 = 51.7	S1 = 114.8	63.1		- 6
	24	H_1	U1 = 76.7	S4 = 164.0	87.3	66.9	30
		E_1	U2 = 63.3	S3 = 138.7	75.4		13
		B_1	U3 = 43.2	S2 = 73.2(b)	(b)		(b)
		F_1	U4 = 79.3	S1 = 155.5	76.2		14

(e) Probable broken inlet to sampling train, data excluded from statistical analysis.

(b) Outlying data, excluded from statistical analysis on the basis of the studentized range test.

TABLE 5. DATA FROM NITROGEN DIOXIDE EXPERIMENTS (BLOCKS 1-24) AT BLOOMINGTON SITE ARRANGED BY BLOCK AND OUTLET POSITION

Hour	Block	Lab	Unspiked Samples, $\mu g/m^3$ (U)	Spiked Samples, $\mu g/m^3$ (S)	Estimated Spiking Rate, $\mu g/m^3$ (S-U)	True Spiking Rate, $\mu g/m^3$ (R)	Difference, percent of (R)
1	1	B_2	U1 = 32.1	S1 = 89.7	57.6	32.6	77
		D_2	U2 = 17.8	S2 = 31.5(a)	(a)		(a)
		C_2	U4 = 51.5	S4 = 88.6	37.1		14
	2	F_2	U1 = 72.8	S1 = 102.8	30.0	32.4	- 8
		A_2	U2 = 45.4	S2 = 78.0	32.6		0.5
		G_2	U3 = 66.7	S3 = 99.1	32.4		0
		E_2	U4 = 40.7	S4 = 65.9	25.2		- 22
2	3	B_2	U2 = 30.3	S2 = 78.3	48.0	32.5	48
		C_2	U3 = 53.3	S3 = 108.0	54.7		68
		D_2	U4 = 32.6	S4 = 59.2	26.6		- 18
	4	G_2	U1 = 40.0	S1 = 68.6	28.6	32.5	- 12
		F_2	U2 = 47.4	S2 = 83.1	35.7		10
		E_2	U3 = 37.6	S3 = 63.9	26.3		- 19
		A_2	U4 = 28.7	S4 = 52.4	23.7		- 27
3	5	C_2	U1 = 43.6	S1 = 65.1	21.5	32.7	- 34
		D_2	U3 = 18.3	S3 = 49.1	30.8		- 6
		B_2	U4 = 23.4	S4 = 55.8	32.4		- 0.9
	6	E_2	U1 = 22.0	S1 = 42.2	20.2	32.5	- 38
		G_2	U2 = 22.9	S2 = 45.7	22.8		- 30
		A_2	U3 = 18.5	S3 = 40.3	21.8		- 33
		F_2	U4 = 38.6	S4 = 61.8	23.2		- 29
4	7	D_2	U1 = 10.1	S1 = 27.5	17.4	32.5	- 46
		C_2	U2 = 6.5	S2 = 47.2	40.7		25
		B_2	U3 = 10.7	S3 = 26.5	15.8		- 51
	8	A_2	U1 = 14.8	S1 = 34.3	19.5	32.6	- 40
		E_2	U2 = 8.3	S2 = 41.2	32.9		1
		F_2	U3 = 29.2	S3 = 51.5	22.3		- 32
		G_2	U4 = 21.0	S4 = 47.6	26.6		- 18

(a) Outlying data, excluded from statistical analysis on the basis of the studentized range test.

TABLE 5. DATA FROM NITROGEN DIOXIDE EXPERIMENTS (BLOCKS 1-24) AT BLOOMINGTON SITE ARRANGED BY BLOCK AND OUTLET POSITION

(continued)

Hour	Block	Lab	Unspiked Samples, $\mu g/m^3$ (U)	Spiked Samples, $\mu g/m^3$ (S)	Estimated Spiking Rate, $\mu g/m^3$ (S-U)	True Spiking Rate, $\mu g/m^3$ (R)	Difference, percent of (R)
5	9	B_2	U2 = 8.4	S2 = 32.3	23.9	32.6	- 27
		A_2	U3 = 9.4	S3 = 37.1	27.7		- 15
		G_2	U4 = 11.4	S4 = 32.4	21.0		- 36
	10	D_2	U5 = 20.6	S5 = 38.6	18.0	32.6	- 45
		F_2	U6 = 18.3	S6 = 46.0	27.7		- 15
		C_2	U7 = 11.7	S7 = 32.5	20.8		- 36
		E_2	U8 = 6.9	S8 = 33.4	26.5		- 19
6	11	B_2	U1 = 16.5	S1 = 47.3	30.8	32.4	- 5
		G_2	U3 = 17.1	S3 = 41.9	24.8		- 23
		A_2	U4 = 21.5	S4 = 47.5	26.0		- 19
	12	E_2	U5 = 13.9	S5 = 52.4	38.5	32.4	19
		C_2	U6 = 24.6	S6 = 60.1	35.5		10
		F_2	U7 = 29.3	S7 = 54.7	25.4		- 22
		D_2	U8 = 15.5	S8 = 46.4	30.9		- 5
7	13	A_2	U1 = 36.7	S1 = 78.5	41.8	32.5	29
		G_2	U2 = 34.3	S2 = 70.5	36.2		11
		B_2	U4 = 38.7	S4 = 69.0	30.3		- 7
	14	C_2	U5 = 46.0	S5 = 87.5	41.5	32.5	28
		D_2	U6 = 36.7	S6 = 77.5	40.8		26
		E_2	U7 = 33.0	S7 = 72.8	39.8		22
		F_2	U8 = 47.0	S8 = 88.7	41.7		28
8	15	G_2	U1 = 78.1	S1 = 114.3	36.2	32.5	11
		A_2	U2 = 84.1	S2 = 128.6	44.5		37
		B_2	U3 = 92.4	S3 = 135.0	42.6		31
	16	F_2	U5 = 97.1	S5 = 128.4	31.3	32.5	- 4
		E_2	U6 = 83.5	S6 = 122.5	39.0		20
		D_2	U7 = 70.8	S7 = 114.0	43.2		33
		C_2	U8 = 114.3	S8 = 133.0	18.7		- 42

TABLE 5. DATA FROM NITROGEN DIOXIDE EXPERIMENTS (BLOCKS 1-24) AT BLOOMINGTON SITE ARRANGED BY BLOCK AND OUTLET POSITION

(continued)

Hour	Block	Lab	Unspiked Samples, $\mu g/m^3$ (U)	Spiked Samples, $\mu g/m^3$ (S)	Estimated Spiking Rate, $\mu g/m^3$ (S-U)	True Spiking Rate, $\mu g/m^3$ (R)	Difference, percent of (R)
9	17	A_2	U1 = 22.3	S1 = 48.5	26.2	32.6	- 20
		C_2	U2 = 16.0	S2 = 57.1	41.1		26
		D_2	U3 = 22.0	S3 = 34.2	12.2		- 63
		G_2	U4 = 17.1	S4 = 38.1	21.0		- 36
	18	F_2	U5 = 33.8	S5 = 76.2	42.4	32.6	30
		B_2	U6 = 22.2	S6 = 68.7	46.5		43
		E_2	U7 = 18.3	S7 = 54.4	36.1		11
10	19	D_2	U1 = 9.0	S1 = 25.4	16.4	32.5	- 50
		G_2	U2 = 19.1	S2 = 36.2	17.1		- 47
		A_2	U3 = 17.4	S3 = 38.9	21.5		- 34
		C_2	U4 = 21.2	S4 = 53.2	32.0		- 2
	20	B_2	U5 = 19.3	S5 = 46.4	27.1	32.5	- 17
		F_2	U7 = 31.9	S7 = 55.5	23.6		- 27
		E_2	U8 = 20.8	S8 = 41.0	20.2		- 38
11	21	G_2	U1 = 19.1	S1 = 28.6	9.5	32.5	- 71
		D_2	U2 = 14.7	S2 = 38.2	23.5		- 28
		C_2	U3 = 18.1	S3 = 43.4	25.3		- 22
		A_2	U4 = 17.4	S4 = 36.2	18.8		- 42
	22	E_2	U5 = 17.5	S5 = 45.3	27.8	32.5	- 14
		F_2	U6 = 30.2	S6 = 74.1(a)	43.9		35
		B_2	U8 = 10.0	S8 = 33.6	23.6		- 27
12	23	C_2	U1 = 7.7	S1 = 37.2	29.5	32.5	- 9
		A_2	U2 = 11.8	S2 = 29.4	17.6		- 46
		G_2	U3 = 5.7	S3 = 24.8	19.1		- 41
		D_2	U4 = 7.7	S4 = 27.3	19.6		- 40
	24	E_2	U6 = 17.4	S6 = 32.7	15.3	32.5	- 53
		B_2	U7 = 10.1	S7 = 21.2	11.1		- 66
		F_2	U8 = 15.4	S8 = 43.4	28.0		- 14

(a) Outlying data, excluded from statistical analysis on the basis of the studentized range test.

TABLE 6. DATA FROM NITROGEN DIOXIDE EXPERIMENTS (BLOCKS 1-24) AT MANHATTAN SITE ARRANGED BY BLOCK AND OUTLET POSITION

Hour	Block	Lab	Unspiked Samples, $\mu g/m^3$ (U)	Spiked Samples, $\mu g/m^3$ (S)	Estimated Spiking Rate, $\mu g/m^3$ (S-U)	True Spiking Rate, $\mu g/m^3$ (R)	Difference, percent of (R)
1	1	E_3	U1 = 102.9	S1 = 211.2	108.3	95.5	13
		A_3	U2 = 114.0	S2 = 239.4	125.4		31
		G_3	U4 = 114.3	S4 = 238.1	123.8		30
	2	C_3	U5 = 70.0(a)	S5 = 99.0(a)	(a)	95.5	(a)
		F_3	U6 = 212.0(b)	S6 = 277.0	(b)		(b)
		D_3	U7 = 137.6	S7 = 297.8	160.2		68
		B_3	U8 = 120.0	S8 = 250.0	130.0		36
2	3	E_3	U2 = 115.3	S2 = 228.3	113.0	95.5	18
		G_3	U3 = 133.4	S3 = 238.1	104.7		10
		A_3	U4 = 119.8	S4 = 243.2	123.4		29
	4	D_3	U5 = 131.1	S5 = 185.6	54.5	95.5	- 43
		C_3	U6 = 84.0(a)	S6 = 101.0(a)	(a)		(a)
		B_3	U7 = 117.0	S7 = 262.0	145.0		52
		F_3	U8 = 144.8	S8 = 289.8	145.0		52
3	5	G_3	U1 = 154.3	S1 = 274.3	120.0	95.6	26
		A_3	U3 = 148.9	S3 = 271.7	122.8		28
		E_3	U4 = 133.4	S4 = 268.5	135.1		41
	6	B_3	U5 = 148.0	S5 = 295.0	147.0	95.6	54
		D_3	U6 = 174.4	S6 = 286.9	112.5		18
		F_3	U7 = 162.8	S7 = 315.6	152.8		60
		C_3	U8 = 62.0 (a)	S8 = 176.0 (a)	(a)		(a)
4	7	A_3	U1 = 155.9	S1 = 276.3	120.4	95.5	26
		G_3	U2 = 154.3	S2 = 278.1	123.8		30
		E_3	U3 = 144.1	S3 = 262.2	118.1		24
	8	F_3	U5 = 186.2	S5 = 331.4	145.2	95.5	52
		B_3	U6 = 158.0	S6 = 301.0	143.0		50
		C_3	U7 = 67.0(a)	S7 = 170.0(a)	(a)		(a)
		D_3	U8 = 182.9	S8 = 309.5	126.6		33

(a) Laboratory C_3 determinations inconsistent with other laboratories, excluded from statistical analysis.

(b) Outlying data, excluded from statistical analysis on the basis of the studentized range test.

TABLE 6. DATA FROM NITROGEN DIOXIDE EXPERIMENTS (BLOCKS 1-24) AT MANHATTAN SITE ARRANGED BY BLOCK AND OUTLET POSITION

(continued)

Hour	Block	Lab	Unspiked Samples, $\mu g/m^3$ (U)	Spiked Samples, $\mu g/m^3$ (S)	Estimated Spiking Rate, $\mu g/m^3$ (S-U)	True Spiking Rate, $\mu g/m^3$ (R)	Difference, percent of (R)
5	9	E_3	U2 = 160.1	S2 = 281.6	121.5	95.7	27
		F_3	U3 = 198.5	S3 = 362.8	164.3		72
		D_3	U4 = 169.2	S4 = 349.6	180.4		89
	10	A_3	U5 = 171.0	S5 = 303.3	132.3	95.7	38
		C_3	U6 = 56.0(a)	S6 = 117.0(a)	(a)		(a)
		G_3	U7 = 173.4	S7 = 287.7	114.3		19
		B_3	U8 = 187.0	S8 = 328.0	141.0		47
6	11	E_3	U1 = 185.9	S1 = 289.8	103.9	95.5	9
		D_3	U3 = 231.5	S3 = 333.2	101.7		6
		F_3	U4 = 217.9	S4 = 356.2	138.3		45
	12	B_3	U5 = 191.0	S5 = 334.0	143.0	95.5	50
		G_3	U6 = 192.4	S6 = 316.2	123.8		30
		C_3	U7 = 81.0(a)	S7 = 129.0(a)	(a)		(a)
		A_3	U8 = 192.9	S8 = 312.9	120.0		26
7	13	F_3	U1 = 201.6	S1 = 349.0	147.4	95.3	55
		D_3	U2 = 136.8	S2 = 288.4	151.6		59
		E_3	U4 = 161.2	S4 = 290.0	128.8		35
	14	G_3	U5 = 169.5	S5 = 281.9	112.4	95.3	18
		A_3	U6 = 172.2	S6 = 297.6	125.4		32
		B_3	U7 = 171.0	S7 = 310.0	139.0		46
		C_3	U8 = 66.0(a)	S8 = 113.0(a)	(a)		(a)
8	15	D_3	U1 = 155.4	S1 = 291.1	135.7	95.5	42
		F_3	U2 = 147.3	S2 = 299.2	151.9		59
		E_3	U3 = 123.6	S3 = 243.9	120.3		26
	16	C_3	U5 = 48.0(a)	S5 = 88.0(a)	(a)	95.5	(a)
		B_3	U6 = 125.0	S6 = 270.0	145.0		52
		A_3	U7 = 128.9	S7 = 242.9	114.0		19
		G_3	U8 = 131.4	S8 = 251.5	120.1		26

(a) Laboratory C_3 determinations inconsistent with other laboratories, excluded from statistical analysis.

TABLE 6. DATA FROM NITROGEN DIOXIDE EXPERIMENTS (BLOCKS 1-24) AT MANHATTAN SITE ARRANGED BY BLOCK AND OUTLET POSITION

(continued)

Hour	Block	Lab	Unspiked Samples, $\mu g/m^3$ (U)	Spiked Samples, $\mu g/m^3$ (S)	Estimated Spiking Rate, $\mu g/m^3$ (S-U)	True Spiking Rate, $\mu g/m^3$ (R)	Difference, percent of (R)
9	17	F_3	U1 = 112.7	S1 = 259.0	146.3	95.5	53
		G_3	U2 = 102.9	S2 = 209.6	106.7		12
		A_3	U3 = 95.2	S3 = 236.3	141.1		48
		D_3	U4 = 117.4	S4 = 249.0	131.6		38
	18	C_3	U5 = 38.0(a)	S5 = 86.0(a)	(a)	95.5	(a)
		E_3	U6 = 94.2	S6 = 211.6	117.4		23
		B_3	U7 = 109.0	S7 = 249.0	140.0		47
10	19	A_3	U1 = 114.3	S1 = 234.2	119.9	95.5	26
		D_3	U2 = 96.2	S2 = 225.3	129.1		35
		F_3	U3 = 132.9	S3 = 267.6	134.7		41
		G_3	U4 = 114.3	S4 = 232.4	118.1		24
	20	E_3	U5 = 108.6	S5 = 222.4	113.8	95.5	19
		C_3	U7 = 41.0(a)	S7 = 84.0(a)	(a)		(a)
		B_3	U8 = 117.0	S8 = 249.0	132.0		38
11	21	D_3	U1 = 118.7	S1 = 248.2	129.5	95.5	36
		A_3	U2 = 119.3	S2 = 246.7	127.4		33
		G_3	U3 = 112.4	S3 = 238.1	125.7		32
		F_3	U4 = 134.6	S4 = 277.4	142.8		50
	22	B_3	U5 = 118.0	S5 = 258.0	140.0	95.5	47
		C_3	U6 = 41.0(a)	S6 = 87.0(a)	(a)		(a)
		E_3	U8 = 105.0	S8 = 237.7	132.7		39
12	23	G_3	U1 = 116.2	S1 = 228.6	112.4	95.3	18
		F_3	U2 = 130.1	S2 = 269.1	139.0		46
		D_3	U3 = 118.8	S3 = 253.4	134.6		41
		A_3	U4 = 119.6	S4 = 240.7	121.1		27
	24	B_3	U6 = 119.0	S6 = 256.0	137.0	95.3	44
		E_3	U7 = 101.6	S7 = 221.6	120.0		26
		C_3	U8 = 76.0(a)	S8 = 163.0(a)	(a)		(a)

(a) Laboratory C_3 determinations inconsistent with other laboratories, excluded from statistical analysis.

TABLE 7. BLOCK STATISTICS (BLOCKS 1-24) FOR UNSPIKED SAMPLES OF NITROGEN DIOXIDE FROM LOS ANGELES

Hour	Block	n	m	s	$\hat{s}$	w	w/$\hat{s}$	CV
1	1	3	87.9	8.0	12.6	15.9	1.27	9
	2	4	55.0	17.6	10.0	40.6	4.08	32
2	3	4	52.0	5.5	9.7	12.8	1.32	11
	4	4	54.6	12.3	9.9	29.3	2.95	23
3	5	4	46.1	3.6	9.3	8.3	0.90	8
	6	4	52.6	9.5	9.8	23.0	2.35	18
4	7	4	54.1	6.5	9.9	14.2	1.44	12
	8	4	62.4	16.3	10.5	34.7	3.29	26
5	9	4	144.1	54.5	17.0	121.3	7.13(a)	38
	10	4	162.7	21.6	18.5	51.1	2.77	13
6	11	4	209.6	26.2	22.2	57.5	2.59	12
	12	4	200.3	8.6	21.5	18.2	0.85	4
7	13	4	183.3	14.9	20.1	35.6	1.77	8
	14	4	186.6	21.8	20.4	49.2	2.42	12
8	15	4	225.4	24.6	23.4	58.9	2.51	11
	16	3	163.5	24.7	18.5	49.2	2.65	15
9	17	3	97.7	11.9	13.3	23.5	1.76	12
	18	4	60.1	11.7	10.4	25.5	2.46	19
10	19	4	60.5	7.3	10.4	16.9	1.63	12
	20	4	61.7	7.1	10.5	16.7	1.59	12
11	21	4	68.3	10.1	11.0	22.6	2.05	15
	22	4	73.0	9.8	11.4	22.2	1.95	13
12	23	4	64.9	9.5	10.7	22.6	2.10	15
	24	4	65.6	16.5	10.8	36.1	3.34	25

(a) Statistically significant at the one percent level indicating that the block contains one or more outlying values.

TABLE 8. BLOCK STATISTICS (BLOCKS 1-24) FOR UNSPIKED SAMPLES OF NITROGEN DIOXIDE FROM BLOOMINGTON

Hour	Block	n	m	s	$\hat{s}$	w	$w/\hat{s}$	CV
1	1	3	33.8	16.9	8.3	33.7	4.07	50
	2	4	56.4	15.7	10.1	32.1	3.19	28
2	3	3	38.7	12.7	8.7	23.0	2.65	33
	4	4	38.4	7.7	8.6	18.7	2.16	20
3	5	3	28.4	13.4	7.9	25.3	3.22	47
	6	4	25.5	8.9	7.6	20.1	2.64	35
4	7	3	9.1	2.3	6.3	4.2	0.66	25
	8	4	18.3	8.9	7.1	20.9	2.96	49
5	9,10	7	12.4	5.1	6.6	13.7	2.08	41
6	11,12	7	19.8	5.6	7.2	15.4	2.15	28
7	13,14	7	38.9	5.5	8.7	14.0	1.61	14
8	15,16	7	88.6	14.3	12.6	43.5	3.45	16
9	17,18	7	21.7	5.9	7.3	17.8	2.43	27
10	19,20	7	19.8	6.7	7.2	22.9	3.19	34
11	21,22	7	18.1	6.1	7.0	20.2	2.87	34
12	23,24	7	10.8	4.3	6.5	11.7	1.81	40

TABLE 9. BLOCK STATISTICS (BLOCKS 1-24) FOR UNSPIKED SAMPLES OF NITROGEN DIOXIDE FROM MANHATTAN

Hour	Block	n	m	s	$\hat{s}$	w	$w/\hat{s}$	CV
1	1,2	6	133.5	40.1	16.2	109.1	6.75(a)	30
2	3,4	6	126.9	11.5	15.6	29.5	1.89	9
3	5,6	6	153.6	14.0	17.8	41.0	2.31	9
4	7,8	6	163.6	17.0	18.6	42.1	2.27	10
5	9,10	6	176.5	13.8	19.6	38.4	1.96	8
6	11,12	6	201.9	18.3	21.6	45.6	2.11	9
7	13,14	6	168.7	20.9	19.0	64.8	3.42	12
8	15,16	6	135.3	13.0	16.3	31.8	1.95	10
9	17,18	6	105.2	9.4	13.9	23.2	1.67	9
10	19,20	6	113.9	11.9	14.6	36.7	2.51	10
11	21,22	6	118.0	9.8	14.9	29.6	1.98	8
12	23,24	6	117.5	9.2	14.9	28.5	1.91	8

(a) Statistically significant at the one percent level indicating that the block contains one or more outlying values.

TABLE 10. BLOCK STATISTICS (BLOCKS 1-24) FOR SPIKED SAMPLES OF NITROGEN DIOXIDE FROM LOS ANGELES

Hour	Block	n	m	s	$\hat{s}$	w	w/$\hat{s}$	CV
1	1	3	171.7	17.6	19.2	34.9	1.82	10
	2	4	131.7	14.7	16.0	35.5	2.21	11
2	3	4	133.3	12.3	16.2	29.4	1.82	9
	4	4	125.7	10.5	15.6	23.8	1.53	8
3	5	4	113.4	19.5	14.6	46.0	3.16	17
	6	4	121.8	10.1	15.2	23.7	1.55	8
4	7	4	131.4	8.8	16.0	19.4	1.21	7
	8	4	144.0	19.5	17.0	42.9	2.52	14
5	9	3	183.9	103.5	20.2	201.0	9.97(a)	56
	10	4	238.7	22.1	24.5	48.5	1.98	9
6	11	3	279.0	26.3	27.7	46.3	1.67	9
	12	4	277.3	11.7	27.5	26.5	0.96	4
7	13	3	262.9	8.0	26.4	14.9	0.56	3
	14	4	270.1	16.5	27.0	38.6	1.43	6
8	15	3	288.1	25.9	28.4	49.9	1.76	9
	16	4	236.7	28.3	24.3	62.8	2.58	12
9	17	4	180.8	7.0	19.9	12.9	0.65	4
	18	4	137.9	22.9	16.5	53.5	3.24	17
10	19	4	123.4	20.4	15.4	47.9	3.12	17
	20	4	136.1	9.8	16.4	19.6	1.20	7
11	21	4	125.5	15.0	15.5	30.2	1.94	12
	22	4	153.9	15.8	17.8	35.6	2.00	10
12	23	4	121.8	11.7	15.2	25.0	1.64	10
	24	4	132.8	41.1	16.1	90.8	5.63(a)	31

(a) Statistically significant at the one percent level indicating that the block contains one or more outlying values.

TABLE 11. BLOCK STATISTICS (BLOCKS 1-24) FOR SPIKED SAMPLES OF NITROGEN DIOXIDE FROM BLOOMINGTON

Hour	Block	n	m	s	$\hat{s}$	w	$w/\hat{s}$	CV
1	1	3	69.9	33.3	11.1	58.2	5.22(a)	48
	2	4	86.4	17.5	12.9	36.9	2.97	20
2	3	3	81.8	24.6	12.1	48.8	4.04	30
	4	4	67.0	12.7	10.9	30.7	2.81	19
3	5	3	56.7	8.0	10.1	16.0	1.58	14
	6	4	47.5	9.8	9.4	21.5	2.30	21
4	7	3	33.7	11.7	8.3	20.7	2.50	35
	8	4	43.6	7.5	9.1	17.2	1.90	17
5	9,10	7	36.0	5.1	8.5	14.0	1.66	14
6	11,12	7	50.0	6.1	9.6	18.2	1.90	12
7	13,14	7	77.8	7.8	11.8	19.7	1.67	10
8	15,16	7	125.1	8.5	15.5	21.0	1.35	7
9	17,18	7	53.9	15.2	9.9	42.0	4.25	28
10	19,20	7	42.4	10.4	9.0	30.1	3.36	25
11	21,22	7	42.8	14.9	9.0	45.5	5.06(a)	35
12	23,24	7	30.9	7.6	8.1	22.2	2.76	25

(a) Statistically significant at the one percent level indicating that the block contains one or more outyling values.

TABLE 12. BLOCK STATISTICS (BLOCKS 1-24) FOR SPIKED SAMPLES OF NITROGEN DIOXIDE FROM MANHATTAN

Hour	Block	n	m	s	$\hat{s}$	w	$w/\hat{s}$	CV
1	1,2	6	252.2	30.8	25.6	86.6	3.39	12
2	3,4	6	241.2	34.8	24.7	104.2	4.22	14
3	5,6	6	285.3	17.9	28.2	47.1	1.67	6
4	7,8	6	293.1	25.5	28.8	69.2	2.40	9
5	9,10	6	318.8	33.3	30.8	81.2	2.63	10
6	11,12	6	323.7	22.7	31.2	66.4	2.13	7
7	13,14	6	302.8	24.6	29.6	67.1	2.27	8
8	15,16	6	266.4	24.4	26.7	56.3	2.11	9
9	17,18	6	235.7	20.8	24.3	49.4	2.04	9
10	19,20	6	238.5	17.0	24.5	45.2	1.85	7
11	21,22	6	251.0	14.9	25.5	39.7	1.56	6
12	23,24	6	244.9	17.9	25.0	47.5	1.90	7

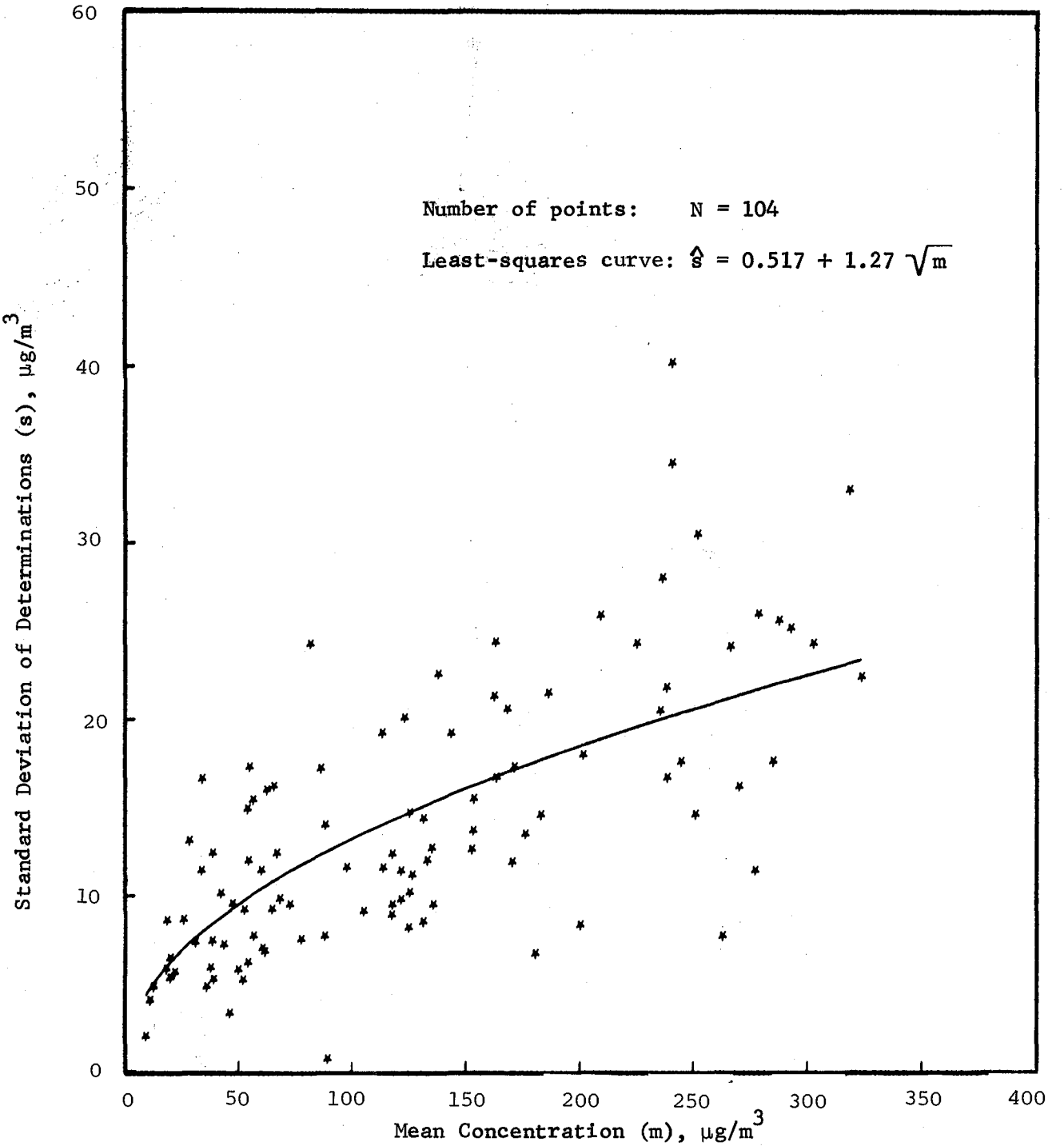


FIGURE 10. SCATTER DIAGRAM AND LEAST-SQUARES CURVE RELATING BETWEEN-LABORATORY STANDARD DEVIATION (REPRODUCIBILITY) TO CONCENTRATION OF NITROGEN DIOXIDE

A least-squares regression equation of the form $\hat{s} = a + b\sqrt{m}$ was fitted to the data points in Figure 10 by the method of weighted least squares. Weights were assigned to the data points in order to compensate for the fact that two assumptions of the statistical method are being violated:

(1) The coordinates of the data points are averages, which are not always computed from the same number of observations;

(2) The variances along the regression curve are not equal.

The appropriate weighting formula is $W = f/(\alpha + \beta \sqrt{m})^2$, where W represents the weight, f denotes the number of degrees of freedom associated with the computed standard deviation $\hat{s}$, α and β denote constant terms in the true regression curve, and m is the mean concentration. The parameters α and β are not known, nor are their least-squares estimates, a and b. An iterative approach is required, using successive estimates of a, b, and W which converge to a least-squares solution. By this procedure, the equation $\hat{s} = 0.517 + 1.27\sqrt{m}$ is obtained as an estimate of the true regression curve $s = \alpha + \beta \sqrt{m}$. The standard deviation of the residuals about the regression line is found to be 3.5 $\mu g/m^3$. This curve summarizes the results of the reproducibility analysis.

It may be noted that the least-squares curve for between-laboratory standard deviations is approximately linear for concentrations between 50 and 300 $\mu g/m^3$. A least squares line (not shown) was fitted to these data and yielded the equation: $\hat{s} = 5.53 + 0.066$ m, with a standard deviation for the residuals equal to 3.7 $\mu g/m^3$. The curve shown in Figure 10 is judged to be preferable to the computed line especially for low concentrations and for providing a more realistic extrapolation of standard deviation to higher nitrogen dioxide concentrations.

A linear regression equation was instrumental in identifying outliers in the basic data by supplying estimates of s for each value of m in Tables 7 through 12. These estimates are listed under column heading $\hat{s}$ in Tables 7 through 12. The ratio of the range to the estimated standard deviation $w/\hat{s}$ was next computed for each block and compared with the 99 percent point of the studentized range [6,7,8]. Six values of $w/\hat{s}$, which are identified

in Tables 7 through 11, were found to be statistically significant by this test. The significant values of $w/\hat{s}$ served to identify blocks containing outlying observations and so, by reference to Tables 4 through 6, the individual outliers were determined. These outliers, together with identification of their location in the experimental design, are listed in Table 13 along with the revised block statistics obtained by removing them from the computations.

Analysis of Repeatability

Experimental Data

The results of the nitrogen dioxide measurements at all sites from Blocks 25 through 32 of the statistical design are presented in Tables 14, 15, and 16. In each of these three tables, the experimental data are arranged by block. For each set of duplicate determinations, the difference (in absolute value) is given. Given also is the coefficient of variation, CV, which is the ratio of the standard deviation of the duplicate determinations to the arithmetic mean of the duplicate determinations, expressed as a percentage of the latter. The spiking concentration for each block, in units of $\mu g/m^3$, is shown in the last column.

Evaluation of Repeatability

The combined data from all three sampling sites were used to explore the relationship between within-laboratory variability and concentration level of nitrogen dioxide. For each homogeneous time period, the block mean and the pooled standard deviation of duplicate determinations were computed for unspiked samples and for spiked samples. The results are given in Table 17. Data for unspiked samples from Block 25 at Los Angeles (see Table 14) are used to illustrate the computations. The number of determinations in this group of data is four, so the numeral 4 appears on the first line of Table 17 in the column headed "n" to denote the sample size on which the block mean is based. This mean, m, is computed from the results shown in Table 14, as follows:

TABLE 13. COMPLETE LIST OF STATISTICAL OUTLIERS AND CORRESPONDING REVISED BLOCK STATISTICS

Site	Hour	Block	Outlier[a]			Revised Statistics[b]		
			Lab	Outlet	Reading	n	m	s
Los Angeles	5	9	B_1	U2	63.7	3	170.9	12.2
Los Angeles	5	9	B_1	S2	69.0	2	241.4	40.5
Los Angeles	12	24	B_1	S2	73.2	3	152.7	12.9
Bloomington	1	1	D_2	S2	31.5	2	89.3	1.0
Bloomington	11	21 + 22	F_2	S6	74.1	6	37.6	6.2
Manhattan	1	1 + 2	F_3	U6	212.0	5	117.8	12.7

(a) Outliers determined with 99 percent confidence by the studentized range test.

(b) Excluding outliers.

TABLE 14. DATA FROM BLOCKS 25-32 OF NITROGEN DIOXIDE EXPERIMENTS AT LOS ANGELES SITE ARRANGED BY BLOCK

		Unspiked Samples, $\mu g/m^3$					Spiked Samples, $\mu g/m^3$					
Hour	Block	Lab	(Ui)	(Uj)	|Ui-Uj|	CV	Lab	(Si)	(Sj)	|Si-Sj|	CV	Spiking
13	25	B_1	U1 = 239.5	U2 = 228.0	11.5	4	A_1	S1 = 310.2	S3 = 308.0	2.2	0.5	66.9
		C_1	U3 = 210.2	U4 = 205.3	4.9	2	H_1	S2 = 305.0	S4 = 290.0	15.0	4	
	26	E_1	U1 = 250.5	U2 = 247.5	3.0	0.9	D_1	S1 = 321.5	S3 = 302.3	19.2	4	66.9
		G_1	U3 = 295.3	U4 = 264.8	30.5	8	F_1	S2 = 380.0	S4 = 363.3	16.7	3	
14	27	C_1	U1 = 291.1	U2 = 290.5	0.6	0.1	H_1	S1 = 389.0	S3 = 395.0	6.0	1	66.9
		B_1	U3 = 312.5	U4 = 318.2	5.7	1	A_1	S2 = (a)	S4 = 386.2	(a)	(a)	
	28	F_1	U1 = 265.9	U2 = 299.4	33.5	8	G_1	S1 = 362.0	S3 = 316.2	45.8	10	66.9
		D_1	U3 = 252.6	U4 = 243.0	9.6	3	E_1	S2 = 306.5	S4 = 283.2	23.3	6	
15	29	H_1	U1 = 205.0	U2 = 203.0	2.0	0.7	C_1	S1 = 253.5	S3 = 271.9	18.4	5	66.9
		A_1	U3 = 224.4	U4 = 228.4	4.0	1	B_1	S2 = 281.6	S4 = 271.4	10.2	3	
	30	G_1	U1 = 160.0	U2 = 156.2	3.8	2	E_1	S1 = 218.5	S3 = 225.9	7.4	2	66.9
		F_1	U3 = 167.4	U4 = 165.1	2.3	1	D_1	S2 = 200.9	S4 = 206.9	6.0	2	
16	31	A_1	U1 = 148.3	U2 = 143.2	5.1	2	B_1	S1 = 220.0	S3 = 211.1	8.9	3	66.9
		H_1	U3 = 147.0	U4 = 134.0	13.0	6	C_1	S2 = 189.9	S4 = 196.8	6.9	2	
	32	D_1	U1 = 80.4	U2 = 74.6	5.8	5	F_1	S1 = 185.5	S3 = 194.6	9.1	3	66.8
		E_1	U3 = 85.0	U4 = 85.5	0.5	0.4	G_1	S2 = 181.0	S4 = 165.7	15.3	6	

(a) Cracked bubbler, data excluded from statistical analysis.

TABLE 15. DATA FROM BLOCKS 25-32 OF NITROGEN DIOXIDE EXPERIMENTS AT BLOOMINGTON SITE ARRANGED BY BLOCK

		Unspiked Samples, $\mu g/m^3$					Spiked Samples, $\mu g/m^3$					
Hour	Block	Lab	(Ui)	(Uj)	|Ui-Uj|	CV	Lab	(Si)	(Sj)	|Si-Sj|	CV	Spiking
13	25	B_2	U1 = 8.0	U2 = 6.0	2.0	20	A	S1 = 32.8	S3 = 32.2	0.6	1	32.5
		C_2	U3 = 9.0	U4 = 9.7	0.7	5			(a)			
	26	E_2	U5 = 8.5	U6 = 4.5	4.0	43	D	S5 = 27.3	S7 = 28.6	1.3	3	32.5
		G_2	U7 = 7.6	U8 = 7.6	0.0	0.0	F	S6 = 37.0	S8 = 48.7	11.7	19	
14	27	C_2	U1 = 10.0	U2 = 14.0	4.0	23			(a)			32.5
		B_2	U3 = 8.0	U4 = 5.0	3.0	32	A	S2 = 35.7	S4 = 33.6	2.1	4	
	28	F_2	U5 = 12.5	U6 = 12.0	0.5	3	G	S5 = 30.5	S7 = 26.7	3.8	9	32.5
		D_2	U7 = 6.3	U8 = 4.2	2.1	28	E	S6 = 33.9	S8 = 35.4	1.5	3	
15	29			(a)			C	S1 = 50.7	S3 = 51.9	1.2	1.7	32.5
		A_2	U3 = 17.7	U4 = 15.8	1.9	8	B	S2 = 46.0	S4 = 42.0	4.0	6	
	30	G_2	U5 = 11.4	U6 = 11.4	0.0	0.0	E	S5 = 43.4	S7 = 45.1	1.7	3	32.5
		F_2	U7 = 16.0	U8 = 16.6	0.6	2	D	S6 = 37.8	S8 = 36.0	1.8	3	
16	31	A_2	U1 = 28.5	U2 = 27.3	1.2	3	B	S1 = 56.0	S3 = 64.0	8.0	9	32.5
				(a)			C	S2 = 63.0	S4 = 63.7	0.7	0.8	
	32	D_2	U5 = 19.7	U6 = 19.7	0.0	0.0	F	S5 = 66.7	S7 = 79.8	13.1	12	32.5
		E_2	U7 = 24.4	U8 = 22.8	1.6	5	G	S6 = 57.2	S8 = 51.4	5.8	7	

(a) Data were not obtained for this cell since only seven laboratories participated in the test.

TABLE 16. DATA FROM BLOCKS 25-32 OF NITROGEN DIOXIDE EXPERIMENTS AT MANHATTAN SITE ARRANGED BY BLOCK

		Unspiked Samples, $\mu g/m^3$					Spiked Samples, $\mu g/m^3$					
Hour	Block	Lab	(Ui)	(Uj)	|Ui-Uj|	CV	Lab	(Si)	(Sj)	|Si-Sj|	CV	Spiking
13	25	E_3	U1 = 122.3	U2 = 124.1	1.8	1	F	S1 = 300.6	S2 = 301.2	0.6	0.1	95.4
		G_3	U3 = 127.6	U4 = 121.9	5.7	3			(a)			
	26	B_3	U5 = 128.0	U6 = 129.0	1.0	0.6	A	S5 = 254.5	S6 = 256.1	1.6	0.4	95.4
		D_3	U7 = 87.0	U8 = 122.5	35.5	24	C	S7 = 173.0	S8 = 171.0	2.0	0.8	
14	27	G_3	U1 = 120.0	U2 = 120.0	0.0	0.0	F	S3 = 278.8	S4 = 278.0	0.8	0.2	95.7
		E_3	U3 = 118.4	U4 = 112.3	6.1	4			(a)			
	28	C_3	U5 = 75.0	U6 = 74.0	1.0	0.9	D	S5 = 267.1	S7 = 264.5	2.6	0.7	95.7
		A_3	U7 = 116.4	U8 = 116.2	0.2	0.1	B	S6 = 260.0	S8 = 252.0	8.0	2	
15	29	F_3	U3 = 120.2	U4 = 113.1	7.1	4	G	S1 = 215.3	S2 = 224.8	9.5	3	95.5
				(a)			E	S3 = 209.0	S4 = 214.5	5.5	2	
	30	D_3	U5 = 104.9	U6 = 100.8	4.1	3	B	S5 = 232.0	S7 = 234.0	2.0	0.6	95.5
		C_3	U7 = 66.0	U8 = 65.0	1.0	1	A	S6 = 228.5	S8 = 225.7	2.8	0.9	
16	31	F_3	U1 = 117.1	U2 = 121.9	4.8	3	E	S1 = 222.2	S2 = 227.5	5.3	2	95.4
				(a)			G	S3 = 232.4	S4 = 236.2	3.8	1	
	32	A_3	U5 = 106.1	U6 = 105.0	1.1	0.7	C	S5 = 153.0	S7 = 155.0	2.0	0.9	95.4
		B_3	U7 = 108.0	U8 = 108.0	0.0	0.0	D	S6 = 174.5	S8 = 236.1	61.6	21	

(a) Data were not obtained for this cell since only seven laboratories participated in the test.

TABLE 17. BLOCK STATISTICS (BLOCKS 25-32) FOR SAMPLES OF NITROGEN DIOXIDE

Site	Sample	Hour	Block	n	m	df	s
Los Angeles	Unspiked	13	25	4	220.8	2	6.3
			26	4	264.5	2	15.3
		14	27	4	303.1	2	2.9
			28	4	265.2	2	17.4
		15	29	4	215.2	2	2.2
			30	4	162.2	2	2.2
		16	31	4	143.1	2	7.0
			32	4	81.4	2	2.9
	Spiked	13	25	4	303.3	2	7.6
			26	4	341.8	2	12.7
		14	27	2	392.0	1	4.2
			28	4	317.0	2	25.7
		15	29	4	269.6	2	10.5
			30	4	213.0	2	4.8
		16	31	4	204.4	2	5.6
			32	4	181.7	2	8.9
Bloomington	Unspiked	13	25,26	8	7.6	4	1.6
		14	27,28	8	9.0	4	1.9
		15	29,30	6	14.8	3	0.8
		16	31,32	6	23.7	3	0.8
	Spiked	13	25,26	6	34.4	3	4.8
		14	27,28	6	32.6	3	1.9
		15	29,30	8	44.1	4	1.7
		16	31,32	8	62.7	4	5.8
Manhattan	Unspiked	13	25,26	8	120.3	4	12.7
		14	27,28	8	106.5	4	2.2
		15	29,30	6	95.0	3	3.4
		16	31,32	6	111.0	3	2.0
	Spiked	13	25,26	6	242.7	3	1.1
		14	27,28	6	266.7	3	3.4
		15	29,30	8	223.0	4	4.1
		16	31,32	8	204.6	4	21.9

$$m = \frac{239.5 + 228.0 + 210.2 + 205.3}{4} = 220.8 ,$$

and the result appears on the first line of Table 17 in the column headed "m". There are two degrees of freedom for measuring repeatability as indicated by the numeral 2 on the first line of Table 17 in the column headed "df". The pooled standard deviation of duplicate determinations, which is the measure of repeatability for the block of data under discussion, is computed as follows:

$$\hat{s} = \sqrt{\frac{(239.5-233.75)^2 + (228.0-233.75)^2 + (210.2-207.75)^2 + (205.3-207.75)^2}{1 + 1}} = 6.3,$$

where 233.75 and 207.75 represent the means of duplicate measurements in Block 25. This result appears on the first line of Table 17 in the column headed "s".

The 32 pairs of values of m and s in Table 17, representing both unspiked and spiked samples from all three sampling sites, are plotted as points of a scatter diagram in Figure 11. It is apparent from this graph that the within-laboratory standard deviation increases with increasing concentration.

A curve of the form $\hat{s} = b\sqrt{m}$ was fitted to the data points by the method of weighted least squares. Here, the appropriate weighting formula is $W = f/(\beta\sqrt{m})^2$. Again, an iterative approach is required, resulting in the equation $\hat{s} = 0.524\sqrt{m}$ with a standard deviation of residuals equal to 2.6 micrograms per cubic meter. A model of the form $\hat{s} = a + b\sqrt{m}$ yields a smaller residual standard deviation of 2.4 $\mu g/m^3$, but also yields an undesirable negative value for a; a model of the form $\hat{s} = a + bm$ yields a value of 2.3 $\mu g/m^3$ for the residual standard deviation. For consistency with the previous analysis of reproducibility, the form $\hat{s} = b\sqrt{m}$ is chosen. Accordingly, the curve of the equation $\hat{s} = 0.524\sqrt{m}$ is shown in Figure 11. This curve summarizes the results of the repeatability analysis.

The preceding equation was used to obtain an approximation of sensitivity as follows. The minimum measured mean concentration is found to be 7.6 $\mu g/m^3$ from Table 17. Substitution of this value for m in the above

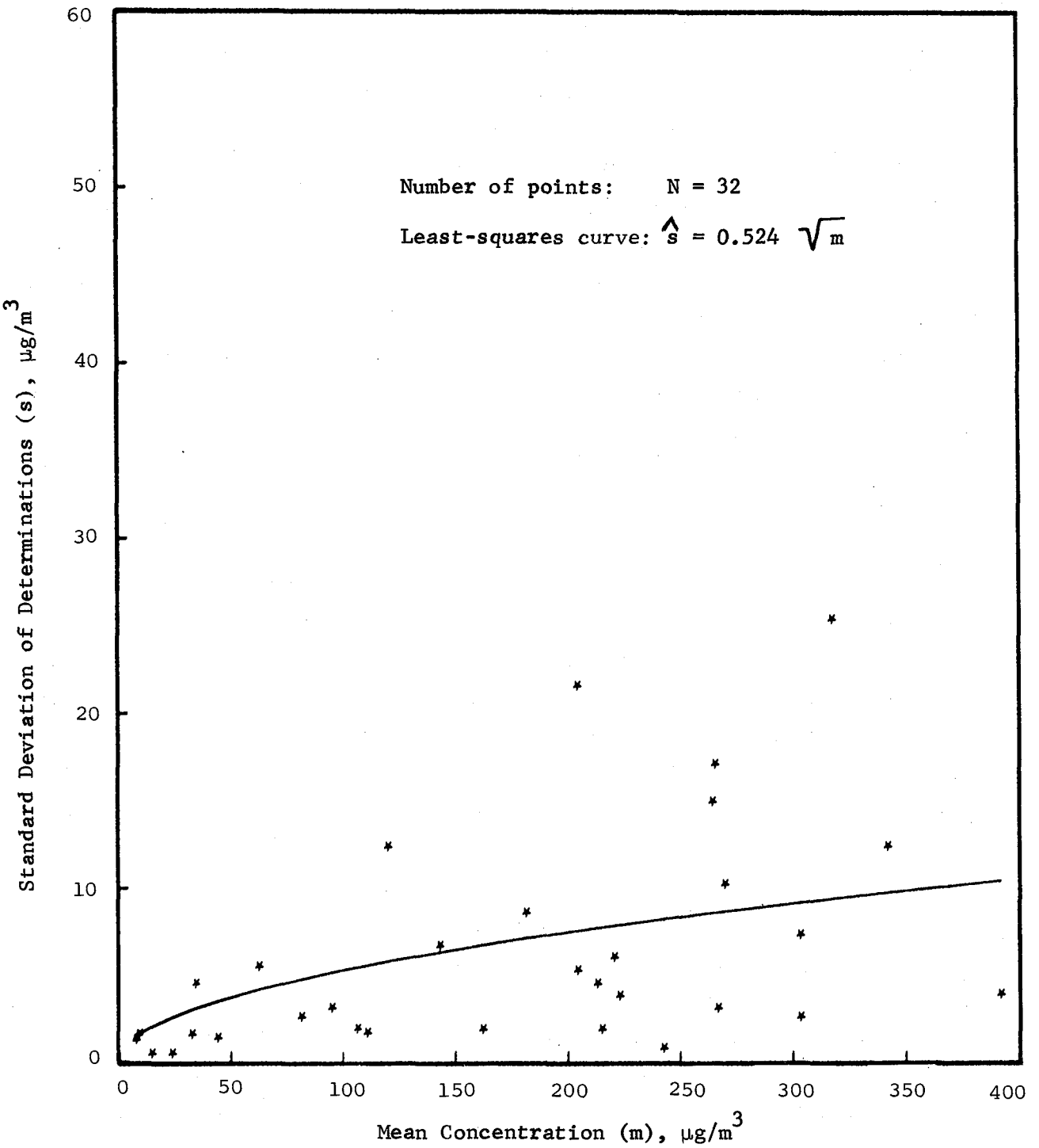


FIGURE 11. SCATTER DIAGRAM AND LEAST-SQUARES CURVE RELATING WITHIN-LABORATORY STANDARD DEVIATION (REPEATABILITY) TO CONCENTRATION OF NITROGEN DIOXIDE

equation yields s = 1.48, and twice this standard deviation, 3 $\mu g/m^3$, is considered to be an approximation of the lower limit of detection of the Test Method.

In the preceding analysis of repeatability, the data reported by all laboratories for Blocks 25 through 32 at each sampling site were combined in order to base the results on the largest possible number of data points. The resulting equation relating the within-laboratory standard deviation (repeatability) to mean concentration constitutes a single, pooled estimate which depicts the performance of the "average" laboratory. This estimate tells nothing about the performance of individual laboratories. In order to develop this type of information, a similar analysis was performed for each laboratory. It was found that the within-laboratory standard deviations for individual laboratories varied considerably. This substantiates the need for a multi-laboratory testing program in establishing a measure of repeatability, and the dangers of basing such measures on the performance of a single laboratory.

Analysis of Accuracy

In addition to providing an estimate of between-laboratory variability (reproducibility) the data from Blocks 1 through 24 of the statistical design provide an estimate of accuracy. The difference (S-U) between the spiked sample determination and the unspiked sample determination, for a given block and a given laboratory, is a measure of the controlled amount of nitrogen dioxide added to the ambient atmosphere. These differences, obtained by each laboratory at each of the three sampling sites, are the basis for the analysis of accuracy.

The percent differences in the last column of Tables 4, 5, and 6 are summarized by the histograms in Figures 12, 13, and 14, respectively. The histogram for Los Angeles in Figure 12, which is based on 87 measurements of the difference, S-U, is fairly symmetrical and indicative of a normal distribution. The distribution has a mean of + 11 percent, which indicates a positive bias, and a standard deviation of 22.0 percent. The hypothesis that the true bias is zero, versus the alternative two-sided hypothesis that the true bias is different from zero, is tested by use of Student's t, as follows:

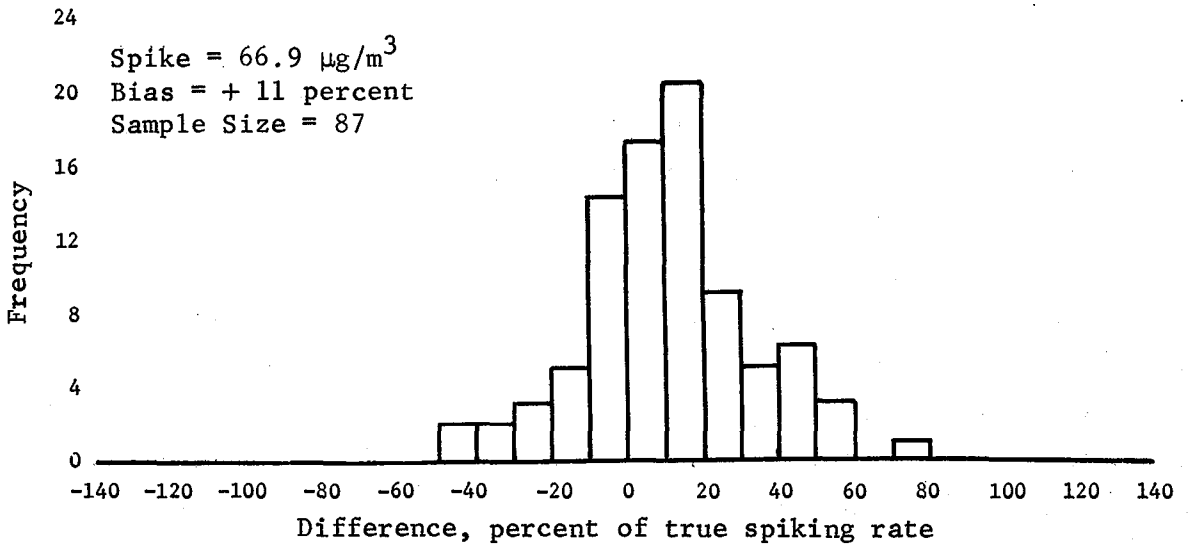


FIGURE 12. HISTOGRAM OF DIFFERENCES IN SPIKE DETERMINATIONS AT LOS ANGELES

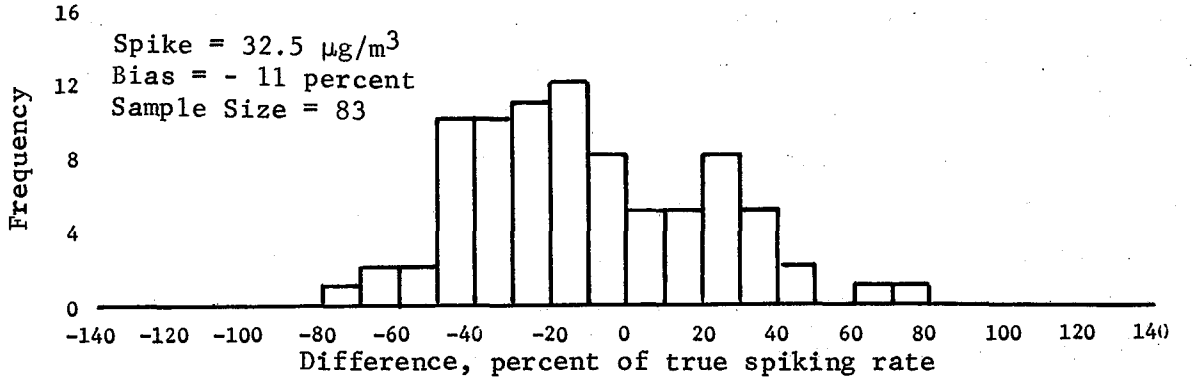


FIGURE 13. HISTOGRAM OF DIFFERENCES IN SPIKE DETERMINATIONS AT BLOOMINGTON

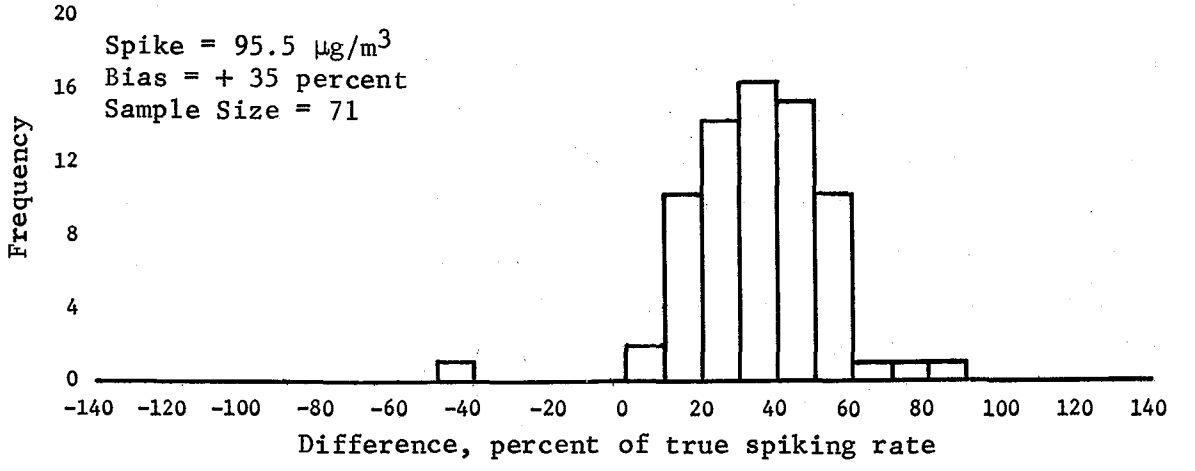


FIGURE 14. HISTOGRAM OF DIFFERENCES IN SPIKE DETERMINATIONS AT MANHATTAN

$$t = \bar{x}\ \sqrt{n}/s = 10.7\ \sqrt{87}/22.0 = 4.54.$$

On n-1 = 86 degrees of freedom, the value for t is statistically significant at the 99 percent level. Therefore, the test hypothesis is rejected and it is concluded that the true bias is probably not zero.

The histogram for Bloomington in Figure 13, which is based on 83 determinations of S-U, departs somewhat from a normal distribution. It is bimodal in appearance, but this is likely a product of sampling. The distribution, centered to the left of zero, is characterized by a mean of -11 percent, which indicates a negative bias, and a standard deviation of 30.7 percent. The hypothesis that the true bias is zero is tested by use of Student's t, as follows:

$$t = \bar{x}\ \sqrt{n}/s = -10.8\ \sqrt{83}/30.7 = -3.21.$$

On n - 1 = 82 degrees of freedom, this value for t is statistically significant at the 99 percent level. Therefore, the test hypothesis is rejected and it is concluded that the true bias is probably not zero.

The histogram for Manhattan in Figure 14, which is based on 71 determinations of S-U, is indicative of a normal distribution. The determinations are centered about a mean with a greater positive deviation than the Los Angeles and Manhattan data. The distribution is characterized by a mean deviation of + 35 percent, which indicates a positive bias, and a standard deviation of 18.4 percent. The hypothesis that the true bias is zero is tested by use of Student's t, as follows:

$$t = \bar{x}\ \sqrt{n}/s = 35.3\ \sqrt{71}/18.4 = 16.2.$$

On n - 1 = 70 degrees of freedom, this value for t is statistically significant at the 99 percent level. Therefore, the test hypothesis is rejected and it is concluded that the true bias is probably not zero.

Although the histograms in Figures 12 through 14 provide a useful summary of overall accuracy at the three test sites, they do not show the performance of individual laboratories. In order to get a comparison of laboratories, the determinations of S-U in Blocks 1 through 24 were averaged

for each laboratory and site combination. These averages, which represent laboratory estimates of spiking concentrations, are shown as vertical shaded bars in Figure 15. The actual spike concentration is shown in the figure by solid, horizontal line segments.

Figure 15 shows that in Los Angeles measurements all but one laboratory overestimated the spiking concentration, and two of these were very high in their estimates. The Bloomington data show that all but two laboratories underestimated the spiking concentration, and three of these were very low in their estimates. At Manhattan, all but one of the laboratories overestimated the spiking concentration by a significant margin, while one laboratory significantly underestimated the spiking concentration.

The bias is seen to vary from laboratory to laboratory. The average bias increases from negative to positive as the nitrogen dioxide concentration in the air increases (in the order Bloomington, Los Angeles, and Manhattan). A separate examination of the relationship of individual estimates (S-U) of the spiking concentration to the nominal nitrogen dioxide level (S+U)/2 for each laboratory was made. This examination indicates that the dependence of the bias on concentration is very small.

An overall measure of bias (accuracy) was obtained by taking a weighted average of the bias values for the three locations, using sample size as the weight. This procedure shows that the overall recovery of nitrogen dioxide from spiked samples exceeded the spiked amount by an average of 18 percent of the true amount.

Analysis of Comparability

A measure of comparability defined as the extent to which the measurements of nitrogen dioxide concentration by different laboratories agree in regard to the differences between different concentrations is afforded by correlation analysis. For nitrogen dioxide concentrations that vary from hour to hour, the same pattern of increase or decrease should be shown by all laboratories. In other words, there should be good correlation between laboratories over an extended time period regardless of their systematic

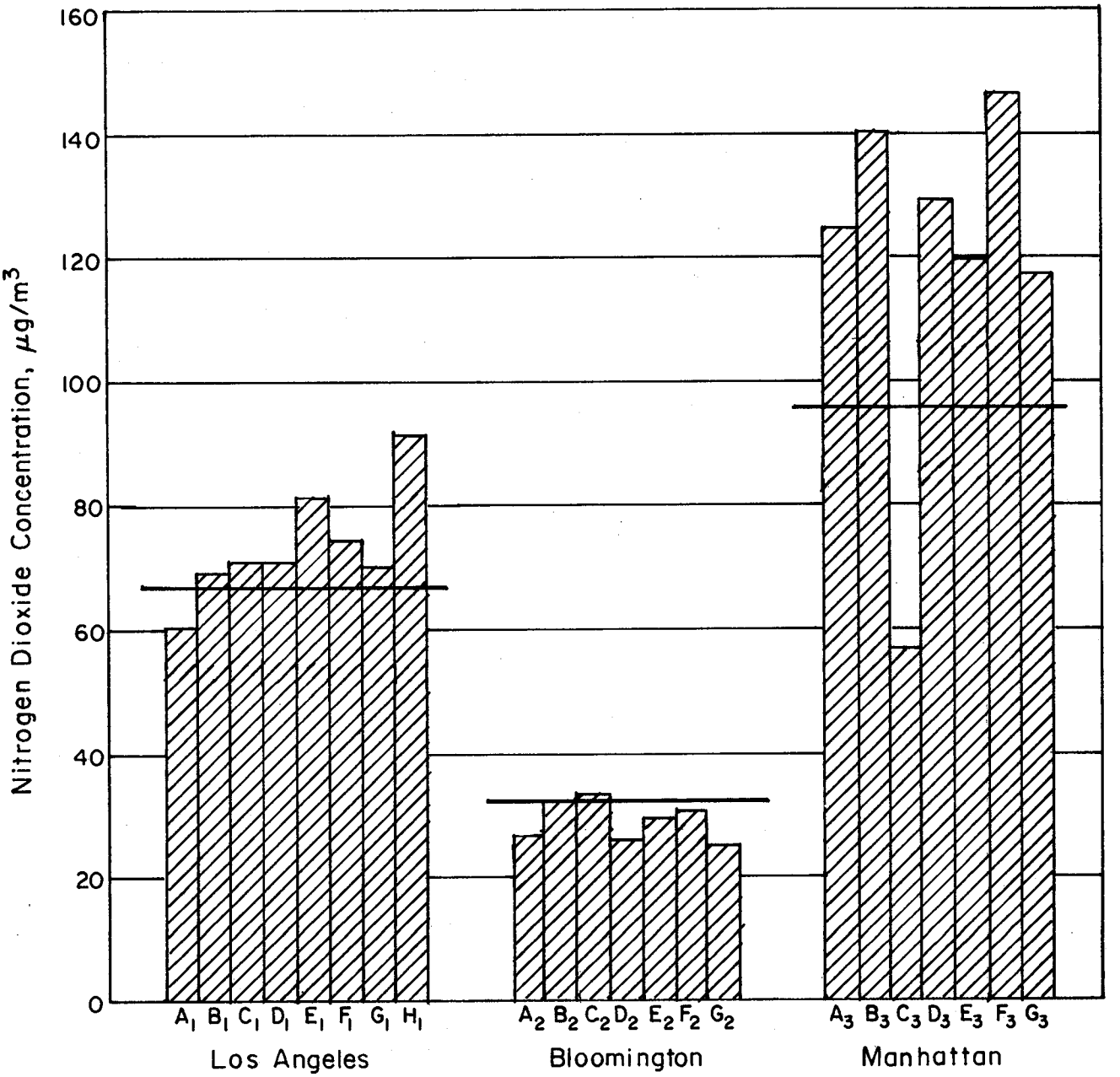


FIGURE 15. COMPARISON OF LABORATORY BIAS AT EACH SITE

Letters are laboratory codes. Shaded bars indicate laboratory estimates of spiking concentration. Bold lines denote actual spiking concentrations.

differences at a given time. This relationship was explored by computing, for each site and sample type, the correlation coefficients between all pairs of laboratories over time periods. For these computations, the nitrogen dioxide measurements were cross-classified in two-way tables according to laboratory and hour. Each pair of adjacent half-hour blocks in the same hour period were combined and treated as one block to give 12 pairs of measurements for each correlation. The results of these computations are shown in Tables 18 through 23. In Tables 22 and 23, laboratory C_3 at Manhattan shows poor correlations with all the other laboratories. On this basis the measurements obtained by laboratory C_3 at Manhattan were omitted from the analyses of reproducibility, repeatability, accuracy, and analysis-of-variance tables.

A total of 140 correlation coefficients for all laboratories, all sites, and all spiked and unspiked samples are shown in these tables. Of these cor elations 115 (82 percent) yield correlation coefficients which are significent at the ninety-five percent level. A feature of the comparability analysis is that it shows that good correlation in the data was obtained using the Test Method; a correlation which demonstrates that although systematic differences may exist which affect accuracy, good agreement in the measurement of concentration patterns and trends can be expected among laboratories using the Test Method.

Analysis of Laboratory, Block, and Outlet Effects Using Latin Squares and Randomized Blocks

The foregoing analysis indicates that laboratory and block effects are substantial, whereas the effect of outlet position is negligible. The significance of these three sources of variation can be tested through the use of analysis of variance techniques applied to the Latin Squares which make up the experimental runs in blocks 1 through 24.

TABLE 18. CORRELATION MATRIX FOR UNSPIKED SAMPLES FROM LOS ANGELES[a]

Laboratory	A_1	B_1	C_1	D_1	E_1	F_1	G_1	H_1
A_1	1.00	0.92	0.98	0.96	0.95	0.94	0.98	0.97
B_1	0.92	1.00	0.83	0.83	0.87	0.85	0.88	0.83
C_1	0.98	0.83	1.00	0.99	0.97	0.95	0.96	0.98
D_1	0.96	0.83	0.99	1.00	0.96	0.94	0.95	0.94
E_1	0.95	0.87	0.97	0.96	1.00	0.98	0.93	0.91
F_1	0.94	0.85	0.95	0.94	0.98	1.00	0.94	0.92
G_1	0.98	0.88	0.96	0.95	0.93	0.94	1.00	0.95
H_1	0.97	0.83	0.98	0.94	0.91	0.92	0.95	1.00

(a) Blocks 1-24 of statistical design.

TABLE 19. CORRELATION MATRIX FOR SPIKED SAMPLES FROM LOS ANGELES[a]

Laboratory	A_1	B_1	C_1	D_1	E_1	F_1	G_1	H_1
A_1	1.00	0.79	0.87	0.96	0.94	0.90	0.56	0.95
B_1	0.79	1.00	0.54	0.73	0.70	0.68	0.09	0.68
C_1	0.87	0.54	1.00	0.95	0.88	0.84	0.48	0.87
D_1	0.96	0.73	0.95	1.00	0.93	0.91	0.53	0.92
E_1	0.94	0.70	0.88	0.93	1.00	0.97	0.46	0.97
F_1	0.90	0.68	0.84	0.91	0.97	1.00	0.33	0.93
G_1	0.56	0.09	0.48	0.53	0.46	0.33	1.00	-0.14
H_1	0.95	0.68	0.87	0.92	0.97	0.93	-0.14	1.00

(a) Blocks 1-24 of statistical design.

TABLE 20. CORRELATION MATRIX FOR UNSPIKED SAMPLES FROM BLOOMINGTON[a]

Laboratory	A_2	B_2	C_2	D_2	E_2	F_2	G_2
A_2	1.00	0.97	0.94	0.89	0.97	0.97	0.93
B_2	0.97	1.00	0.96	0.94	0.97	0.92	0.86
C_2	0.94	0.96	1.00	0.90	0.97	0.94	0.90
D_2	0.89	0.94	0.90	1.00	0.89	0.80	0.75
E_2	0.97	0.97	0.97	0.89	1.00	0.94	0.91
F_2	0.97	0.92	0.94	0.80	0.94	1.00	0.98
G_2	0.93	0.86	0.90	0.75	0.91	0.98	1.00

(a) Blocks 1-24 of statistical design.

TABLE 21. CORRELATION MATRIX FOR SPIKED SAMPLES FROM BLOOMINGTON[a]

Laboratory	A_2	B_2	C_2	D_2	E_2	F_2	G_2
A_2	1.00	0.93	0.88	0.86	0.97	0.92	0.92
B_2	0.93	1.00	0.93	0.78	0.93	0.94	0.91
C_2	0.88	0.93	1.00	0.82	0.91	0.89	0.91
D_2	0.86	0.78	0.82	1.00	0.89	0.74	0.70
E_2	0.97	0.93	0.91	0.89	1.00	0.93	0.88
F_2	0.92	0.94	0.89	0.74	0.93	1.00	0.90
G_2	0.92	0.91	0.91	0.70	0.88	0.90	1.00

(a) Blocks 1-24 of statistical design.

TABLE 22. CORRELATION MATRIX FOR UNSPIKED SAMPLES FROM MANHATTAN[a]

Laboratory	A_3	B_3	C_3	D_3	E_3	F_3	G_3
A_3	1.00	0.98	0.43	0.81	0.99	0.77	0.98
B_3	0.98	1.00	0.35	0.79	0.97	0.78	0.97
C_3	0.43	0.35	1.00	0.47	0.40	0.52	0.47
D_3	0.81	0.79	0.47	1.00	0.82	0.69	0.83
E_3	0.99	0.97	0.40	0.82	1.00	0.76	0.99
F_3	0.77	0.78	0.52	0.69	0.76	1.00	0.75
G_3	0.98	0.97	0.47	0.83	0.99	0.75	1.00

(a) Blocks 1-24 of statistical design.

TABLE 23. CORRELATION MATRIX FOR SPIKED SAMPLES FROM MANHATTAN[a]

Laboratory	A_3	B_3	C_3	D_3	E_3	F_3	G_3
A_3	1.00	0.99	0.39	0.74	0.95	0.97	0.94
B_3	0.99	1.00	0.43	0.76	0.96	0.98	0.96
C_3	0.39	0.43	1.00	0.34	0.40	0.37	0.44
D_3	0.74	0.76	0.34	1.00	0.67	0.74	0.75
E_3	0.95	0.96	0.40	0.67	1.00	0.96	0.94
F_3	0.97	0.98	0.37	0.74	0.96	1.00	0.95
G_3	0.94	0.96	0.44	0.75	0.94	0.95	1.00

(a) Blocks 1-24 of statistical design.

In Table 24 is shown a summary of the results of applying analysis of variance to the twelve Latin Squares in the data matrix (Table 4) from the Los Angeles samples. Entries in the table denote the level of statistical significance in units of fractiles of the F-distribution. Statistical significance is indicated by a value for the F-fractile of 95 percent or greater. In the column headed "Laboratory", there are four F-fractiles which are significant and several more which approach significance. In the column headed "Block" there are five F-fractiles which are significant and two more which exceed the 90 percent level. In the column headed "Outlet", on the other hand, there are no significant F-fractiles at the 95 percent level.

In Table 25 are shown the F-fractiles obtained by applying analysis of variance to the six completed Latin Squares in the data matrix (Table 5) from the Bloomington samples. The other six Latin Squares in the data matrix were not completed, because only seven laboratories participated at Bloomington. In this case, four of the six F-fractiles for laboratory and all six F-fractiles for block are significant at the 95 percent level, whereas only one of the six F-fractiles for outlet is significant.

In Table 26 are shown the F-fractiles obtained by applying analysis of variance to the six completed Latin Squares in the data matrix (Table 6) from the Manhattan samples. Again, the other six Latin Squares in the data matrix were not completed because only seven laboratories participated at Manhattan. In this case, five of the six F-fractiles for laboratory are significant at the 95 percent level (and also at the 99 percent level); three of the six F-fractiles for block are significant at the 95 percent level, whereas none of the F-fractiles for outlet are significant. These results are in agreement with the results for Los Angles and Bloomington in Tables 24 and 25, respectively.

The analysis of variance of the Latin Squares in the data matrices of the Los Angeles, Bloomington, and Manhattan data provides additional evidence that the outlet position at which samples were taken did not have a significant effect on the test data. In most cases, significant variability was noted between laboratories and between blocks. Between-laboratory variability is a parameter of primary interest in this study. Variations

TABLE 24. F-FRACTILES OBTAINED FROM LATIN SQUARE ANALYSIS OF NITROGEN DIOXIDE MEASUREMENTS OF LOS ANGELES SAMPLES

Data Set		F-fractile, percent[a]		
Blocks	Sample Type	Laboratory	Block	Outlet
1,3,5,7	Unspiked	43	(95)	55
	Spiked	74	47	48
2,4,6,8	Unspiked	(98)	61	94
	Spiked	85	91	87
9,11,13,15	Unspiked	(96)	(99)	77
	Spiked	79	(97)	70
10,12,14,16	Unspiked	(98)	(95)	45
	Spiked	47	92	43
17,19,21,23	Unspiked	63	63	48
	Spiked	87	(99.8)	42
18,20,22,24	Unspiked	92	70	48
	Spiked	(96)	60	49

(a) F-fractiles enclosed in parentheses indicate a real effect.

TABLE 25. F-FRACTILES OBTAINED FROM LATIN SQUARE ANALYSIS OF NITROGEN DIOXIDE MEASUREMENTS OF BLOOMINGTON SAMPLES

Data Set		F-fractile, percent[a]		
Blocks	Sample Type	Laboratory	Block	Outlet
1,3,5,7	Unspiked	(b)	(b)	(b)
	Spiked	(b)	(b)	(b)
2,4,6,8	Unspiked	(99.7)	(99.9)	82.1
	Spiked	(99.8)	(99.9)	39.5
9,11,13,15	Unspiked	(b)	(b)	(b)
	Spiked	(b)	(b)	(b)
10,12,14,16	Unspiked	87.2	(99.97)	49.5
	Spiked	(98.9)	(99.997)	(95.9)
17,19,21,23	Unspiked	32.8	(95.7)	3.2
	Spiked	(99.1)	(97.5)	61.0
18,20,22,24	Unspiked	(b)	(b)	(b)
	Spiked	(b)	(b)	(b)

(a) F-fractiles enclosed in parentheses indicate a real effect.
(b) F-fractile not computed because of missing data.

TABLE 26. F-FRACTILES OBTAINED FROM LATIN SQUARE ANALYSIS OF NITROGEN DIOXIDE MEASUREMENTS OF MANHATTAN SAMPLES

Data Set		F-fractile, percent[a]		
Blocks	Sample Type	Laboratory	Block	Outlet
1,3,5,7	Unspiked	(b)	(b)	(b)
	Spiked	(b)	(b)	(b)
2,4,6,8	Unspiked	(99.93)	84.6	93.9
	Spiked	(99.93)	(97.5)	69.3
9,11,13,15	Unspiked	(b)	(b)	(b)
	Spiked	(b)	(b)	(b)
10,12,14,16	Unspiked	(99.98)	(99.8)	40.2
	Spiked	(99.997)	(99.95)	63.4
17,19,21,23	Unspiked	89.9	84.2	48.1
	Spiked	(99.87)	93.1	87.9
18,20,22,24	Unspiked	(b)	(b)	(b)
	Spiked	(b)	(b)	(b)

(a) F-fractiles enclosed in parentheses indicate a real effect.
(b) F-fractile not computed becuase of missing data.

between blocks include the natural changes in the ambient nitrogen dioxide level with time; an effect which is not significant in evaluating the Test Method.

Due to a change in the statistical design, beginning with Block 9 at Bloomington all seven laboratories sampled concurrently, and each pair of blocks in the same hour were combined into a single block of 60 minutes. This change, together with the elimination (by the Latin Square analysis) of sampling outlet position as a significant variable, permits the study of the data for Blocks 9 through 24 at Bloomington as a two-way table in which the rows represnnt laboratories and the columns represent hours; and similarly for Blocks 1 through 24 at Manhattan. The advantage lies in consolidating several small sets of data, which require separate analyses, into a single set of data which require only a single analysis with more degrees of freedom for significance tests.

Before analyzing these two-way tables, data which were questionable for either physical or statistical reasons were replaced by least-squares estimates computed from the formula[9]

$$E = \frac{L + bB - S}{(\ -1)\ (b-1)},$$

where E = estimated value
= number of laboratories
b = number of blocks
L = sum of values reported by laboratory with missing value
B = sum of values in same block as missing value
S = sum of all values in two-way table.

Tables 27 through 30 present the analysis of variance for each of the two-way tables. The first column of each table indicates that the total variability in the data can be separated into three sources, associated with the variability between laboratories, the time variation, and the variability caused by the interaction of laboratory and time effects. The second column, listed the degrees of freedom, indicates the number of independent comparisons that can be made between pairs of laboratory averages, pairs of hourly averages, and pairs of laboratory-by-hour interaction effects. The third column of each table gives the mean square, or variance, associated with each source of

TABLE 27. VARIANCE ANALYSIS OF UNSPIKED SAMPLES FROM BLOOMINGTON[a]

Source	Degrees of Freedom	Mean Square	Variance Ratio	F-fractile
Laboratory	6	180.74	5.11	> 99.9
Hour	7	4599.09	130.	> 99.9
Interaction	42	35.38	--	

(a) Based on blocks 9-24 of design, ignoring outlet position.

TABLE 28. VARIANCE ANALYSIS OF SPIKED SAMPLES FROM BLOOMINGTON[a]

Source	Degrees of Freedom	Mean Square	Variance Ratio	F-fractile
Laboratory	6	370.99	9.34	> 99.9
Hour	7	6776.58	171.	> 99.9
Interaction	41	39.72	--	

(a) Based on blocks 9-24 of design, ignoring outlet position. Data obtained by Laboratory F_2 for block 22 was excluded from analysis.

TABLE 29. VARIANCE ANALYSIS OF UNSPIKED SAMPLES FROM MANHATTAN[a]

Source	Degrees of Freedom	Mean Square	Variance Ratio	F-fractile
Laboratory	5	1310.18	13.7	> 99.9
Hour	11	5520.76	57.9	> 99.9
Interaction	54	95.33	--	

(a) Based on blocks 1-24 of design, ignoring outlet position. Data obtained by Laboratory F_3 for block 2 was excluded from analysis.

TABLE 30. VARIANCE ANALYSIS OF SPIKED SAMPLES FROM MANHATTAN[a]

Source	Degrees of Freedom	Mean Square	Variance Ratio	F-fractile
Laboratory	5	5020.01	25.0	> 99.9
Hour	11	6226.42	31.0	> 99.9
Interaction	55	200.66	--	

(a) Based on blocks 1-24 of design, ignoring outlet position.

variability. The fourth column gives the variance ratio, or F-ratio. A small variance ratio signifies that the average determinations are in close agreement, while a large variance ratio indicates that there are considerable differences in the average determinations. The last column of each table shows the percentage point of the F-distribution associated with the variance ratio on the same line of the table. This percentage point, or F-fractile, is a measure of the statistical significance attached to the particular effect on test. High percentages are associated with high significance, and low percentages are associated with low significance.

The variability attributed to laboratory, hour, and interaction in Tables 27 through 30 are composed of variations from the following sources.

Laboratory

(a) Reproducibility
(b) Repeatability
(c) Laboratory-hour interaction
(d) Unidentified sources

Hour

(a) Hourly variations in the ambient nitrogen dioxide level
(b) Repeatability
(c) Laboratory-hour interaction
(d) Unidentified sources

Interaction

(a) Laboratory-hour interaction
(b) Repeatability
(c) Unidentified sources

Reproducibility and repeatability have been defined and discussed previously in this report. The laboratory-hour interaction indicates the influence of time related changes on the variability of the measurements made by the various laboratories.

A comparison of the composition of the laboratory and interaction variations show that they contain the same components with the exception that the laboratory variation contains the reproducibility term. The variance ratios of the laboratory-to-interaction sources shows that reproducibility, a parameter of principle interest in this study, is much more significant than the combined variations due to repeatability, laboratory-hour interaction, and unidentified sources of variation. Furthermore, the small magnitude of the mean square of the interaction variations demonstrates that no significant sources of unidentified variation was overlooked in the analysis of variance. The latter observations confirms that sources of variation in the study were limited to those which were identified and taken into consideration in the experiment design.

DISCUSSION AND CONCLUSIONS

The conclusions regarding the accuracy and precision of ASTM Method D1607 for measuring nitrogen dioxide in the atmosphere which may be drawn from the interlaboratory study are as follows:

(1) The average standard deviation, s_b, for between-laboratory variability (reproducibility) is given by the equation:

$$s_b = 0.517 + 1.27 \sqrt{m} ,$$

where, s_b and, m, the mean concentration of nitrogen dioxide are expressed in $\mu g/m^3$.

(2) The average standard deviation, s_w, for within-laboratory variability (repeatability) is given by the equation:

$$s_w = 0.524 \sqrt{m} ,$$

where, s_w, and, m, the mean concentration of nitrogen dioxide are expressed in $\mu g/m^3$.

(3) Based on data at three different geographic sites, measurements may, on the average, overestimate the true nitrogen dioxide concentration 18 percent. The most significant bias (+35 percent) was noted in measurements made at Manhattan. Bias in the measurements at Los Angeles and Bloomington was +11 and -11 percent, respectively. The bias a Manhattan may suggest the presence of an interferring substance in the atmosphere.

(4) The lower limit of detection of nitrogen dioxide (sensitivity) by the method is estimated to be about 3 $\mu g/m^3$ based on the repeatability at the lowest measured concentration.

The results of the interlaboratory study validate that ASTM Method D1607 is a sensitive, accurate, and precise technique for measurement of nitrogen dioxide in the atmosphere. The establishment of the accuracy and precision of the method is an important "breakthrough" since knowledge of these parameters are essential when applying a test method. For example, meaningful comparison of data from various laboratories or from various locations by the same laboratory and comparison of test data with air quality standards require quantitative measures of the variability of the method used to obtain the test data. Currently, ASTM Method D1607 is the only method of measuring nitrogen dioxide in the atmosphere for which quantitative accuracy and precision data have been generated.

RECOMMENDATIONS

Based on the results of this study, it is the general recommendation that no substantial changes are necessary in ASTM Method D1607 to achieve results of the quality represented by the reported statistical parameters. However, there are a few revisions and recommendations which might clarify and improve the Test Method.

(1) The option of using a flexible fluorocarbon sampling line instead of glass or stainless steel as specified by the Test Method is recommended. The use of the fluorocarbon sampling line in this study did not have any deleterious effect on the nitrogen dioxide measurements, therefore, it would be appropriate to include the fluorocarbon sampling line as a third acceptable option.

(2) Acetone was added to the absorbing reagent to avoid the remote possibility of fading of the developed color by SO_2, if present. This may have been an unneccessary precaution for these tests, but the fortuitous presence of SO_2 was not predictable. It is recommended that acetone be a specified component of the absorbing reagent in Paragraph 7.4, and that it may be omitted as an option if interference from SO_2 is definitely not anticipated. It is not evident that one percent acetone would have any detrimental effects on storage stability of the solution.

(3) It is recommended that the Test Method be amended to state specifically that the dichromate-sulfuric acid cleaning procedure need only be used periodically, whenever the bubbler has been contaminated. This would supplement and support the instruction in Paragraph 6.1.3 which indicates that rinsing and drying is an adequate preparation for reuse of a bubbler. The instruction for acid cleaning in Paragraph 6.1.2 was interpreted by one or two participating laboratories as a required step to precede the rinsing step specified in Paragraph 6.1.3.

(4) A sampling train arrangement, incorporating a dry test meter, as shown in Figure 1 of this report is recommended for performing the Test Method.

(5) It is recommended that a precautionary statement be included in the Test Method suggesting a periodic supervisory review to assure compliance with critical procedural details. This should counteract evolutionary changes that otherwise may occur when the method is followed repeatedly by one operator.

(6) Additional study is recommended to determine the cause of the positive bias as observed in the Manhattan test results.

Finally, it is recommended that the accuracy and precision data obtained in this study be incorporated into the description of the Test Method.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of Mr. Walter V. Cropper, Manager-Special Projects, ASTM, throughout the planning and conduct of this study. Also of immeasurable value in the experimental design and statistical analysis of the resulting data was the advice and suggestions of Drs. John Mandel, Frank Grubbs, and Emil Jebe, all of whom are members of ASTM Committee E-11 on Statistical Methods.

We express to Dr. R. H. Johns, ASTM Research Associate, National Bureau of Standards, our appreciation for his competent work in the development and performance of the spiking procedures.

Lastly, our sincere appreciation is extended to the following organizations and personnel for their cooperation in the ASTM threshold test program.

California Department of Health

Kenneth Smith
Mohamade Shekhvadeh
William Wehrmeister

George D. Clayton and Associates

George Clayton
Louis Gendernalik
Jack Barton
Ted Held
Del Malzahn
Don Russell

Arthur D. Little, Inc.

Cliff Summers
Walter Smith
Art Benson
Karl Werner

Midwest Research Institute

Fred Bergman
Nick Stich
Frank Hanis

Public Service Electric and Gas Company (New Jersey)

John Tomshaw
Ed Cooper
Eric Wirth
George Durr
Frank DeCicco
Reuben Wasser
Ken Harris

Research Triangle Institute

Cliff Decker
Denny Wagoner

Walden Research Corporation

John Driscoll
Jim Becker
Roland Hebert

Western Electric Company

Gene Dennison
Barret Broyde
Frank Zado
Robert Menichelli
Dave Green
Ike Smith

REFERENCES

(1) Annual Book of ASTM Standards, Part 23, American Society of Testing Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

(2) ASTM Manual for Conducting an Interlaboratory Study of a Test Method, ASTM STP 335, American Society for Testing Materials (1963).

(3) Mandel, J., "Repeatability and Reproducibility", Materials Research and Standards, 11, No. 8, 8-16 (Aug., 1971).

(4) "Tentative Recommended Practice for Statements on Precision and Accuracy", ASTM Method D 2906.

(5) "Use of the Terms Precision and Accuracy as Applied to Measurement of a Property of a Material", ASTM Method E 177.

(6) "Standard Recommended Practice for Dealing with Outlying Observations", ASTM Method E 178.

(7) Grubbs, F. E., "Procedures for Detecting Outlying Observations in Samples", Technometrics, 11, No. 1, 1-21 (Feb., 1969).

(8) Natrella, M.G., Experimental Statistics, National Bureau of Standards Handbook 91, Table A-10 (1963).

(9) Snedecor, G. W., Statistical Methods, 4th Edition, 268 (1946).

APPENDIX

REPRINT OF ASTM

STANDARD METHOD OF TEST FOR NITROGEN DIOXIDE CONTENT OF THE ATMOSPHERE (GREISS-SALTZMAN REACTION)

Designation: D 1607 - 69

Standard Method of Test for NITROGEN DIOXIDE CONTENT OF THE ATMOSPHERE (GRIESS-SALTZMAN REACTION)[1]

This Standard is issued under the fixed designation D 1607; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 This method[2] covers the manual determination of nitrogen dioxide (NO_2) in the atmosphere in the range from 0.005 ppm to about 5 ppm (0.01 to 10 μg/liter) when sampling is conducted in fritted bubblers. The method is preferred when high sensitivity is needed.

1.2 Concentrations from 5 to 100 ppm in industrial atmospheres and in gas burner stacks also may be sampled by employing evacuated bottles or glass syringes. For higher concentrations, for automotive exhaust, or for samples relatively high in sulfur dioxide content, or both, other methods should be applied. See for example ASTM Method D 1608, Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenol Disulfonic Acid Procedure).[3]

2. Summary of Method

2.1 The NO_2 is absorbed in an azo-dye forming reagent (**1**).[4] A stable pink color is produced within 15 min which may be read visually or in an appropriate instrument at 550 nm.

3. Significance

3.1 Nitrogen dioxide plays an important role in photochemical smog-forming reactions and in sufficient concentrations is deleterious to health, agriculture, materials, and visibility.

3.2 In combustion processes such as in internal combustion engines or in furnaces, significant amounts of nitric oxide (NO) may be produced by combination of atmospheric nitrogen and oxygen; later at ordinary temperatures reaction of NO with oxygen yields NO_2. The latter gas also may be produced in industrial processes involving nitric acid, nitrates, use of explosives, and welding.

3.3 Since ambient concentrations of NO_2 fluctuate, air quality standards are established in terms of both the mean values and peak values never to be exceeded, or to be exceeded less frequently than a specified fraction of the time. Sampling times should be specified together with the peak concentrations, since shorter times yield higher values.

4. Definitions

4.1 For definitions of terms used in this method, refer to the ASTM Definitions D 1356, Terms Relating to Atmospheric Sampling and Analysis.[3]

5. Interferences

5.1 A 10-fold ratio of sulfur dioxide (SO_2) to NO_2 produces no effect. A 30-fold ratio slowly bleaches the color to a slight extent. The addition of 1 percent acetone to the reagent before use retards the fading by forming a temporary addition product with SO_2. This permits reading within 4 to 5 h (instead of the 45 min required without the acetone) without appreciable interferences. Interference from SO_2 may be a problem in some stack gas samples (see 1.2).

5.2 A 5-fold ratio of ozone to NO_2 will cause a small interference, the maximal effect occurring in 3 h. The reagent assumes a slightly orange tint.

5.3 *Peroxyacylnitrate* (PAN) can give a

[1] This method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres.

Current edition effective Oct. 3, 1969. Originally issued 1958. Replaces D 1607 - 60.

[2] Adapted from "Selected Methods for the Measurement of Air Pollutants," *PHS Publication No. 999-AP-11*, May, 1965. A similar version has been submitted to the Intersociety Committee.

[3] *Annual Book of ASTM Standards*, Part 23.

[4] The boldface numbers in parentheses refer to the list of references appended to this method.

response of approximately 15 to 35 percent of an equivalent molar concentration of NO_2 (2). In ordinary ambient air the concentrations of PAN are too low to cause any significant error.

5.4 The interferences from other nitrogen oxides and other gases that might be found in polluted air are negligible. However, if the evacuated bottle or syringe method is used to sample concentrations above 5 ppm, interference from NO (due to oxidation to NO_2) is possible; see 8.4.

5.5 If strong oxidizing of reducing agents are present, the colors should be determined within 1 h, if possible, to minimize any loss.

6. Apparatus

6.1 *Absorber*—The sample is absorbed in an all-glass bubbler with a 60-μm maximum pore diameter frit similar to that illustrated in Fig. 1.[5]

6.1.1 The porosity of the fritted bubbler, as well as the sampling flow rate, affect absorption efficiency. An efficiency of over 95 percent may be expected with a flow rate of 0.4 liters/min or less and a maximum pore diameter of 60 μm. Frits having a maximum pore diameter less than 60 μm will have a higher efficiency but will require an inconvenient pressure drop for sampling; see equation in 6.1.2. Considerably lower efficiencies are obtained with coarser frits, but these may be utilized if the flow rate is reduced.

6.1.2 Since the quality control by some manufacturers is rather poor, it is desirable to measure periodically the porosity of an absorber as follows: Carefully clean the apparatus with dichromate-concentrated sulfuric acid solution ($K_2Cr_2O_7$ - H_2SO_4) and then rinse it thoroughly with distilled water. Assemble the bubbler, add sufficient distilled water to barely cover the fritted portion, and measure the vacuum required to draw the first perceptible stream of air bubbles through the frit. Then calculate the maximum pore diameter as follows:

$$\text{Maximum pore diameter, } \mu m = 30s/P$$

where:

s = surface tension of water at the test temperature in dynes/cm (73 at 18 C, 72 at 25 C, and 71 at 31 C), and

P = measured vacuum, mm Hg.

6.1.3 Rinse the bubbler thoroughly with water and allow to dry before using. A rinsed and reproducibly drained bubbler may be used if the volume, r, of retained water is added to that of the absorbing reagent for the calculation of results. This correction may be determined as follows: Pipet into a drained bubbler exactly 10 ml of a colored solution (such as previously exposed absorbing reagent) of absorbance (A_1). Assemble the bubbler and rotate to rinse the inside with the solution. Rinse the fritted portion by pumping gently with a rubber bulb. Read the new absorbance, A_2 of the solution. Then:

$$10A_1 = (10 + r)A_2$$

or:

$$r = 10\,[(A_1/A_2) - 1]$$

6.2 *Air-Metering Device*—A glass rotameter capable of accurately measuring a flow of 0.4 liter/min is suitable. A wet test meter is convenient to check the calibration.

6.3 *Sampling Probe*—A glass or stainless steel tube 6 to 10 mm in diameter provided with a downward-facing intake (funnel or tip) is suitable. A small loosely fitting plug of glass wool may be inserted, when desirable, in the probe to exclude water droplets and particulate matter. The dead volume of the system should be kept minimal to permit rapid flushing during sampling to avoid losses of nitrogen dioxide on the surfaces.

6.4 *Grab-Sample Bottles*—Ordinary glass-stoppered borosilicate glass bottles of 30 to 250-ml sizes are suitable if provided with a mating ground joint attached to a stopcock for evacuation. Calibrate the volume by weighing with connecting piece, first empty, then filled to the stopcock with distilled water.

6.5 *Glass Syringes*—Fifty or one hundred-milliliter syringes are convenient (although less accurate than bottles) for sampling.

6.6 *Air Pump*—A suction pump capable of drawing the required sample flow for intervals of up to 30 min is suitable. A tee connection at the intake is desirable. The inlet connected to the sampling train should have an appropriate trap and needle valve, preferably of stainless steel. The second inlet should have a valve for bleeding in a large excess flow of clean air to prevent condensation of acetic

[5] Corning Glass Works Drawing XA-8370 specifies this item with 12/5 ball and socket joints. Ace Glass, Inc., specifies this item as No. 7530.

acid vapors from the absorbing reagent, with consequent corrosion of the pump. Alternatively, soda lime may be used in the trap. A filter and critical orifice may be substituted for the needle valve (3).

6.7 *Spectrophotometer or Colorimeter*—A laboratory instrument suitable for measuring the pink color at 550 nm, with stoppered tubes or cuvettes. The wavelength band width is not critical for this determination.

7. Reagents and Materials

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Absorbing Reagent*—Dissolve 5 g of anhydrous sulfanilic acid (or 5.5 g of $NH_2 \cdot C_6H_4SO_3H \cdot H_2O$) in almost a liter of water containing 140 ml of glacial acetic acid. Gentle heating is permissible to speed up the process. To the cooled mixture, add 20 ml of the 0.1 percent stock solution of *N*-(1-naphthyl)-ethylenediamine dihydrochloride, and dilute to 1 liter. Avoid lengthy contact with air during both preparation and use, since discoloration of reagent will result because of absorption of NO_2. The solution will be stable for several months if kept well-stoppered in a brown bottle in the refrigerator. The absorbing reagent would be allowed to warm to room temperature before use.

7.3 *N-(1-Naphthyl)-Ethylenediamine Dihydrochloride, Stock Solution (0.1 percent)*—Dissolve 0.1 g of the reagent in 100 ml of water. Solution will be stable for several months if kept well-stoppered in a brown bottle in the refrigerator. (Alternatively, weighed small amounts of the solid reagent may be stored.)

7.4 *Nitrite-Free Water*—All solutions are made in nitrite-free water. If available distilled or deionized water contains nitrite impurities (produces a pink color when added to absorbing reagent), redistill it in an all-glass still after adding a crystal each of potassium permanganate (KM_nO_4) and of barium hydroxide.

7.5 *Sodium Nitrite, Standard Solution (0.0203 g/liter)*—One milliliter of this working solution of sodium nitrite ($NaNO_2$) produces a color equivalent to that of 10 μl of NO_2 (10 ppm in 1 liter of air at 760 mm Hg and 25 C, see 11.2.1). Prepare fresh just before use by dilution from a stronger stock solution containing 2.03 g of the reagent grade granular solid (calculated as 100 percent/liter). It is desirable to assay the solid reagent, especially if it is old. The stock solution is stable for 90 days at room temperatures, and for a year in a brown bottle under refrigeration.

8. Sampling

8.1 *Choice of Methods*—Three methods are described below. Concentrations below 5 ppm are sampled by the bubbler method. Higher concentrations may be sampled by the evacuated bottle method, or more conveniently (but less accurately) by the glass syringe method. The latter method is more useful when appreciable concentrations (for example, 20 ppm) of NO are suspected.

8.2 *Bubbler Method*—Assemble, in order, a sampling probe (optional), a glass rotameter, fritted absorber, and pump. Use ground-glass connections upstream from the absorber. Butt-to-butt glass connections with slightly-greased vinyl or pure gum rubber tubing also may be used for connections without losses if lengths are kept minimal. The sampling rotameter may be used upstream from the bubbler provided occasional checks are made to show that no nitrogen dioxide is lost. The rotameter must be kept free from spray or dust. Pipet 10.0 ml of absorbing reagent into a dry fritted bubbler (see 6.1.3). Draw an air sample through it at the rate of 0.4 liter/min (or less) long enough to develop sufficient final color (about 10 to 30 min). Note the total air volume sampled. Measure and record the sample air temperature and pressure.

8.3 *Evacuated Bottle Method*—Sample in

[6] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N.Y., and the "United States Pharmacopeia."

bottles of appropriate size containing 10.0 ml (or other convenient volume) of absorbing reagent. For 1-cm spectrophotometer cells, a 5+1 ratio of air sample volume to reagent volume will cover a concentration range up to 100 ppm; a 25+1 ratio suffices to measure down to 2 ppm. Wrap a wire screen or glass-fiber-reinforced tape around the bottle for safety purposes. Grease the joint lightly with silicone or fluorocarbon grease. If a source of vacuum is available at the place of sampling, it is best to evacuate just before sampling to eliminate any uncertainty about loss of vacuum. A three-way Y stopcock connection is convenient. Connect one leg to the sample source, one to the vacuum pump, and third to a tee attached to the bottle and to a mercury manometer or accurate gage. In the first position of the Y stopcock, the bottle is evacuated to the vapor pressure of the absorbing reagent. In the second position of the Y stopcock the vacuum pump draws air through the sampling line to thoroughly flush it. The actual vacuum in the sample bottle is read on the manometer. In the third position of the Y stopcock the sampling line is connected to the evacuated bottle and the sample is collected. The stopcock on the bottle is then closed. Allow 15 min with occasional shaking for complete absorption and color development. For calculations of the standard volume of the sample, record the temperature and the pressure. The latter is the difference between the filled and evacuated conditions, and the uncorrected volume is that of the bottle plus that of the connection up to the stopcock minus the volume of absorbing reagent.

8.4 *Glass Syringe Method*—Ten milliliters of absorbing reagent is kept in a capped 50 (or 100)-ml glass syringe, and 40 (or 90) ml of air is drawn in at the time of sampling. The absorption of NO_2 is completed by capping and shaking vigorously for 1 min, after which the air is expelled. (When appreciable concentrations (for example, 20 ppm) of NO are suspected, interference caused by the oxidation of NO to NO_2 is minimized by expelling the air sample immediately after the absorption period.) Additional air may be drawn in and the process repeated several times if necessary, to develop sufficient final color.

8.5 *Effects of Storage*—Colors may be preserved, if well stoppered, with only 3 to 4 percent loss in absorbance per day; however, if strong oxidizing or reducing gases are present in the sample in concentrations considerably exceeding that of the NO_2, the colors should be determined as soon as possible to minimize any loss. See Section 5 for effects of interfering gases on stability.

9. Calibration and Standardization

9.1 Add graduated amounts of $NaNO_2$ solution up to 1 ml (measured accurately in a graduated pipet or small buret) to a series of 25-ml volumetric flasks, and dilute to the marks with absorbing reagent. Mix, allow 15 min for complete color development, and read the colors (see 10.1).

9.1.1 Good results can be obtained with these small volumes of standard solution if they are carefully measured. Making the calibration solutions up to 25 ml total volume, rather than the 10-ml volume used for samples, facilitates accuracy. If preferred, even larger volumes may be used with correspondingly larger volumetric flasks.

9.1.2 Using nitrite solution is much more convenient than preparing accurately known gas samples for standardizing. See 11.2 for stoichiometric relationships.

9.2 Plot the absorbances of the standard colors against the milliliters of standard solution. The plot follows Beer's law. Draw the straight line through the origin giving the best fit, and determine the slope, S (the value of milliliters of $NaNO_2$ intercepted at absorbance of exactly 1.0).

9.3 Greatest accuracy is achieved by standardizing with accurately known gas samples in a precision flow dilution system (**4,5,6**). The recently developed permeation tube technique (**7**) appears promising. If this method is used, the stoichiometric factor is eliminated from the calculations.

10. Measurement of Color

10.1 After collection or absorption of the sample, a red-violet color appears. Color development is complete within 15 min at room temperatures. Compare with standards visually or transfer to stoppered cuvettes and read in a spectrophotometer at 550 nm, using unexposed reagent as a reference. Alternatively, distilled water may be used as a reference, and the absorbance of the reagent blank

deducted from that of the sample.

10.2 Colors too dark to read may be quantitatively diluted with unexposed absorbing reagent. The measured absorbance is then multiplied by the dilution factor.

11. Calculations

11.1 For convenience, standard conditions are taken as 760 mm Hg and 25 C, at which the molar gas volume is 24.47 liters. (This is very close to the standard conditions used (**8**) for air-handling equipment, of 29.92 in. Hg, 70 F, and 50 percent relative humidity, at which the molar gas volume is 24.76 liters, of 1.2 percent greater.)

11.1 Ordinarily the correction of the sample volume to these standard conditions is slight and may be omitted; however, for greatest accuracy, it may be made by means of the perfect gas equation.

11.2 Standardization is based upon the empirical observation (**1,5**) that 0.72 mol $NaNO_2$ produces the same color as 1 mol NO_2.

NOTE—Recently Stratmann and Buck (**9**) reported a stoichiometric relationship of 1.0. Subsequently they found (**10**) decreasing values at concentrations above 0.3 ppm, approaching approximately the 0.7 figure at a few ppm. Shaw (**11**) confirmed the 0.72 value and suggested that higher values could be obtained erroneously if inadequate corrections for blanks were made. It is recommended that no change be made in the widely used 0.72 value at present.

11.2.1 One milliliter of the working standard solution contains 2.03×10^{-5} g $NaNO_2$. Since the molecular weight of $NaNO_2$ is 69.00 g, this is equivalent to:

$$[(2.03 \times 10^{-5})/69.00] \times (24.47/0.72) = 1.00 \times 10^{-5} \text{ liter, or } 10 \ \mu l \text{ of } NO_2.$$

11.2.2 Calculate the standardization factor, K, defined as the number of microliters of NO_2 required by 1 ml of absorbing reagent to give an absorbance of exactly 1:

$$K = (S \times 10)/25 = 0.40S$$

where:

S = slope of the calibration plot (see 9.2).

The factor 10 represents the strength (μl/ml) of the standard solution and factor 25 represents the total volume of the colored standards. For 1-cm cells, the value of K is about 0.73.

11.3 Compute the concentration of NO_2 in the sample as follows:

$$NO_2, \text{ ppm} = \text{absorbance} \times K/V$$

where:

K = standardization factor, and

V = volume of air sample, at standard conditions, in liters/ml of absorbing reagent.

11.3.1 If V is a simple multiple of K, calculations are simplified. Thus, for the K value of 0.73 previously cited, if exactly 7.3 liters of air are sampled through a bubbler containing 10 ml of absorbing reagent, $K/V = 1$, and the absorbance is also parts per million directly.

11.3.2 For exact work, an allowance may be made in the calculations for sampling efficiency and for fading of the color using the following equation:

$$NO_2, \text{ ppm} = \text{corrected absorbance} \times K/VE$$

where:

E = sampling efficiency.

For a bubbler, E is estimated from prior tests using two absorbers in series (**6**) (see 6.1.1). For a bottle or syringe, $E = 1.0$. The absorbance is corrected for fading of the color (see 8.5) when there is a prolonged interval between sampling and measurement of the absorbance.

12. Precision and Accuracy

12.1 A precision of 1 percent of the mean can be achieved with careful work (**4**); the limiting factors are the measurements of the volume of the air sample and of the absorbance of the color.

12.2 At present, accuracy data are not available.

REFERENCES

(1) Saltzman, B. E., "Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere," *Analytical Chemistry*, ANCHA, Vol 26, 1954, pp. 1949–55.

(2) Terraglio, F. P., Calif. State Dept. of Public Health. Unpublished data, 1964.

(3) Lodge, J. P., Jr., Pate, J. B., Ammons, B. E., and Swanson, G. A., "The Use of Hypodermic Needles as Critical Orifices in Air Sampling," *Journal of the Air Pollution Control Association*, JPCAA, Vol 16, 1966, pp. 197–200.

(4) Thomas, M. D., and Amtower, R. E., "Gas Dilution Apparatus for Preparing Reprodu-

cible Dynamic Gas Mixtures in any Desired Concentration and Complexity," *Journal of the Air Pollution Control Association*, JPCAA, Vol 16, 1966, pp. 618–23.
(5) Saltzman, B. E., and Wartburg, A. F., Jr., "Precision Flow Dilution System for Standard Low Concentrations of Nitrogen Dioxide," *Analytical Chemistry*, ANCHA, Vol 37, 1865, pp. 1261–4.
(6) Saltzman, B. E., "Preparation and Analysis of Calibrated Low Concentrations of Sixteen Toxic Gases," *Analytical Chemistry*, ANCHA, Vol 33, 1961, pp. 1103–4.
(7) O'Keefe, A. E., and Ortman, G. C., "Primary Standards for Trace Gas Analysis," *Analytical Chemistry*, ANCHA, Vol 38, 1966, pp. 760–3.
(8) ASTM Committee D-22, "Terms Relating to Atmospheric Sampling and Analysis, D 1356–60," *ASTM Standards on Methods of Atmospheric Sampling and Analysis*, 2nd Edition, 1962, Philadelphia, Pa.
(9) Stratmann, H., and Buck, M., "Messung von Stickstoffdioxid in der Atmosphäre," *Journal of the Air and Water Pollution Institute*, Vol 10, 1966, pp. 313–26.
(10) Stratmann, H., personal communication, September, 1966.
(11) Shaw, J. T., "The Measurement of Nitrogen Dioxide in the Air," *Atmospheric Environmental*, ATENB, 1967, pp. 81–5.

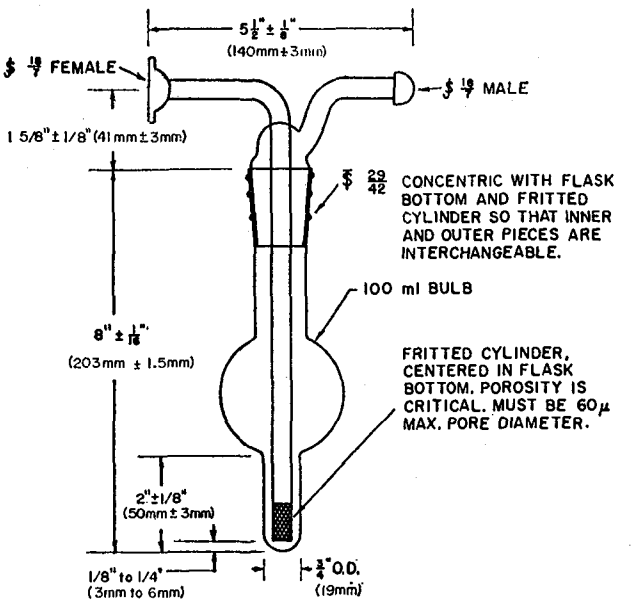


FIG. 1 Fritted Bubbler for Sampling Nitrogen Dioxide.