THRESHOLD

Interlaboratory Cooperative Study of the Precision and Accuracy of the Measurement of SULFUR DIOXIDE CONTENT IN THE ATMOSPHERE using ASTM Method D 2914

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FINAL REPORT

on

INTERLABORATORY COOPERATIVE STUDY OF THE PRECISION AND ACCURACY OF THE MEASUREMENT OF SULFUR DIOXIDE CONTENT IN THE ATMOSPHERE USING ASTM METHOD D 2914

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INTERLABORATORY COOPERATIVE STUDY OF THE PRECISION AND ACCURACY OF THE MEASUREMENT OF SULFUR DIOXIDE CONTENT IN THE ATMOSPHERE USING ASTM METHOD D 2914

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 sulfur dioxide by the West-Gaeke method according to ASTM Method D 2914[(1)*]. The evaluation of D 2914 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 nitrogen dioxide, lead, dustfall, total sulfation, and particulate matter in Phase 1.

Project Threshold, a multiphase program, is sponsored by American Society for Testing and 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 sulfur dioxide in ambient air and in ambient air spiked with known quantities of sulfur 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 2914 for measuring sulfur dioxide in the atmosphere. The laboratories performed a total of 704 measurements of sulfur dioxide over the concentration range of about 7 to 300 $\mu g/m^3$ (0.003 to 0.12 ppm) in ambient air and spiked-ambient air at Los Angeles, California; Bloomington, Indiana; and Manhattan, New York.

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* References at end of report.

Statistical analyses of the sulfur 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 sulfur dioxide, m, as follows:

$$s_b = 1.61 \sqrt{m},$$

where, s_b, and, m, are given in $\mu g/m^3$. This relation yields standard deviations of 4 and 28 $\mu g/m^3$, respectively, at concentrations of 7 and 300 $\mu g/m^3$, the sulfur dioxide concentration extremes 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:

$$s_w = 0.701 \sqrt{m},$$

where, s_w, and, m, are given in $\mu g/m^3$. This relation yields standard deviations of 2 $\mu g/m^3$ and 11 $\mu g/m^3$, respectively, at concentrations of 7 and 250 $\mu g/m^3$, the sulfur dioxide concentration extremes which were studied.

- The bias of the measurements of the sulfur dioxide recovered from spiked-ambient samples was -22, -6, and -4 percent at Los Angeles, Bloomington, and Manhattan, respectively. The bias does not appear to be dependent on concentration. As a measure of the overall bias of the method the recovery of sulfur dioxide from spiked samples at all sites, based on the spiked amount, was an average of 11 percent less than the amount added.

- 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 118 (84 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 sulfur dioxide concentration was observed by all laboratories using the Test Method.

- An estimated minimum concentration of sulfur dioxide that can be detected based on statistical considerations is about 4 $\mu g/m^3$.

EXPERIMENTAL PROGRAM

ASTM Test Method D 2914

The Tentative Method of Test for Sulfur Dioxide Content of the Atmosphere (West-Gaeke Method), D 2914, is reproduced in the Appendix to this report. The method is applicable to measurement of ambient concentrations in the range of about 10 to 13,000 $\mu g/m^3$ (0.003 to 5 ppm) of sulfur dioxide. A sample of the ambient atmosphere is drawn through potassium tetrachloromercurate (TCM) solution in a midget impinger. The sulfur dioxide in the air reacts with the reagent solution to form a stable dichlorosulfitomercurate complex, which later is combined with pararosanaline and formaldehyde to give a highly colored product whose concentration is measured with a spectrophotometer. The intensity of color of the product is directly related to the concentration of sulfur dioxide by calibration with solutions containing known quantities of sulfite ion, or by using known concentrations of sulfur dioxide in dry air prepared with a permeation tube.

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 concerning the performance of the site tests and analyses. The references in parentheses inserted in some items specify the numbered paragraph in the Test Method where the option is described.

Preparation

Sufficient TCM absorbing reagent for all scheduled tests plus an adequate surplus was prepared at each laboratory and brought to the test site for use in the midget impingers. Spare midget impingers were provided by each laboratory to permit the use of a clean impinger containing fresh absorbing reagent for each sampling period.

The TCM absorbing reagent was adjusted, if necessary, to pH = 5.2 (6.3).

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 ambient or spiked-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 impinger (5.5).

No prefilter was used (5.5).

One midget impinger was used as the absorber [5.1 (b)].

Collection

A uniform sampling rate and time were used by all laboratories for taking simultaneous samples. The rate was nominally 2 liters per minute and sampling periods were varied from 30 to 90 minutes according to instructions of the Coordinating Laboratory. The duration of the sampling period was adjusted as the concentration of SO_2 varied in the ambient atmosphere. Both a calibrated dry test meter and a glass rotameter were recommended for use in the sampling train. If samples were not to be analyzed on-site, the collected samples were transferred immediately to stoppered flasks for storage and transportation to the home laboratory for analysis. Enough flasks were provided to store 32 samples plus 4 reagent blanks (one for each half-day session) (8.1). The storage flasks were refrigerated at 3 to 7 C until they were taken back to the home laboratory. Each flask was coded with a letter and number to relate it uniquely to the time of sampling recorded on each laboratory's data form. Samples in their transporting flasks were returned to refrigeration after reaching the home laboratory until there was opportunity for analysis. A correction for the time that the sample was not under refrigeration during transport was estimated and applied (11).

Analysis

Variation A of this method (2.1 and 2.1.1) was used at a pH of 1.6 and with spectrophotometric measurement at 548 nm and a band width of <16 nm. The wavelength calibration of the spectrophotometer was verified. Color was read by a

spectrophotometer as specified, using water as a reference. Unexposed reagent was used for blank correction. Each laboratory used Harleco (Hartman-Leddon Company) solution of purified pararosaniline (PRA) for analysis (A. H. Thomas Company, Item No. 64327). Portions of a Harleco PRA solution which had been assayed by Dr. Johns, ASTM Fellow at the National Bureau of Standards, were made available for each laboratory to check against its own solution assay (6.9.2). Calibration curves were prepared using standard sulfite solution (6.12.4) by the procedure described in the Test Method (9). A copy of the calibration curve (9.2) was submitted as part of the data obtained by each Cooperating Laboratory.

The preceding requirements and a copy of the Test Method constituted the pretest instructions to the participating laboratories. Each laboratory was visited to review the instructions orally and inspect the apparatus to be used in the field tests, but the laboratories were not specifically required to rehearse the test procedure under supervision prior to performance of the actual site tests. Any pretest preparation other than stated above was at the discretion of the individual laboratories, therefore, the results should represent the accuracy and precision obtainable by a compentent laboratory with "normal" preparation to conduct the Test Method.

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) the midget impinger containing sulfur dioxide absorbing solution, (3) desiccant/absorbent to protect measuring and pumping apparatus downstream, (4) measuring apparatus for pressure, temperature, sample flow rate, and sample volume, and (5) 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

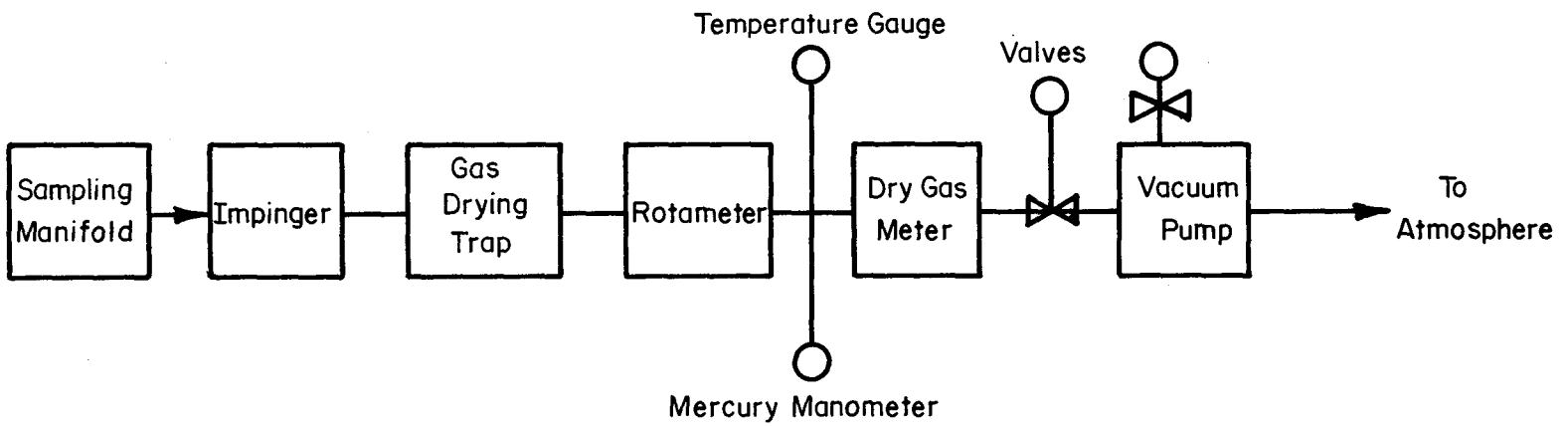
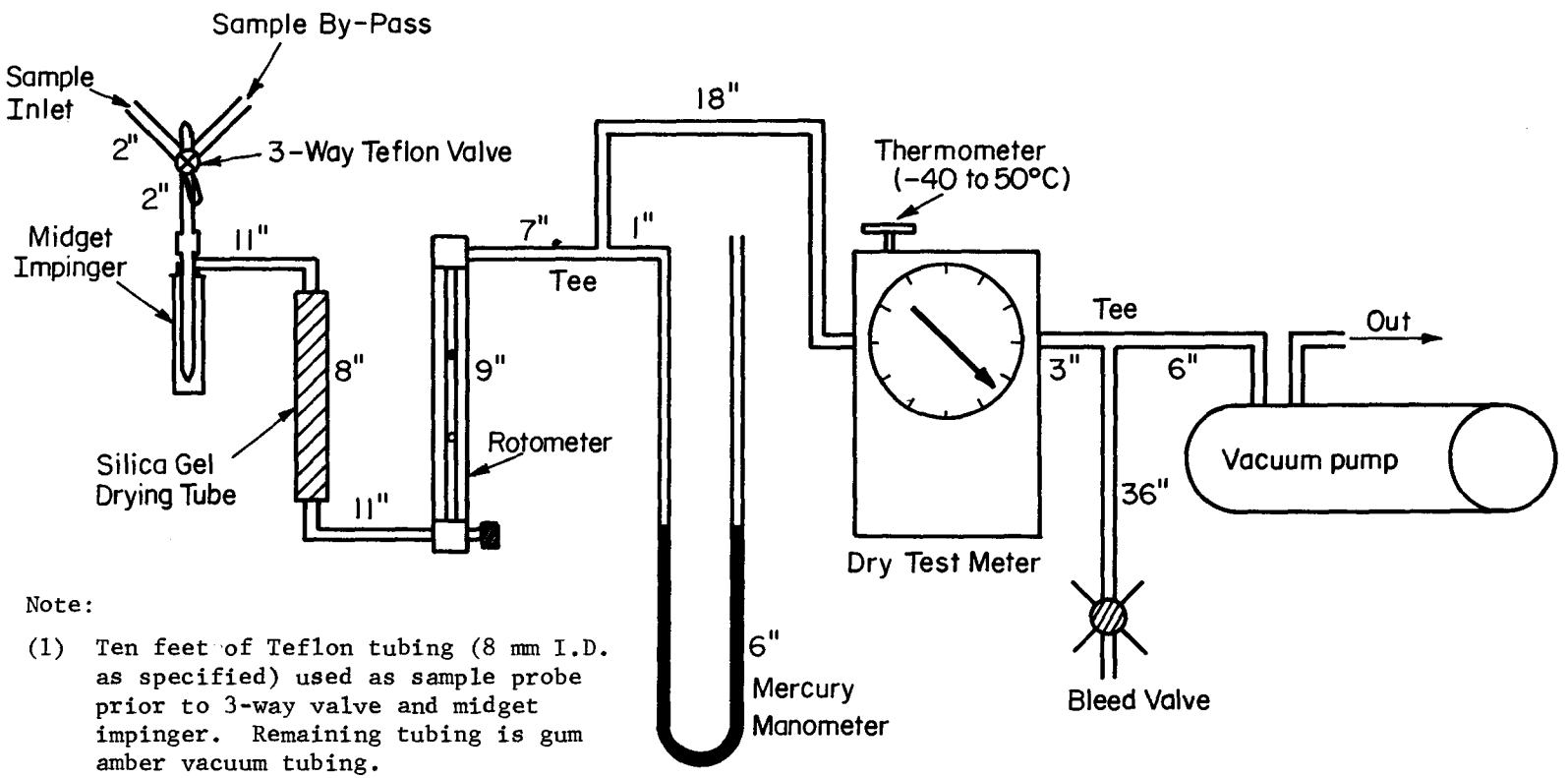


FIGURE 1. SCHEMATIC ARRANGEMENT OF SAMPLING APPARATUS FOR ASTM METHOD D2914



Note:

(1) Ten feet of Teflon tubing (8 mm I.D. as specified) used as sample probe prior to 3-way valve and midget impinger. Remaining tubing is gum amber vacuum tubing.

(2) 3-way valve to midget impinger is a butt joint connection.

FIGURE 2. SAMPLING APPARATUS FOR ASTM METHOD D 2914

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 sulfur 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 sulfur 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 sulfur dioxide sampling trains. A photo of the sampling manifold is presented in Figure 6.

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). Sulfur 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 sulfur dioxide above ambient level could be calculated from the known flow rates of added sulfur dioxide and ambient air in the branch line, and was measured as the difference between the sulfur 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.

FIGURE 3. SAMPLING APPARATUS FOR ASTM METHOD D 2914

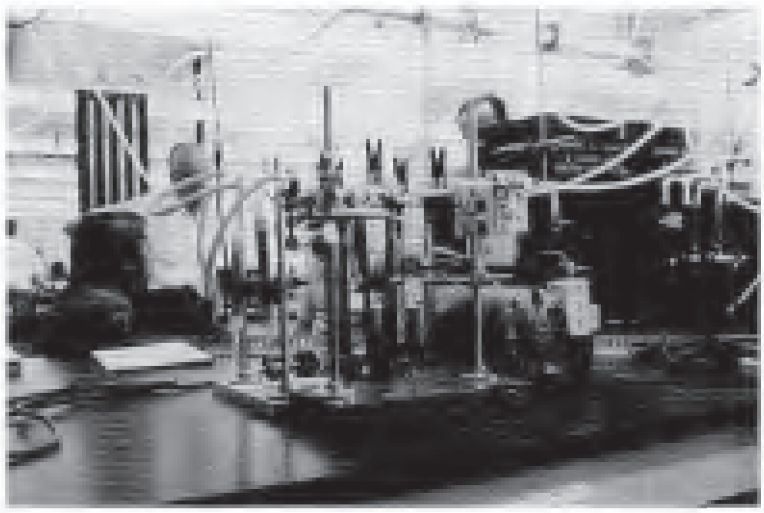


FIGURE 4. PARALLEL-SAMPLING TRAINS FOR CONCURRENT MEASUREMENTS BY ASTM METHOD D 2914

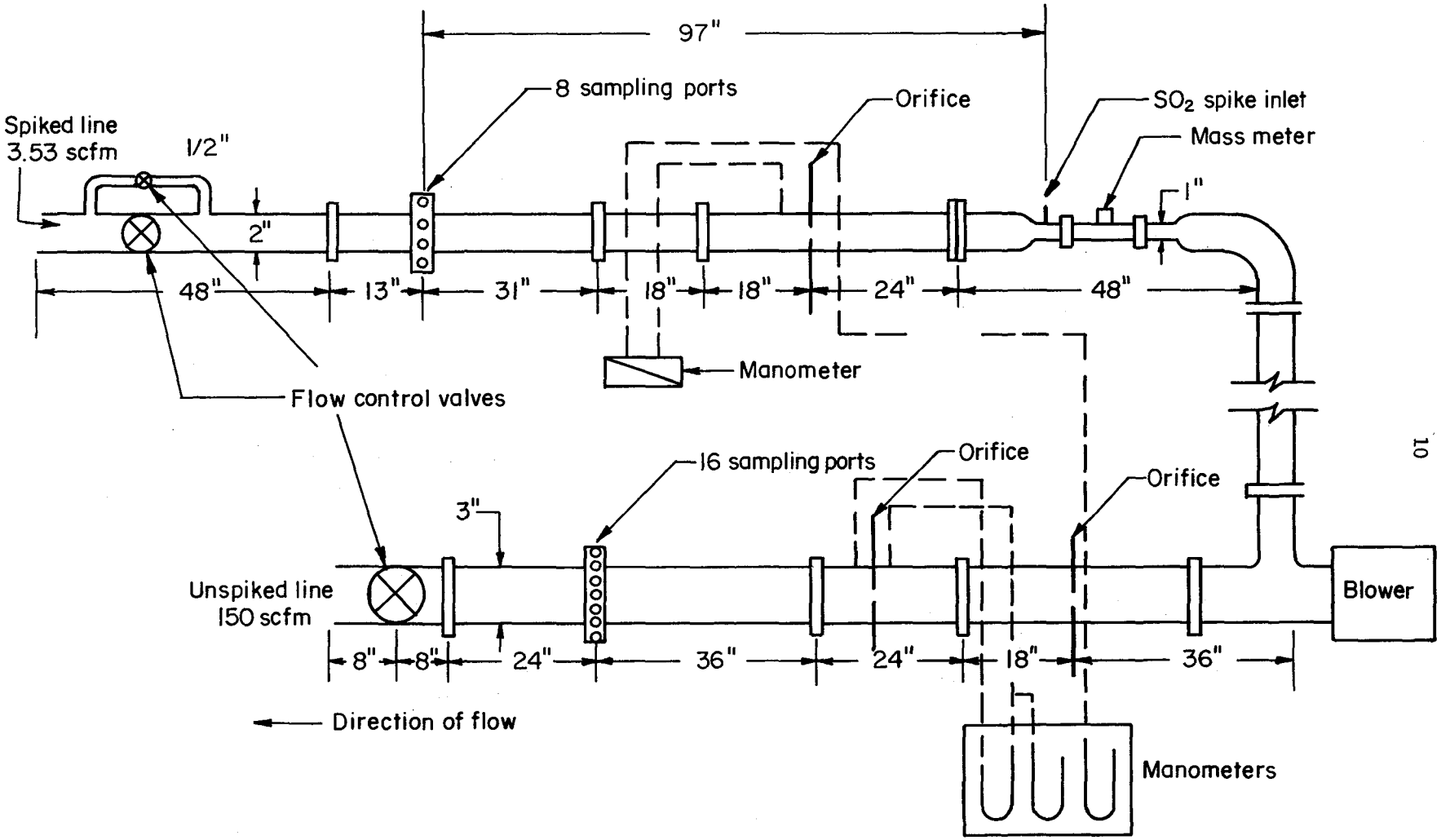


FIGURE 5. SAMPLE GENERATING SYSTEM USED FOR EVALUATION OF ASTM METHOD D 2914 FOR DETERMINING SULFUR DIOXIDE IN THE ATMOSPHERE

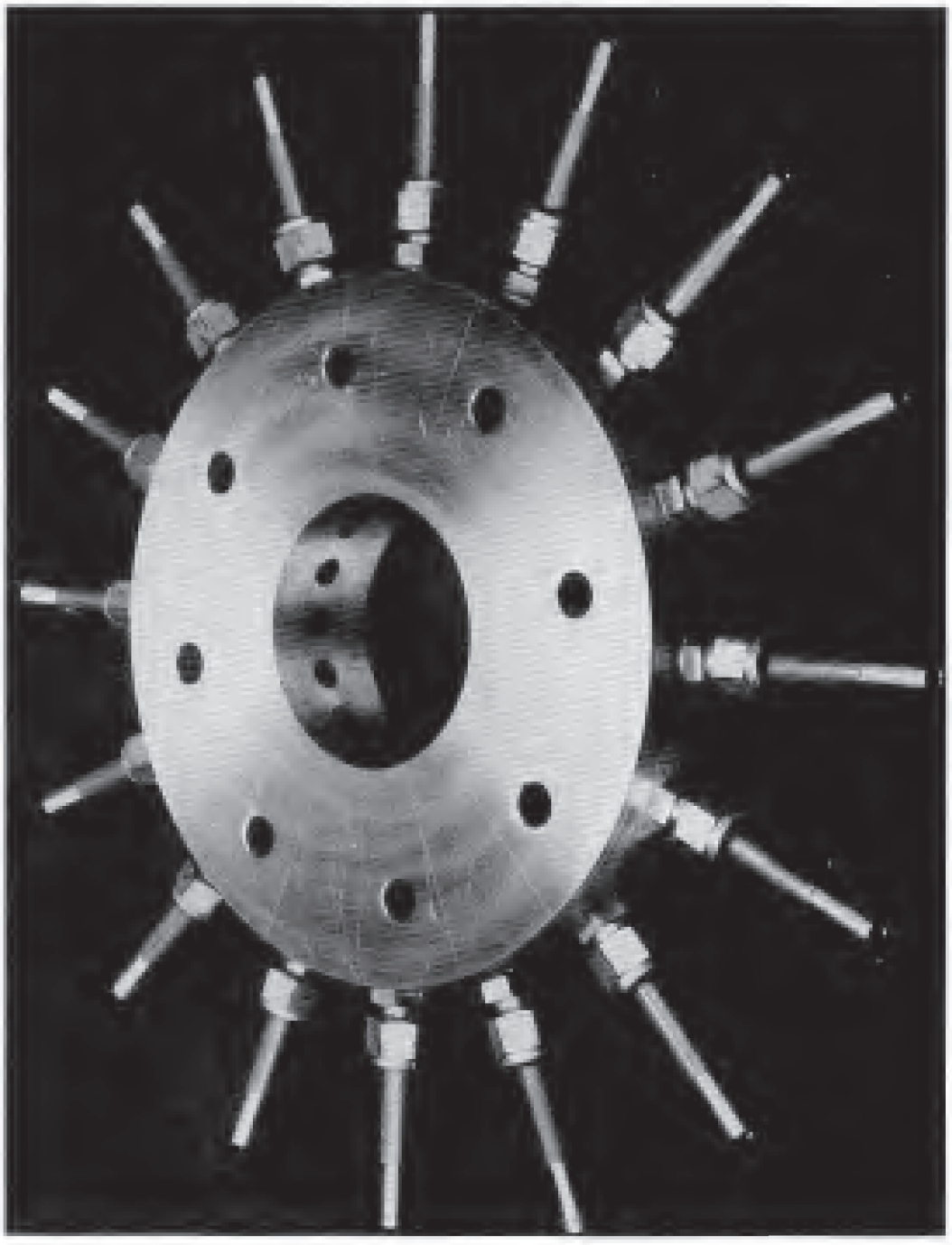


FIGURE 6. SIXTEEN-POSITION SAMPLING MANIFOLD USED IN UNSPIKED SAMPLE LINE

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

Spiking Procedure

The addition of sulfur 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 sulfur dioxide has been added. The system used to generate the known sulfur 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 sulfur dioxide supply. Dry air from a cylinder was used as a carrier gas to introduce the sulfur 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 about 31, 30, and 87 $\mu g/m^3$, 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 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. Thereafter, for all the Bloomington and Manhattan tests, the procedure was modified so that all participating laboratories sampled simultaneously for 30 to 90 minutes, rather than sampling for one-half hour in two alternating groups. The change in sampling procedure was made for the following reasons.

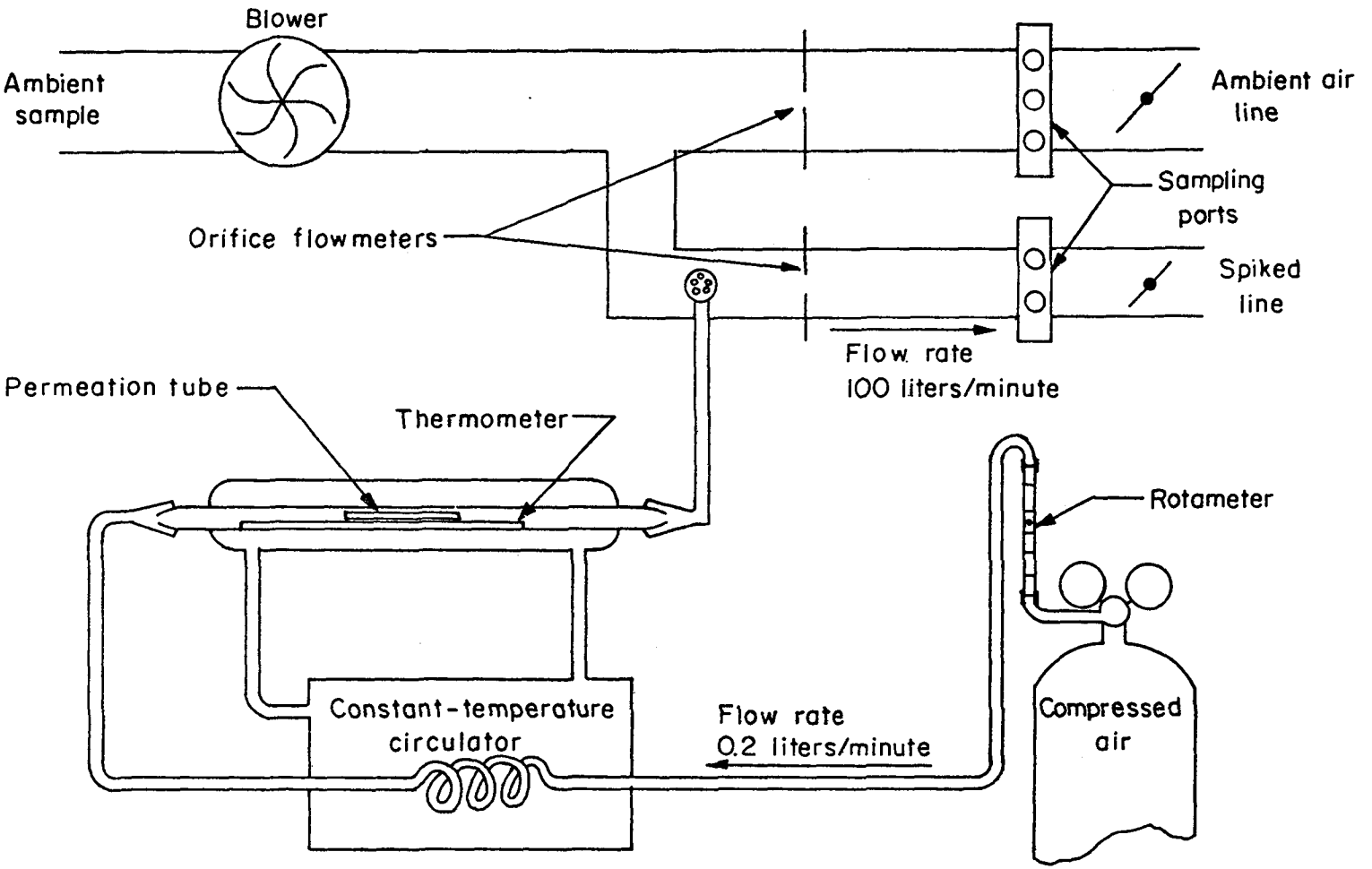


FIGURE 7. SULFUR DIOXIDE SPIKE GENERATION SYSTEM

(1) The ambient sulfur dioxide concentrations were so low at Bloomington that a longer sampling time was desirable to collect a larger sample of sulfur 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. Ambient air was drawn into the sample generating system through an intake line which extended well above the roof height. A photo of the intake line arrangement is shown in Figure 8. Similar sample system intake line installations were used at the other test sites. The interior 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 consecutive half-day sampling periods on August 18, 19, and 20, 1971. The ambient level of sulfur dioxide ranged from about 10 to 70 $\mu g/m^3$ 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 interior sampling system at the site is shown in Figure 9. The ambient sample line and sampling manifold is shown in the upper foreground and the sulfur dioxide-spiked-ambient-sample line and sampling manifold can be seen in the background. Similar experimental arrangements were 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 27 and 28, 1971. The ambient level of sulfur dioxide at the Bloomington site ranged from about 10 to 30 $\mu g/m^3$.

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 on lower 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 12 and 13, 1973. Ambient levels of sulfur 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.

FIGURE 8. SULFUR DIOXIDE SAMPLING SYSTEM INTAKE LINE AT LOS ANGELES TEST SITE

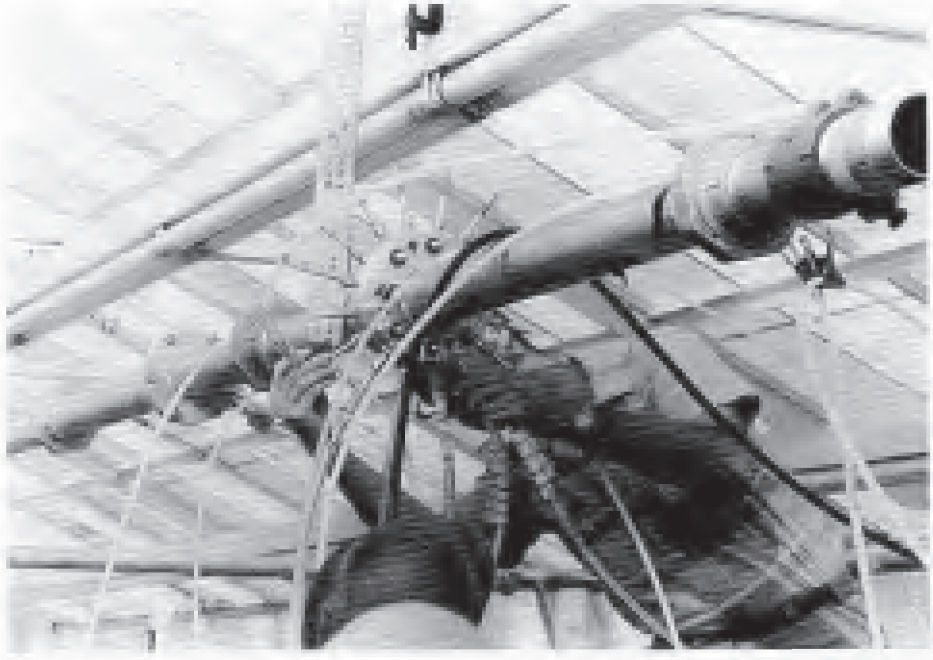


FIGURE 9. SAMPLE GENERATING SYSTEM ARRANGEMENT USED FOR SULFUR DIOXIDE MEASUREMENTS AT THE BLOOMINGTON TEST SITE

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 sulfur dioxide in the atmosphere, if all extraneous variables are held constant.

(2) Measurement of laboratory-to-laboratory variability in determining atmospheric levels of sulfur 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 sulfur dioxide on accuracy and precision of the measurements.

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

It was also recognized that the ambient concentration of sulfur 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 sulfur dioxide concentrations were expected while at Bloomington, a more rural area, lower concentrations were expected. The changes of sulfur dioxide concentration with time were expected to occur due to variations in source emissions and in climatological and meteorological conditions. The study of site- and time-related variations of ambient sulfur 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 sulfur 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. Linking of the Latin Squares was provided through the use of a balanced incomplete block design, which was superimposed on the design structure as a whole, 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 designed to provide a measure of the repeatability of the Test Method.

The sampling pattern, after randomization, of sulfur dioxide experiments at the Los Angeles site is shown in Table 1. Eight laboratories participated in the test. Concurrent sampling for 30-minute periods was performed in two groups of four laboratories each. During the process of randomizing the sampling pattern, 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.

The sampling pattern of the test at the Bloomington site is shown in Table 2. Only seven laboratories participated in the experiments, consequently data were not obtained for several cells of the Latin Squares of the sampling pattern. In accordance with the sampling pattern, concurrent sampling was performed by all seven laboratories. Sampling periods of 60 to 90 minutes were used for the test blocks.

Seven laboratories participated in the Manhattan test, consequently several of the Latin Squares in the sampling pattern also have empty data cells. In all blocks the seven laboratories sampled simultaneously. Sampling times of 30 to 60 minutes were used for the test blocks. The sampling pattern of the Manhattan test is shown in Table 3.

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

Time Period	Block	Sampling Outlet Position[a] U1 U2 U3 U4[b]	S1 S2 S3 S4[c]
1	1	H_1 A_1 C_1 E_1	C_1 E_1 H_1 A_1
	2	F_1 G_1 B_1 D_1	F_1 G_1 D_1 B_1
2	3	C_1 E_1 H_1 A_1	A_1 H_1 C_1 E_1
	4	D_1 B_1 F_1 G_1	D_1 F_1 B_1 G_1
3	5	A_1 H_1 E_1 C_1	H_1 A_1 E_1 C_1
	6	B_1 D_1 G_1 F_1	G_1 B_1 F_1 D_1
4	7	E_1 C_1 A_1 H_1	E_1 C_1 A_1 H_1
	8	G_1 F_1 D_1 B_1	B_1 D_1 G_1 F_1
5	9	A_1 G1 E1 B1	E1 G1 B1 A1
	10	F_1 C1 H1 D1	C1 H1 F1 D1
6	11	B_1 E1 G1 A1	A1 E1 G1 B1
	12	C_1 F1 D1 H1	F1 D1 H1 C1
7	13	E_1 B1 A1 G1	B1 A1 E1 G1
	14	D_1 H1 F1 C1	D1 F1 C1 H1
8	15	G_1 A1 B1 E1	G1 B1 A1 E1
	16	H_1 D1 C1 F1	H1 C1 D1 F1
9	17	G1 H1 B1 C1	H1 G1 B1 C1
	18	E1 F1 A1 D1	E1 D1 A1 F1
10	19	B1 C1 H1 G1	G1 C1 H1 B1
	20	F1 A1 D1 E1	F1 A1 D1 E1
11	21	C1 B1 G1 H1	B1 H1 C1 G1
	22	D1 E1 F1 A1	D1 E1 F1 A1
12	23	H1 G1 C1 B1	C1 B1 G1 H1
	24	A1 D1 E1 F1	A1 F1 E1 D1
13	25	F1 A1 A1 F1	G1 D1 G1 D1
	26	B1 H1 H1 B1	E1 C1 E1 C1
14	27	A1 G1 G1 A1	D1 F1 D1 F1
	28	H1 B1 B1 H1	C1 E1 C1 E1
15	29	D1 F1 F1 D1	A1 G1 A1 G1
	30	C1 E1 E1 C1	B1 H1 B1 H1
16	31	G1 D1 D1 G1	F1 A1 F1 A1
	32	E1 C1 C1 E1	H1 B1 H1 B1

(a) Letter entries are laboratory code designations.
(b) Ui = unspiked sample collected from the i^{th} outlet.
(c) Si = spiked sample collected from the i^{th} outlet.

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

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

(a) Letter entries are laboratory code designations.
(b) Ui = unspiked sample collected from the i^{th} outlet.
(c) Si = spiked sample collected from the i^{th} outlet.

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

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

(a) Letter entries are laboratory code designations.
(b) Ui = unspiked sample collected from the i^{th} outlet.
(c) Si = spiked sample collected from the i^{th} outlet.

STATISTICAL ANALYSIS OF SULFUR 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 sulfur 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 sulfur 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".

Accuracy

In a portion of the experiments, the laboratories performed analyses of an ambient sample and a duplicate ambient sample to which a known sulfur dioxide spike was added. The difference between sulfur dioxide analyses for each such pair of samples serves as a measure of the concentration of sulfur dioxide added to the sample. Small 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 sulfur dioxide concentrations by different laboratories agree in regard to the differences between different concentrations. As sulfur dioxide concentrations vary from sampling period to sampling period, the same pattern of increasing or decreasing concentration 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 sulfur dioxide were performed at the three test 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 sulfur 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 time period, block, and laboratory according to the sampling patterns presented in Tables 1, 2, and 3. The next two columns contain the measurements of the sulfur 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 time period, block, and laboratory combination, between the measured sulfur dioxide concentration in the spiked sample and the measured concentration of sulfur dioxide in the unspiked sample. Column 7 shows the spiking rate that was used to provide a known increase in the concentration of sulfur 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.

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

Time Period	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	H_1	U1 = 31.1	S3 = 31.1	0.0	30.9	-100
		A_1	U2 = 27.8	S4 = 45.9	18.1		- 41
		C_1	U3 = 22.8	S1 = 44.9	22.1		- 28
		E_1	U4 = 37.2	S2 = 98.6(a)	(a)		(a)
	2	F_1	U1 = 29.4	S1 = 18.7	- 10.7	30.9	-135
		G_1	U2 = 19.2	S2 = 26.0	6.8		- 78
		B_1	U3 = 18.5	S4 = 37.0	18.5		- 40
		D_1	U4 = 22.1	S3 = 35.4	13.3		- 57
2	3	C_1	U1 = 37.0	S3 = 58.7	21.7	31.0	- 27
		E_1	U2 = 28.8	S4 = 55.8	27.0		- 13
		H_1	U3 = 25.9	S2 = 31.1	5.2		- 83
		A_1	U4 = 24.2	S1 = 47.1	22.9		- 26
	4	D_1	U1 = 14.6	S1 = 34.9	20.3	31.0	- 35
		B_1	U2 = 8.8	S3 = 35.3	26.5		- 15
		F_1	U3 = 28.1	S2 = 38.5	10.4		- 66
		G_1	U4 = 16.7	S4 = 35.8	19.1		- 38
3	5	A_1	U1 = 24.9	S2 = 44.8	19.9	31.0	- 36
		H_1	U2 = 5.2	S1 = 31.1	25.9		- 16
		E_1	U3 = 27.6	S3 = 56.8	29.2		- 6
		C_1	U4 = 27.5	S4 = 57.1	29.6		- 5
	6	B_1	U1 = 4.8	S2 = 21.8	17.0	31.0	- 45
		D_1	U2 = 6.9	S4 = 30.9	24.0		- 23
		G_1	U3 = 7.0	S1 = 30.8	23.8		- 23
		F_1	U4 = 15.7	S3 = 28.4	12.7		- 59
4	7	E_1	U1 = 22.0	S1 = 47.3	25.3	31.0	- 18
		C_1	U2 = 2.3	S2 = 23.6	21.3		- 31
		A_1	U3 = 12.1	S3 = 40.0	27.9		- 10
		H_1	U4 = 10.4	S4 = 39.0	28.6		- 8
	8	G_1	U1 = 7.0	S3 = 20.3	13.3	31.0	- 57
		F_1	U2 = 2.7	S4 = 33.9	31.2		0.5
		D_1	U3 = 4.9	S2 = 25.6	20.7		- 33
		B_1	U4 = 2.3	S1 = 23.5	21.2		- 32

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

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

Time Period	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	A_1	U1 = 29.9	S4 = 58.3	28.4	30.9	- 8
		G_1	U2 = 15.3	S2 = 31.9	16.6		- 46
		E_1	U3 = 41.6	S1 = 65.0	23.4		- 24
		B_1	U4 = 16.8	S3 = 48.8	32.0		4
	10	F_1	U1 = 31.4	S3 = 60.3	28.9	30.9	- 6
		C_1	U2 = 46.0	S1 = 66.5	20.5		- 34
		H_1	U3 = 25.6	S2 = 46.3	20.7		- 33
		D_1	U4 = 26.6	S4 = 56.2	29.6		- 4
6	11	B_1	U1 = 55.3	S4 = 71.0	15.7	30.9	- 49
		E_1	U2 = 73.9	S2 = 92.0	18.1		- 41
		G_1	U3 = 49.5	S3 = 64.9	15.4		- 50
		A_1	U4 = 74.2	S1 = 101.1	26.9		- 13
	12	C_1	U1 = 76.9	S4 = 105.4	28.5	30.9	- 8
		F_1	U2 = 54.4	S1 = 80.0	25.6		- 17
		D_1	U3 = 66.9	S2 = 85.7	18.8		- 39
		H_1	U4 = 62.0	S3 = 82.6	20.6		- 33
7	13	E_1	U1 = 73.9	S3 = 97.2	23.3	30.9	- 25
		B_1	U2 = 55.3	S1 = 76.3	21.0		- 32
		A_1	U3 = 70.9	S2 = 89.4	18.5		- 40
		G_1	U4 = 50.1	S4 = 66.3	16.2		- 48
	14	D_1	U1 = 43.7	S1 = 70.3	26.6	31.0	- 14
		H_1	U2 = 44.0	S4 = 75.0	31.0		0
		F_1	U3 = 37.2	S2 = 65.3	28.1		- 9
		C_1	U4 = 56.7	S3 = 91.4	34.7		12
8	15	G_1	U1 = 3.9(a)	S1 = 30.1(a)	(a)	31.0	(a)
		A_1	U2 = 62.4	S3 = 84.2	21.8		- 30
		B_1	U3 = 21.0	S2 = 51.8	30.8		- 1
		E_1	U4 = 39.1	S4 = 71.0	31.9		3
	16	H_1	U1 = 15.0	S1 = 41.4	26.4	31.0	- 15
		D_1	U2 = 14.1	S3 = 47.6	33.5		- 8
		C_1	U3 = 28.0	S2 = 55.8	27.8		- 10
		F_1	U4 = 14.2	S4 = 39.4	25.2		- 19

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

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

Time Period	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	G_1	U1 = 63.6	S2 = 83.2	19.6	31.0	- 37
		H_1	U2 = 46.7	S1 = 67.7	21.0		- 32
		B_1	U3 = 62.3	S3 = 86.8	24.5		- 21
		C_1	U4 = 75.4	S4 = 102.7	27.3		- 12
	18	E_1	U1 = 52.3	S1 = 113.2	60.9	31.0	96
		F_1	U2 = 75.0	S4 = 80.7	5.7		- 82
		A_1	U3 = 91.2	S3 = 110.6	19.4		- 37
		D_1	U4 = 83.3	S2 = 99.8	16.5		- 47
10	19	B_1	U1 = 66.3	S4 = 95.0	28.7	31.0	- 7
		C_1	U2 = 68.4	S2 = 93.3	24.9		- 20
		H_1	U3 = 54.9	S3 = 81.0	26.1		- 16
		G_1	U4 = 64.5	S1 = 86.6	22.1		- 29
	20	F_1	U1 = 48.4	S1 = 71.7	23.3	30.9	- 25
		A_1	U2 = 57.2	S2 = 89.2	32.0		4
		D_1	U3 = 54.0	S3 = 79.3	25.3		- 18
		E_1	U4 = 31.6	S4 = 95.7	64.1		107
11	21	C_1	U1 = 43.5	S3 = 74.0	30.5	30.9	- 1
		B_1	U2 = 27.8	S1 = 55.8	28.0		- 9
		G_1	U3 = 29.6	S4 = 57.0	27.4		- 11
		H_1	U4 = 28.7	S2 = 47.1	18.4		- 40
	22	D_1	U1 = 26.6	S1 = 59.9	33.3	30.9	8
		E_1	U2 = 11.1	S2 = 48.9	37.8		22
		F_1	U3 = 21.0	S3 = 54.8	33.8		9
		A_1	U4 = 43.2	S4 = 72.7	29.5		- 5
12	23	H_1	U1 = 10.4	S4 = 36.6	26.2	31.1	- 16
		G_1	U2 = 16.9	S3 = 38.9	22.0		- 29
		C_1	U3 = 16.9	S1 = 44.9	28.0		- 10
		B_1	U4 = 18.5	S2 = 45.8	27.3		- 12
	24	A_1	U1 = 38.3	S1 = 66.8	28.5	31.1	- 8
		D_1	U2 = 19.4	S4 = 50.3	30.9		- 1
		E_1	U3 = 6.7	S3 = 44.7	38.0		22
		F_1	U4 = 6.8	S2 = 40.3	33.5		8

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

Time Period	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	A_2	U2 = 21.6	S2 = 39.1	17.5	30.3	- 42
		C_2	U3 = 44.0	S3 = 56.3	12.3		- 59
		E_2	U4 = 25.2	S4 = 42.9	17.7		- 42
	2	F_2	U5 = 18.0	S5 = 30.9	12.9	30.3	- 57
		G_2	U6 = 42.1	S6 = 50.3	8.2		- 73
		B_2	U7 = 43.7	S7 = 55.6	11.9		- 60
		D_2	U8 = 1.9(a)	S8 = 18.6(a)	(a)		(a)
2	3	C_2	U1 = 28.0	S1 = 80.3	52.3	30.4	72
		E_2	U2 = 29.8	S2 = 43.5	13.7		- 55
		A_2	U4 = 20.2	S4 = 45.9	25.7		- 15
	4	D_2	U5 = 1.9(a)	S5 = 16.7(a)	(a)	30.4	(a)
		B_2	U6 = 37.2	S6 = 68.9	31.7		5
		F_2	U7 = 21.2	S7 = 50.8	29.6		- 3
		G_2	U8 = 27.4	S8 = 42.5	15.1		- 50
3	5	A_2	U1 = 18.3	S1 = 48.1	29.8	30.4	- 2
		E_2	U3 = 23.9	S3 = 40.3	16.4		- 46
		C_2	U4 = 18.8	S4 = 77.4	58.6		93
	6	B_2	U5 = 32.1	S5 = 69.3	37.2	30.4	22
		D_2	U6 = 18.6(a)	S6 = 53.7(a)	(a)		(a)
		G_2	U7 = 23.3	S7 = 54.3	31.0		2
		F_2	U8 = 21.8	S8 = 40.1	18.3		- 40
4	7	E_2	U1 = 24.6	S1 = 47.0	22.4	30.3	- 26
		C_2	U2 = 24.8	S2 = 64.8	40.0		32
		A_2	U3 = 16.4	S3 = 44.0	27.6		- 9
	8	G_2	U5 = 15.2	S5 = 48.2	33.0	30.3	9
		F_2	U6 = 20.8	S6 = 51.1	30.3		0
		D_2	U7 = 19.1(a)	S7 = 45.2(a)	(a)		(a)
		B_2	U8 = 32.4	S8 = 57.4	25.0		- 17

(a) Laboratory D_2 determinations inconsistent with other laboratories, excluded from statistical analysis on the basis of the correlations with other laboratories given in Tables 20 and 21.

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

Time Period	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	A_2	U1 = 21.6	S1 = 50.9	29.3	30.3	- 3
		G_2	U2 = 16.6	S2 = 50.6	34.0		12
		E_2	U3 = 21.8	S3 = 44.5	22.7		- 25
		B_2	U4 = 24.8	S4 = 54.2	29.4		- 4
	10	F_2	U5 = 19.1	S5 = 51.0	31.9	30.3	5
		C_2	U6 = 24.4	S6 = 62.3	37.9		25
		D_2	U8 = 17.0(a)	S8 = 50.7(a)	(a)		(a)
6	11	B_2	U1 = 35.3	S1 = 59.5	24.2	30.3	- 1
		E_2	U2 = 20.2	S2 = 47.3	27.1		- 11
		G_2	U3 = 22.9	S3 = 49.3	26.4		- 13
		A_2	U4 = 22.5	S4 = 52.4	29.9		- 1
	12	C_2	U5 = 21.5	S5 = 81.4	59.9	30.3	98
		F_2	U6 = 26.2	S6 = 50.8	24.6		- 19
		D_2	U7 = 23.4(a)	S7 = 64.5(a)	(a)		(a)
7	13	E_2	U1 = 13.5	S1 = 39.2	25.7	30.3	- 15
		B_2	U2 = 21.2	S2 = 50.3	29.1		- 4
		A_2	U3 = 5.6	S3 = 36.9	31.3		3
		G_2	U4 = 22.0	S4 = 44.3	22.3		- 26
	14	D_2	U5 = 6.4(a)	S5 = 45.4(a)	(a)	30.3	(a)
		F_2	U7 = 12.4	S7 = 34.6	22.2		- 27
		C_2	U8 = 16.0	S8 = 10.1	- 5.9		-119
8	15	G_2	U1 = 15.1	S1 = 51.4	36.3	30.3	20
		A_2	U2 = 0.5	S2 = 31.2	30.7		1
		B_2	U3 = 10.4	S3 = 39.9	29.5		- 1
		E_2	U4 = 10.6	S4 = 26.0	15.4		- 49
	16	D_2	U6 = 0.0(a)	S6 = 26.0(a)	(a)	30.3	(a)
		C_2	U7 = 9.6	S7 = 17.9	8.3		- 73
		F_2	U8 = 6.4	S8 = 31.6	25.2		- 17

(a) Laboratory D_2 determinations inconsistent with other laboratories, excluded from statistical analysis on the basis of the correlations with other laboratories given in Tables 20 and 21.

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

Time Period	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	G_2	U1 = 30.7	S1 = 65.4	34.7	30.2	15
		B_2	U3 = 20.8	S3 = 50.4	29.6		- 4
		C_2	U4 = 25.1	S4 = 73.7	48.6		61
	18	E_2	U5 = 18.2	S5 = 37.8	19.6	30.2	- 35
		F_2	U6 = 17.6	S6 = 48.9	31.3		4
		A_2	U7 = 11.9	S7 = 42.1	30.2		0
		D_2	U8 = 13.8(a)	S8 = 38.0(a)	(a)		(a)
10	19	B_2	U1 = 17.7	S1 = 61.3	43.6	30.3	43
		C_2	U2 = 13.6	S2 = 66.4	52.8		74
		G_2	U4 = 15.5	S4 = 46.3	30.8		2
	20	F_2	U5 = 14.8	S5 = 49.9	35.1	30.3	16
		A_2	U6 = 11.4	S6 = 44.6	33.2		10
		D_2	U7 = 8.0(a)	S7 = 43.6(a)	(a)		(a)
		E_2	U8 = 18.2	S8 = 34.9	16.7		- 45
11	21	C_2	U1 = 3.9	S1 = 53.9	50.0	30.4	64
		B_2	U2 = 13.9	S2 = 41.4	27.5		- 11
		G_2	U3 = 15.6	S3 = 44.6	29.0		- 5
	22	D_2	U5 = 2.9(a)	S5 = 72.5(a)	(a)	30.4	(a)
		E_2	U6 = 14.3	S6 = 32.1	17.8		- 41
		F_2	U7 = 6.3	S7 = 28.6	22.3		- 27
		A_2	U8 = 5.3	S8 = 35.1	29.8		- 2
12	23	G_2	U2 = 10.3	S2 = 42.2	31.9	30.3	5
		C_2	U3 = 10.1	S3 = 61.9	51.8		71
		B_2	U4 = 10.9	S4 = 41.0	30.1		- 1
	24	A_2	U5 = 0.0	S5 = 31.9	31.9	30.3	5
		D_2	U6 = 23.1(a)	S6 = 50.5(a)	(a)		(a)
		E_2	U7 = 2.3	S7 = 36.8	34.5		14
		F_2	U8 = 5.1	S8 = 34.0	28.9		- 5

(a) Laboratory D_2 determinations inconsistent with other laboratories, excluded from statistical analysis on the basis of the correlations with other laboratories given in Tables 20 and 21.

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

Time Period	Block	Lab	Unspiked Samples, $\mu g/m^3$ (U)	Spiked Samples, $\mu g/m^3$ (S)	Estimated Spiked Rate, $\mu g/m^3$ (S-U)	True Spiking Rate, $\mu g/m^3$ (R)	Difference, percent of (R)
1	1	F_3	U2 = 167.8	S2 = 295.1	127.3	87.0	46
		G_3	U3 = 225.1	S3 = 277.3	52.2		- 40
		B_3	U4 = 230.0	S4 = 365.0	135.0		55
	2	C_3	U5 = 204.8	S5 = 290.9	86.1	87.0	- 1
		D_3	U6 = 207.6	S6 = 308.8	101.2		16
		E_3	U7 = 169.0	S7 = 244.0	75.0		- 14
		A_3	U8 = 212.5	S8 = 294.0	81.5		- 6
2	3	G_3	U1 = 215.6	S1 = 253.0	37.4	86.9	- 34
		B_3	U2 = 227.0	S2 = 284.0	57.0		- 34
		F_3	U4 = 150.7	S4 = 287.4	136.7		57
	4	A_3	U5 = 195.5	S5 = 278.1	82.6	86.9	- 5
		E_3	U6 = 163.0	S6 = 242.0	79.0		- 9
		C_3	U7 = 201.7	S7 = 293.0	91.3		5
		D_3	U8 = 194.3	S8 = 311.5	117.2		35
3	5	F_3	U1 = 108.4	S1 = 156.0	47.6	86.9	- 45
		B_3	U3 = 166.0	S3 = 255.0	89.0		2
		G_3	U4 = 162.2	S4 = 203.7	41.5		- 52
	6	E_3	U5 = 114.0	S5 = 198.0	84.0	86.9	- 3
		A_3	U6 = 144.1	S6 = 223.6	79.5		- 9
		D_3	U7 = 146.2	S7 = 255.6	109.4		26
		C_3	U8 = 138.0	S8 = 232.5	94.5		9
4	7	B_3	U1 = 203.0(a)	S1 = 229.0	(a)	86.9	(a)
		G_3	U2 = 125.5	S2 = 182.2	56.7		- 35
		F_3	U3 = 95.6	S3 = 170.0	74.4		- 14
	8	D_3	U5 = 135.8	S5 = 234.3	98.5	86.9	13
		C_3	U6 = 114.1	S6 = 200.0	85.9		- 1
		A_3	U7 = 118.9	S7 = 205.4	86.5		- 0.5
		E_3	U8 = 98.0	S8 = 177.0	79.0		- 9

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

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

Time Period	Block	Lab	Unspiked Samples, $\mu g/m^3$ (U)	Spiked Samples, $\mu g/m^3$ (S)	Estimated Spiked Rate, $\mu g/m^3$ (S-U)	True Spiking Rate, $\mu g/m^3$ (R)	Difference, percent of (R)
5	9	F_3	U1 = 104.0	S1 = 168.6	64.6	86.9	- 26
		D_3	U2 = 122.5	S2 = 239.6	117.1		35
		B_3	U3 = 140.0	S3 = 232.0	92.0		6
		E_3	U4 = 102.0	S4 = 182.0	80.0		- 8
	10	C_3	U5 = 120.5	S5 = 200.3	79.8	86.9	- 8
		G_3	U6 = 136.0	S6 = 194.1	58.1		- 33
		A_3	U8 = 119.1	S8 = 210.1	91.0		5
6	11	E_3	U1 = 103.0	S1 = 185.0	82.0	86.9	- 6
		B_3	U2 = 138.0	S2 = 231.0	93.0		7
		D_3	U3 = 141.1	S3 = 218.3	77.2		- 11
		F_3	U4 = 106.4	S4 = 178.3	71.9		- 17
	12	G_3	U5 = 138.3	S5 = 188.9	50.6	86.9	- 42
		C_3	U6 = 117.9	S6 = 210.8	92.9		7
		A_3	U7 = 123.1	S7 = 206.5	83.4		- 4
7	13	B_3	U1 = 148.0	S1 = 240.0	92.0	86.9	6
		E_3	U2 = 106.0	S2 = 188.0	82.0		- 6
		F_3	U3 = 105.8	S3 = 181.1	75.3		- 13
		D_3	U4 = 141.1	S4 = 250.2	109.1		26
	14	A_3	U5 = 130.8	S5 = 219.6	88.8	86.9	2
		C_3	U7 = 125.2	S7 = 208.0	82.8		- 5
		G_3	U8 = 139.9	S8 = 196.8	56.9		- 35
8	15	D_3	U1 = 199.7	S1 = 319.5	119.8	86.9	38
		F_3	U2 = 159.8	S2 = 275.2	115.4		33
		E_3	U3 = 156.0	S3 = 238.0	82.0		- 6
		B_3	U4 = 209.0	S4 = 275.0	66.0		- 24
	16	A_3	U6 = 188.0	S6 = 275.3	87.3	86.9	0.5
		G_3	U7 = 200.0	S7 = 245.7	45.7		- 47
		C_3	U8 = 178.2	S8 = 267.4	89.2		3

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

Time Period	Block	Lab	Unspiked Samples, $\mu g/m^3$ (U)	Spiked Samples, $\mu g/m^3$ (S)	Estimated Spiked Rate, $\mu g/m^3$ (S-U)	True Spiking Rate, $\mu g/m^3$ (R)	Difference, percent of (R)
9	17	D_3	U1 = 228.9	S1 = 354.1	125.2	86.7	44
		E_3	U3 = 192.0	S3 = 266.0	74.0		- 15
		G_3	U4 = 269.7	S4 = 277.0	7.3		- 92
	18	B_3	U5 = 248.0	S5 = 333.0	85.0	86.7	- 2
		C_3	U6 = 219.3	S6 = 301.3	82.0		- 5
		F_3	U7 = 204.6	S7 = 300.2	95.6		10
		A_3	U8 = 229.8	S8 = 312.5	82.7		- 5
10	19	E_3	U1 = 116.0	S1 = 195.0	79.0	86.7	- 9
		G_3	U2 = 157.0	S2 = 202.2	45.2		- 48
		D_3	U4 = 159.7	S4 = 282.2	122.5		41
	20	C_3	U5 = 112.1	S5 = 217.7	105.6	86.7	22
		F_3	U6 = 131.8	S6 = 165.7	33.9		- 61
		A_3	U7 = 150.5	S7 = 234.7	84.2		- 3
		B_3	U8 = 161.0	S8 = 253.0	92.0		6
11	21	G_3	U1 = 157.0	S1 = 188.6	31.6	86.8	- 64
		E_3	U2 = 106.0	S2 = 186.0	80.0		- 8
		D_3	U3 = 143.8	S3 = 247.6	103.8		20
	22	A_3	U5 = 128.4	S5 = 219.9	91.5	86.8	5
		B_3	U6 = 218.0(a)	S6 = 235.0	(a)		(a)
		C_3	U7 = 125.7	S7 = 210.1	84.4		- 3
		F_3	U8 = 124.9	S8 = 200.2	75.3		- 13
12	23	D_3	U2 = 173.0	S2 = 266.2	93.2	86.9	7
		G_3	U3 = 152.8	S3 = 206.6	53.8		- 38
		E_3	U4 = 120.0	S4 = 200.0	80.0		- 8
	24	F_3	U5 = 147.6	S5 = 207.7	60.1	86.9	- 31
		A_3	U6 = 153.4	S6 = 238.7	85.3		- 2
		B_3	U7 = 162.0	S7 = 258.0	96.0		10
		C_3	U8 = 101.5	S8 = 232.1	130.6		50

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

Evaluation of Reproducibility

The sulfur dioxide measurements in Tables 4 through 6 were analyzed to provide the descriptive block statistics which are presented 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 deviations, $w/\hat{s}$; and the coefficient of variation, CV, in percent.

The 96 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.

A curve of the form $\hat{s} = b\sqrt{m}$ 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, and

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

The appropriate weighting formula is $W = f/m$ where W represents the weight, f denotes the number of degrees of freedom associated with the computed standard deviation $\hat{s}$, and m is the mean concentration. By this procedure, the equation $\hat{s} = 1.61\sqrt{m}$ is obtained as an estimate of the true regression curve $s = \beta\sqrt{m}$. The standard deviation of the residuals about the regression line is found to be 3.0 $\mu g/m^3$. 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: $\hat{s} = 4.80 + 0.105\ m$, with a standard deviation for the residuals equal to 3.1 $\mu g/m^3$. 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 sulfur dioxide concentrations. A model of the form $\hat{s} = a + b\sqrt{m}$ yields a smaller residual standard deviation of 2.9 $\mu g/m^3$, but also yields an undesirable negative value for a.

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

Time Period	Block	n	m	s	$\hat{s}$	w	w/$\hat{s}$	CV
1	1	4	29.7	6.0	9.3	14.4	1.54	20
	2	4	22.3	5.0	8.6	10.9	1.26	22
2	3	4	29.0	5.7	9.3	12.8	1.38	20
	4	4	17.0	8.1	8.1	19.3	2.37	48
3	5	4	21.3	10.8	8.5	22.4	2.62	51
	6	4	8.6	4.8	7.3	10.9	1.49	56
4	7	4	11.7	8.1	7.6	19.7	2.58	69
	8	4	4.2	2.2	6.9	4.7	0.68	52
5	9	4	25.9	12.3	9.0	26.3	2.93	47
	10	4	32.4	9.4	9.6	20.4	2.13	29
6	11	4	63.2	12.7	12.5	24.7	1.98	20
	12	4	65.0	9.4	12.7	22.5	1.78	14
7	13	4	62.5	11.6	12.4	23.8	1.91	19
	14	4	45.4	8.2	10.8	19.5	1.80	18
8	15	4	31.6	25.1	9.5	58.5	6.15(a)	79
	16	4	17.8	6.8	8.2	13.9	1.69	38
9	17	4	62.0	11.8	12.4	28.7	2.32	19
	18	4	75.4	16.8	13.7	38.9	2.85	22
10	19	4	63.5	6.0	12.5	13.5	1.08	9
	20	4	47.8	11.4	11.0	25.6	2.32	24
11	21	4	32.4	7.4	9.6	15.7	1.64	23
	22	4	25.5	13.4	8.9	32.1	3.59	53
12	23	4	15.7	3.6	8.0	8.1	1.01	23
	24	4	17.8	14.9	8.2	31.6	3.85	84

(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 SULFUR DIOXIDE FROM BLOOMINGTON

Time Period	Block	n	m	s	$\hat{s}$	w	w/$\hat{s}$	CV
1	1,2	7	28.1	16.0	9.2	42.1	4.59	57
2	3,4	7	23.6	11.1	8.8	35.1	4.01	47
3	5,6	7	22.4	4.8	8.6	13.7	1.59	21
4	7,8	7	21.8	5.8	8.6	16.8	1.96	27
5	9,10	7	20.8	3.3	8.5	8.4	0.99	16
6	11,12	7	24.2	4.2	8.8	12.8	1.45	17
7	13,14	7	13.8	6.4	7.8	16.4	2.10	46
8	15,16	7	7.5	5.5	7.2	15.1	2.09	73
9	17,18	7	19.8	6.5	8.4	18.8	2.24	33
10	19,20	7	14.2	3.6	7.9	10.2	1.30	25
11	21,22	7	8.9	5.5	7.4	12.7	1.73	62
12	23,24	7	8.8	7.6	7.4	23.1	3.14	86

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

Time Period	Block	n	m	s	$\hat{s}$	w	w/$\hat{s}$	CV
1	1,2	7	202.4	24.9	25.7	62.2	2.42	12
2	3,4	7	192.5	27.2	24.7	76.3	3.09	14
3	5,6	7	139.8	22.0	19.7	57.6	2.92	16
4	7,8	7	127.3	36.3	18.6	107.4	5.79(a)	29
5	9,10	7	120.6	14.4	17.9	38.0	2.12	12
6	11,12	7	124.0	15.7	18.2	38.1	2.09	13
7	13,14	7	128.1	16.9	18.6	42.2	2.26	13
8	15,16	7	184.4	20.6	24.0	53.0	2.21	11
9	17,18	7	227.5	26.0	28.0	77.7	2.77	11
10	19,20	7	141.2	21.0	19.9	48.9	2.46	15
11	21,22	7	143.4	36.6	20.1	112.0	5.58(a)	26
12	23,24	7	144.3	24.9	20.2	71.5	3.55	17

(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 SULFUR DIOXIDE FROM LOS ANGELES

Time Period	Block	n	m	s	$\hat{s}$	w	w/$\hat{s}$	CV
1	1	4	55.1	29.8	11.7	67.5	5.75(a)	54
	2	4	29.3	8.6	9.3	18.3	1.97	29
2	3	4	48.2	12.4	11.1	27.6	2.49	26
	4	4	36.1	1.6	9.9	3.6	0.36	4
3	5	4	47.4	12.3	11.0	26.0	2.36	26
	6	4	28.0	4.3	9.2	9.1	0.99	15
4	7	4	37.5	10.0	10.1	23.7	2.35	27
	8	4	25.8	5.8	9.0	13.6	1.52	22
5	9	4	51.0	14.4	11.3	33.1	2.92	28
	10	4	53.3	8.5	11.6	20.2	1.75	16
6	11	4	82.2	17.1	14.3	36.2	2.53	21
	12	4	88.4	11.6	14.9	25.4	1.71	13
7	13	4	82.3	13.7	14.3	30.9	2.16	17
	14	4	75.5	11.3	13.7	26.1	1.91	15
8	15	4	59.3	23.6	12.1	54.1	4.46(a)	40
	16	4	46.0	7.4	10.9	16.4	1.51	16
9	17	4	85.1	14.4	14.6	35.0	2.40	17
	18	4	101.1	14.8	16.1	32.5	2.02	15
10	19	4	89.0	6.4	14.9	14.0	0.94	7
	20	4	84.0	10.6	14.5	24.0	1.66	13
11	21	4	58.5	11.3	12.1	26.9	2.23	19
	22	4	59.1	10.1	12.1	23.8	1.97	17
12	23	4	41.5	4.5	10.4	9.2	0.88	11
	24	4	50.5	11.6	11.3	26.5	2.35	23

(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 SULFUR DIOXIDE FROM BLOOMINGTON

Time Period	Block	n	m	s	$\hat{s}$	w	w/$\hat{s}$	CV
1	1,2	7	42.0	13.8	10.5	37.7	3.59	33
2	3,4	7	49.8	20.4	11.2	63.6	5.66(a)	41
3	5,6	7	54.7	14.1	11.7	37.3	3.19	26
4	7,8	7	51.0	7.4	11.3	20.8	1.83	15
5	9,10	7	52.0	5.4	11.4	17.8	1.56	10
6	11,12	7	58.0	12.0	12.0	34.1	2.84	21
7	13,14	7	37.2	13.1	10.0	39.9	3.97	35
8	15,16	7	32.0	10.9	9.5	33.5	3.51	34
9	17,18	7	50.8	13.8	11.3	35.9	3.17	27
10	19,20	7	49.6	10.9	11.2	31.5	2.81	22
11	21,22	7	44.0	15.2	10.7	43.9	4.11	35
12	23,24	7	42.6	10.5	10.5	30.0	2.84	25

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

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

Time Period	Block	n	m	s	$\hat{s}$	w	w/$\hat{s}$	CV
1	1,2	7	296.4	36.5	34.6	121.0	3.50	12
2	3,4	7	278.4	23.8	32.9	69.5	2.12	9
3	5,6	7	217.8	35.3	27.1	99.6	3.67	16
4	7,8	7	199.7	25.1	25.4	64.3	2.53	13
5	9,10	7	203.8	25.6	25.8	71.0	2.75	13
6	11,12	7	202.7	19.3	25.7	52.7	2.05	10
7	13,14	7	212.0	26.1	26.6	69.1	2.60	12
8	15,16	7	270.9	26.3	32.1	81.5	2.54	10
9	17,18	7	306.3	30.5	35.5	88.1	2.48	10
10	19,20	7	221.5	38.8	27.5	116.5	4.24	18
11	21,22	7	212.5	23.2	26.6	61.6	2.31	11
12	23,24	7	229.9	26.2	28.3	66.2	2.34	11

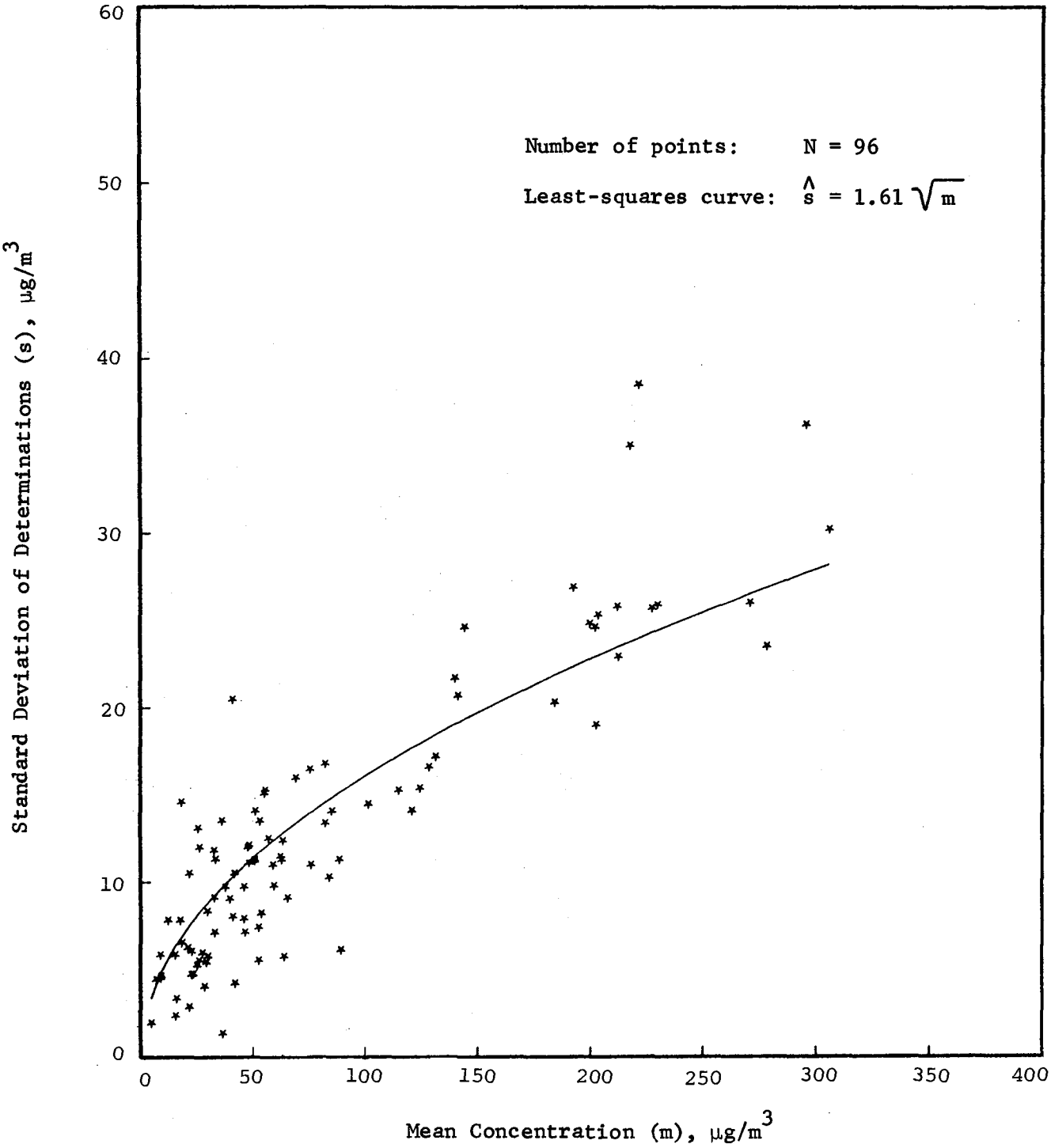


FIGURE 10. SCATTER DIAGRAM AND LEAST-SQUARES CURVE RELATING BETWEEN-LABORATORY STANDARD DEVIATION (REPRODUCIBILITY) TO CONCENTRATION OF SULFUR DIOXIDE

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

A total of 176 measurements of sulfur dioxide were performed at the three test sites in accordance with Blocks 25 through 32 of the experimental design: 64 runs were completed at Los Angeles by 8 laboratories; 56 runs were completed at Bloomington by 7 laboratories; and 56 runs were completed at Manhattan by 7 laboratories.

The results of the sulfur 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.

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

Site	Time Period	Block	Outlier[a]			Revised Statistics[b]		
			Lab	Outlet	Reading	n	m	s
Los Angeles	8	15	G	U1	3.9	3	40.8	20.8
Los Angeles	1	1	E	S2	98.6	3	40.6	8.3
Los Angeles	8	15	G	S1	30.1	3	69.0	16.3
Bloomington	1	1&2	D	U8	1.9	6	32.4	12.1
Bloomington	2	3&4	D	U5	1.9	6	27.3	6.2
Bloomington	3	5&6	D	U6	18.6	6	23.0	5.0
Bloomington	4	7&8	D	U7	19.1	6	22.4	6.3
Bloomington	5	9&10	D	U8	17.0	6	21.4	3.1
Bloomington	6	11&12	D	U7	23.4	6	24.8	5.5
Bloomington	7	13&14	D	U5	6.4	6	15.1	6.1
Bloomington	8	15&16	D	U6	0.0	6	8.8	4.9
Bloomington	9	17&18	D	U8	13.8	6	20.7	6.5
Bloomington	10	19&20	D	U7	8.0	6	15.2	2.6
Bloomington	11	21&22	D	U5	2.9	6	8.5	6.1
Bloomington	12	23&24	D	U6	23.1	6	6.5	4.7
Bloomington	1	1&2	D	S8	18.6	6	45.9	10.0
Bloomington	2	3&4	D	S5	16.7	6	55.3	15.6
Bloomington	3	5&6	D	S6	53.7	6	54.9	15.4
Bloomington	4	7&8	D	S7	45.2	6	52.1	7.7
Bloomington	5	9&10	D	S8	50.7	6	52.2	5.8
Bloomington	6	11&12	D	S7	64.5	6	56.8	12.8
Bloomington	7	13&14	D	S5	45.4	6	35.9	13.8
Bloomington	8	15&16	D	S6	26.0	6	33.0	11.6
Bloomington	9	17&18	D	S8	38.0	6	53.1	13.8
Bloomington	10	19&20	D	S7	43.6	6	50.6	11.5
Bloomington	11	21&22	D	S5	72.5	6	39.3	9.3
Bloomington	12	23&24	D	S6	50.5	6	41.3	10.8
Manhattan	4	7&8	B	U1	203.0	6	114.7	15.6
Manhattan	11	21&22	B	U6	218.0	6	131.0	17.5

(a) All laboratory D_2 determinations classified as outliers on the basis of correlations between laboratories. Other outliers determination with 99 percent confidence by the studentized range test.
(b) Excluding outliers.

TABLE 14. DATA FROM BLOCKS 25-32 OF SULFUR DIOXIDE EXPERIMENTS AT LOS ANGELES SITE ARRANGED BY BLOCK AND OUTLET POSITION

Time Period	Block	Unspiked Samples, $\mu g/m^3$ Lab	(Ui)	(Uj)	|Ui-Uj|	CV	Spiked Samples, $\mu g/m^3$ Lab	(Si)	(Sj)	|Si-Sj|	CV	Spike
13	25	F_1	U1 = 15.1	U4 = 8.8	6.3	37.	G_1	S1 = 45.5	S3 = 46.1	0.6	0.9	30.8
		A_1	U2 = 48.5(a)	U3 = 52.5(a)	(a)	(a)	D_1	S2 = 53.0	S4 = 55.6	2.6	3.	
	26	B_1	U1 = 17.0	U4 = 18.5	1.5	6.	E_1	S1 = 32.0	S3 = 41.5	9.5	18.	30.8
		H_1	U2 = 15.4	U3 = 15.4	0.0	0.0	C_1	S2 = 55.3	S4 = 55.0	0.3	0.4	
14	27	A_1	U1 = 32.7	U4 = 25.7	7.0	17.	D_1	S1 = 51.4	S3 = 50.6	0.8	1.	30.8
		G_1	U2 = 18.7	U3 = 24.4	5.7	19.	F_1	S2 = 30.1	S4 = 31.8	1.7	4.	
	28	H_1	U1 = 5.1	U4 = 5.1	0.0	0.0	C_1	S1 = 45.8	S3 = 65.8	20.0	25.	30.9
		B_1	U2 = 15.0	U3 = 7.0	8.0	51.	E_1	S2 = 27.9	S4 = 39.8	11.9	25.	
15	29	D_1	U1 = 11.2	U4 = 10.6	0.6	4.	A_1	S1 = 56.3	S3 = 58.9	2.6	3.	30.9
		F_1	U2 = 11.0	U3 = 7.3	3.7	29.	G_1	S2 = 28.6	S4 = 41.0	12.4	25.	
	30	C_1	U1 = 12.4	U4 = 7.9	4.5	31.	B_1	S1 = 37.8	S3 = 43.5	5.7	10.	30.9
		E_1	U2 = 3.0	U3 = 9.8	6.8	75.	H_1	S2 = 41.1	S4 = 30.9	10.2	20.	
16	31	G_1	U1 = 5.8	U4 = 5.8	0.0	0.0	F_1	S1 = 27.7	S3 = 11.9	15.8	56.	30.9
		D_1	U2 = 9.3	U3 = 8.8	0.5	4.	A_1	S2 = 49.2	S4 = 52.8	3.6	5.	
	32	E_1	U1 = 4.4	U4 = 18.3	13.9	87.	H_1	S1 = 36.1	S3 = 30.9	5.2	11.	30.9
		C_1	U2 = 17.0	U3 = 16.7	0.3	1.	B_1	S2 = 47.0	S4 = 45.0	2.0	3.	

(a) Apparently spiked samples obtained by mistake, data excluded from statistical analysis.

TABLE 15. DATA FROM BLOCKS 25-32 OF SULFUR DIOXIDE EXPERIMENTS AT BLOOMINGTON SITE ARRANGED BY BLOCK AND OUTLET POSITION

Time Period	Block	Unspiked Samples, $\mu g/m^3$ Lab	(Ui)	(Uj)	Ui-Uj	CV	Spiked Samples, $\mu g/m^3$ Lab	(Si)	(Sj)	Si-Sj	CV	Spike
13	25	F_2	U1 = 33.5	U4 = 31.9	1.6	3.	G_2	S1 = 67.1	S3 = 53.6	13.5	16.	30.3
		A_2	U2 = 29.8	U3 = 29.8	0.0	0.0	D_2	S2 = 68.0	S4 = 72.2	4.2	4.	
	26	B_2	U5 = 35.8	U8 = 36.6	0.8	2.	E_2	S5 = 46.0	S7 = 53.3	7.3	10.	30.3
				(a)			C_2	S6 = (b)	S8 = (b)	(b)	(b)	
14	27	A_2	U1 = 55.6	U4 = 54.7	0.9	1.	D_2	S1 =100.1	S3 = 98.0	2.1	1.	30.3
		G_2	U2 = 65.7	U3 = 64.2	1.5	2.	F_2	S2 = 83.7	S4 = 84.7	1.0	0.8	
	28			(a)			C_2	S5 = (b)	S7 = (b)	(b)	(b)	30.3
		B_2	U6 = 62.0	U7 = 63.4	1.4	2.	E_2	S6 = 67.8	S8 = 77.0	9.2	9.	
15	29	D_2	U1 = 19.1	U4 = 14.3	4.8	20.	A_2	S1 = 39.1	S3 = 39.7	0.6	1.	30.3
		F_2	U2 = 11.5	U3 = 14.9	3.4	18.	G_2	S2 = 49.8	S4 = 48.6	1.2	2.	
	30	C_2	U5 = (b)	U8 = (b)	(b)	(b)	B_2	S5 = 46.2	S7 = 48.7	2.5	4.	30.3
		E_2	U6 = 12.9	U7 = 12.8	0.1	0.6			(a)			
16	31	G_2	U1 = 15.1	U4 = 17.5	2.4	10.	F_2	S1 = 42.6	S3 = 42.1	0.5	0.8	30.3
		D_2	U2 = 10.4	U3 = 10.4	0.0	0.0	A_2	S2 = 40.2	S4 = 40.1	0.1	0.2	
	32	E_2	U5 = 12.8	U8 = 17.6	4.8	22.			(a)			30.3
		C_2	U6 = (b)	U7 = (b)	(b)	(b)	B_2	S6 = 46.5	S8 = 46.3	0.2	0.0	

(a) Data were not obtained for this cell since only seven laboratories participated in the test.
(b) Reagent contaminated, data excluded from statistical analysis.

TABLE 16. DATA FROM BLOCKS 25-32 OF SULFUR DIOXIDE EXPERIMENTS AT MANHATTAN SITE ARRANGED BY BLOCK AND OUTLET POSITION

Time Period	Block	Unspiked Samples, $\mu g/m^3$ Lab	(Ui)	(Uj)	|Ui-Uj|	CV	Spiked Samples, $\mu g/m^3$ Lab	(Si)	(Sj)	|Si-Sj|	CV	Spike
13	25	C_3	U1 = 132.9	U4 = 135.3	2.4	1.	D_3	S1 = 175.7	S3 = 183.7	8.0	3.	86.9
		F_3	U2 = 132.5	U3 = 133.3	0.8	0.4	A_3	S2 = 231.5	S4 = 219.1	12.4	4.	
	26	E_3	U5 = 120.0	U8 = 112.0	8.0	5.	B_3	S5 = 244.0	S7 = 247.0	3.0	0.9	86.9
				(a)			G_3	S6 = 241.6	S8 = 203.9	37.7	12.	
14	27	F_3	U1 = 136.8	U4 = 142.4	5.6	3.	A_3	S1 = 227.2	S3 = 226.1	1.1	0.3	86.7
		D_3	U2 = 117.1	U3 = 127.8	10.7	6.	C_3	S2 = 237.9	S4 = 232.5	5.4	2.	
	28	E_3	U6 = 133.0	U7 = 126.0	7.0	4.	G_3	S5 = 253.9	S7 = 210.3	43.6	13.	86.7
				(a)			B_3	S6 = 232.0	S8 = 235.0	3.0	0.9	
15	29	A_3	U1 = 169.0	U4 = 165.6	3.4	1.	F_3	S1 = 238.4	S3 = 232.6	5.8	2.	86.7
		C_3	U2 = 174.1	U3 = 190.7	16.6	6.	D_3	S2 = 183.7	S4 = 207.7	24.0	9.	
	30	G_3	U5 = 179.6	U8 = 148.1	31.5	14.	E_3	S5 = 210.0	S7 = 211.0	1.0	0.3	86.7
		B_3	U6 = 188.0	U7 = 192.0	4.0	1.			(a)			
16	31	D_3	U1 = (b)	U4 = 85.2	(b)	(b)	C_3	S1 = 248.3	S3 = 218.9	29.4	9.	87.0
		A_3	U2 = 161.1	U3 = 155.8	5.3	2.	F_3	S2 = 233.2	S4 = 231.8	1.4	0.4	
	32	B_3	U5 = 177.0	U8 = 188.0	11.0	4.	E_3	S6 = 210.0	S8 = 202.0	8.0	3.	87.0
		G_3	U6 = 164.9	U7 = 137.9	27.0	13.			(a)			

(a) Data were not obtained for this cell since only seven laboratories participated in the test.
(b) Laboratory D_3 obtained only one determination for Block 31.

Evaluation of Repeatability

The combined data from all three sampling sites were used to examine the relationship between within-laboratory variability and concentration level of sulfur 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 spiked samples from Block 25 at Los Angeles given in 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 ninth 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:

$$m = \frac{45.5 + 46.1 + 53.0 + 55.6}{4} = 50.1,$$

and the result appears on the ninth 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 ninth 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:

$$s = \sqrt{\frac{(45.5 - 45.8)^2 + (46.1 - 45.8)^2 + (53.0 - 54.3)^2 + (55.6 - 54.3)^2}{1 + 1}} = 1.3,$$

where, 45.8 and 54.3 represent the means of duplicate measurements in Block 25. This result appears on the ninth 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 using the appropriate weighting formula, $W = f/m$. This results in the equation $\hat{s} = 0.701\sqrt{m}$ with a standard deviation of residuals equal to 2.5 $\mu g/m^3$. A model of the form $\hat{s} = a + b\sqrt{m}$ yields a larger residual standard deviation of 2.6 $\mu g/m^3$; a model of the form $\hat{s} = a + bm$ also yields a value of 2.6 $\mu g/m^3$ for the residual standard deviation. For

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

Site	Sample	Time Period	Block	n	m	df	s
Los Angeles	Unspiked	13	25	2	12.0	1	4.4
			26	4	16.6	2	0.8
		14	27	4	25.4	2	4.5
			28	4	8.1	2	4.0
		15	29	4	10.0	2	1.9
			30	4	8.3	2	4.1
		16	31	4	7.4	2	0.2
			32	4	14.1	2	7.0
	Spiked	13	25	4	50.1	2	1.3
			26	4	46.0	2	4.8
		14	27	4	41.0	2	0.9
			28	4	44.8	2	11.6
		15	29	4	46.2	2	6.3
			30	4	38.3	2	5.8
		16	31	4	35.4	2	8.1
			32	4	39.8	2	2.8
Bloomington	Unspiked	13	25,26	6	32.9	3	0.7
		14	27,28	6	60.9	3	0.9
		15	29,30	6	14.2	3	2.4
		16	31,32	6	14.0	3	2.2
	Spiked	13	25,26	6	60.0	3	6.5
		14	27,28	6	85.2	3	3.9
		15	29,30	6	45.4	3	1.2
		16	31,32	6	43.0	3	0.2
Manhattan	Unspiked	13	25,26	6	127.7	3	3.4
		14	27,28	6	130.5	3	5.7
		15	29,30	8	175.9	4	12.7
		16	31,32	6	164.1	3	12.1
	Spiked	13	25,26	8	218.3	4	14.4
		14	27,28	8	231.9	4	15.6
		15	29,30	6	213.9	3	10.1
		16	31,32	6	224.0	3	12.4

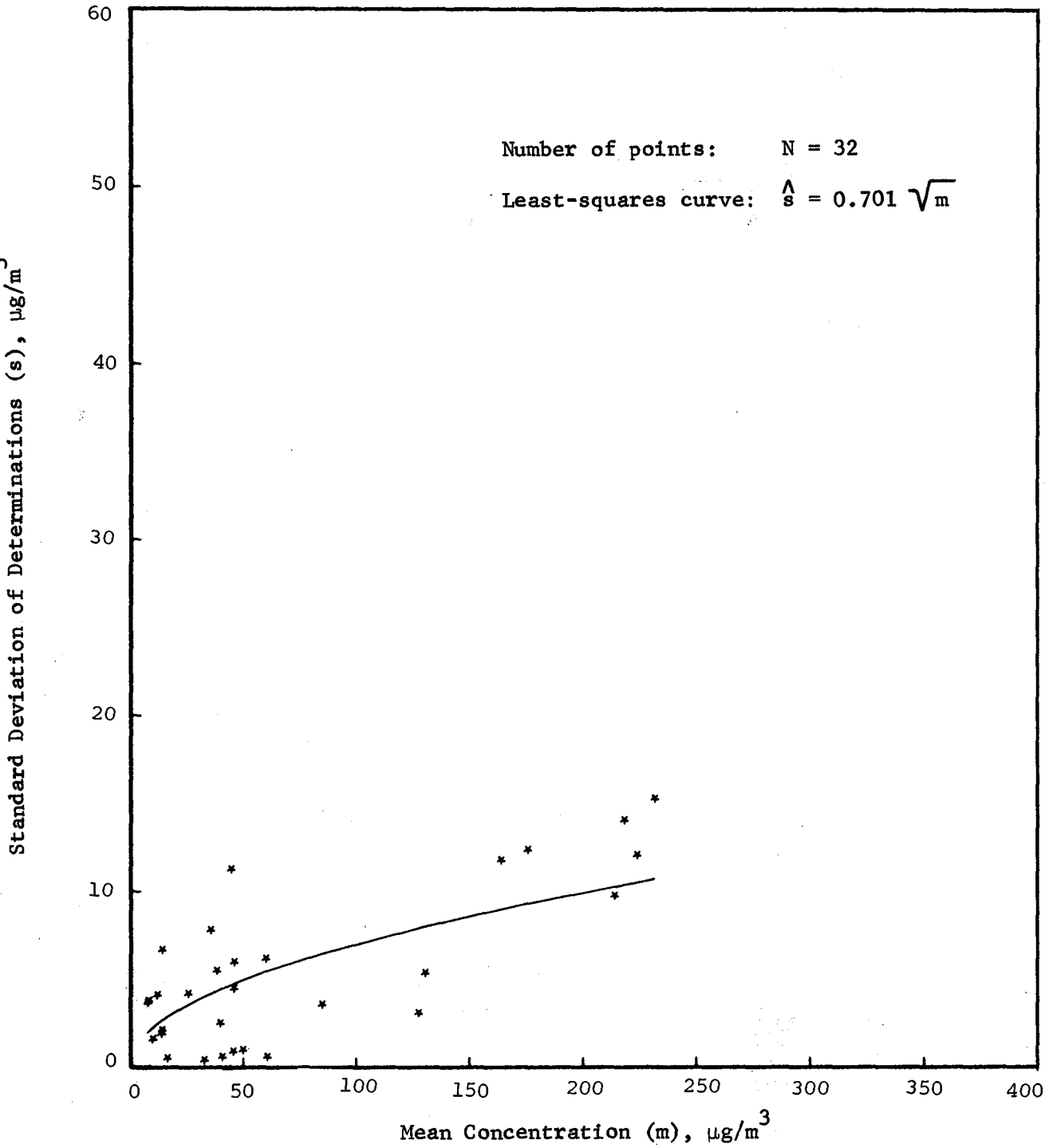


FIGURE 11. SCATTER DIAGRAM AND LEAST-SQUARES CURVE RELATING WITHIN-LABORATORY STANDARD DEVIATION (REPEATABILITY) TO CONCENTRATION OF SULFUR DIOXIDE

consistency with the previous analysis of reproducibility, the form $\hat{s} = b\sqrt{m}$ is chosen. Accordingly, the curve of the equation $\hat{s} = 0.701\sqrt{m}$ 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 7.4 $\mu g/m^3$ from Table 17. Substitution of this value for m in the above equation yields s = 1.91 and twice this standard deviation, about 4 $\mu g/m^3$, 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 multilaboratory testing program in establishing a measure of repeatability, and emphasizes the danger 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 sulfur 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 94 measurements of the difference, S-U, is fairly symmetrical and indicative of a normal distribution. The distribution has a mean of -22 percent, which indicates a negative bias, and a standard deviation of 31.1 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:

$$t = \bar{x}\sqrt{n}/s = -22.0\sqrt{94}/31.1 = -6.86.$$

On n-1 = 93 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 72 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 -6 percent, which indicates a slight negative bias, and a standard deviation of 38.6 percent. The hypothesis that the true bias is zero is tested by use of Student's t, as follows:

$$t = \bar{x}\sqrt{n}/s = -5.5\sqrt{72}/38.6 = -1.21.$$

On n-1 = 71 degrees of freedom, the value for t is not statistically significant at the 99 percent level. Therefore, the hypothesis of zero bias is not rejected by the t-test.

The histogram for Manhattan in Figure 14, which is based on 82 determinations of S-U, is moderately indicative of a normal distribution. The determinations are centered about a mean with a smaller negative deviation than the Los Angeles and Manhattan data. The distribution is characterized by a mean deviation of -4 percent, which indicates a negative bias, and a standard deviation of 27.6 percent. The hypothesis that the true bias is zero is tested by use of Student's t, as follows:

$$t = \bar{x}\sqrt{n}/s = -4.4\sqrt{82}/27.6 = -1.44.$$

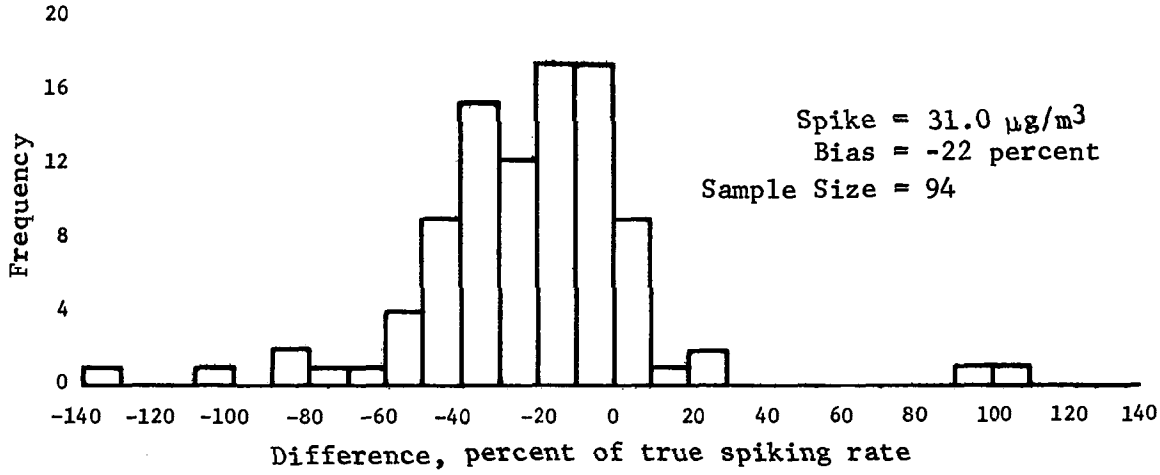


FIGURE 12. HISTOGRAM OF DIFFERENCES IN SPIKING ESTIMATES FOR LOS ANGELES

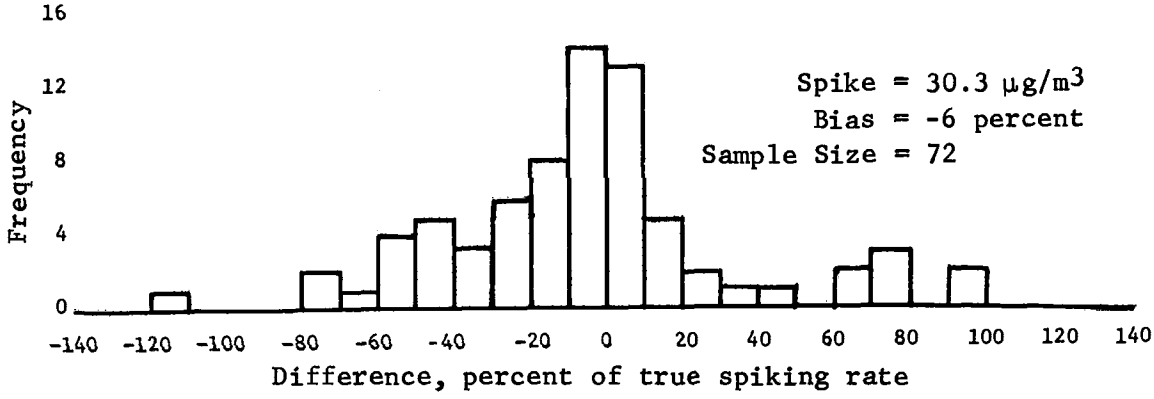


FIGURE 13. HISTROGRAM OF DIFFERENCES IN SPIKING ESTIMATES FOR BLOOMINGTON

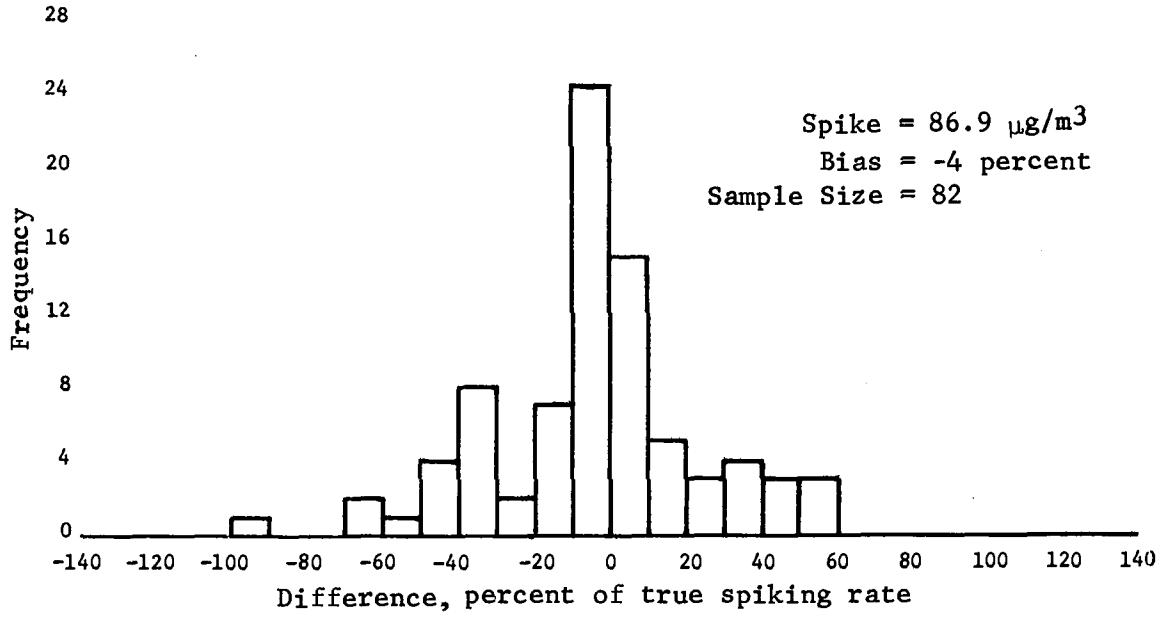


FIGURE 14. HISTOGRAM OF DIFFERENCES IN SPIKING ESTIMATES FOR MANHATTAN

On n-1 = 81 degrees of freedom, this value for t is not statistically significant at the 99 percent level. Therefore, the hypothesis of zero bias is not rejected by the t-test.

Although the histograms in Figures 12 through 14 provide a useful summary of over-all 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 underestimated the spiking concentration, and three of these were very low in their estimates. The Bloomington data show that all but two laboratories underestimated the spiking concentration, and one of these was very low in its estimate. At Manhattan, all but two of the laboratories underestimated the spiking concentration, one by a significant margin, while one laboratory significantly overestimated the spiking concentration.

The bias is seen to vary from laboratory to laboratory. The overall bias departs significantly from zero only at Los Angeles. A separate examination of the relationship of individual estimates (S-U) of the spiking concentration to the nominal sulfur 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 sulfur dioxide from spiked samples was less than the spiked amount by an average of 11 percent of the true amount.

Analysis of Comparability

A measure of comparability defined as the extent to which the measurements of sulfur dioxide concentration by different laboratories agree in regard to the differences between different concentrations is afforded by correlation analysis. For sulfur 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

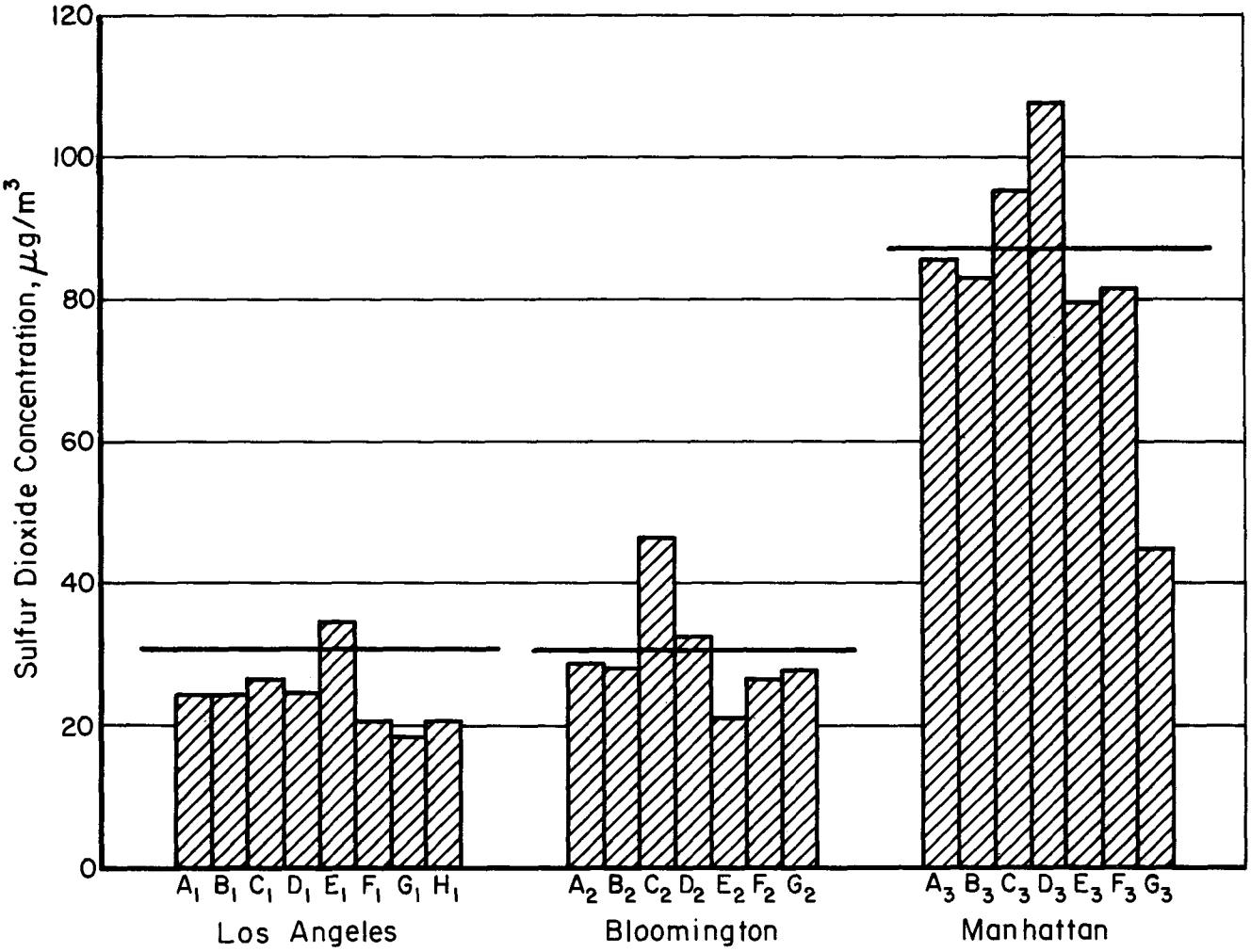


FIGURE 15. COMPARISON OF LABORATORY BIAS OF SULFUR DIOXIDE SPIKE MEASUREMENTS AT EACH SITE

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

should be good correlation between laboratories over an extended time period regardless of their systematic 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 all time periods. For these computations, the sulfur dioxide measurements were cross-classified in two-way tables according to laboratory and time period. Each pair of adjacent half-hour blocks in the same time 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 20 and 21, laboratory D_2 at Bloomington shows poor correlations with all the other laboratories. On this bias the measurements obtained by laboratory D_2 at Bloomington were omitted from the analyses of reproducibility, repeatability, accuracy, and analysis of variance tables. In Table 21, laboratory G_2 shows poor correlations with all the other laboratories, based on spiked samples from Bloomington. However, since in Table 20 laboratory G_2 shows fairly good correlations with all the other laboratories except laboratory D_2, and since all laboratory G_2 values in Table 5 look reasonable, all laboratory G_2 determinations for spiked samples at Bloomington are included in the statistical analysis.

A total of 140 correlation coefficients for all laboratories, all sites, and all spiked and unspiked samples are shown in these tables. Of these correlations 118 (84 percent) yield correlation coefficients which are significant 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 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	0.88	0.80	0.86	0.65	0.76	0.77	0.71
B_1	0.88	1.00	0.89	0.92	0.61	0.83	0.96	0.90
C_1	0.80	0.89	1.00	0.91	0.66	0.92	0.88	0.90
D_1	0.86	0.92	0.91	1.00	0.62	0.94	0.93	0.88
E_1	0.65	0.61	0.66	0.62	1.00	0.66	0.52	0.68
F_1	0.76	0.83	0.92	0.94	0.66	1.00	0.87	0.86
G_1	0.77	0.96	0.88	0.93	0.52	0.87	1.00	0.90
H_1	0.71	0.90	0.90	0.88	0.68	0.86	0.90	1.00

(a) Blocks 1 through 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	0.91	0.86	0.94	0.65	0.86	0.84	0.84
B_1	0.91	1.00	0.87	0.93	0.72	0.87	0.94	0.90
C_1	0.86	0.87	1.00	0.92	0.69	0.90	0.90	0.87
D_1	0.94	0.93	0.92	1.00	0.69	0.94	0.91	0.88
E_1	0.65	0.72	0.69	0.69	1.00	0.53	0.64	0.67
F_1	0.86	0.87	0.90	0.94	0.53	1.00	0.86	0.91
G_1	0.84	0.94	0.90	0.91	0.64	0.86	1.00	0.87
H_1	0.84	0.90	0.87	0.88	0.67	0.91	0.87	1.00

(a) Blocks 1 through 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	0.89	0.76	0.21	0.88	0.93	0.55
B_2	0.89	1.00	0.86	0.63	0.85	0.84	0.71
C_2	0.76	0.86	1.00	-0.04	0.71	0.65	0.83
D_2	0.21	0.06	-0.04	1.00	-0.12	0.36	-0.31
E_2	0.88	0.85	0.71	-0.12	1.00	0.83	0.57
F_2	0.93	0.84	0.65	0.36	0.83	1.00	0.47
G_2	0.55	0.71	0.83	-0.31	0.57	0.47	1.00

(a) Blocks 1 through 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	0.79	0.67	0.17	0.74	0.81	0.22
B_2	0.79	1.00	0.61	-0.19	0.63	0.63	0.05
C_2	0.67	0.61	1.00	0.14	0.55	0.62	0.20
D_2	0.17	-0.19	0.14	1.00	0.03	-0.02	-0.09
E_2	0.74	0.63	0.55	0.03	1.00	0.61	-0.02
F_2	0.81	0.63	0.62	-0.02	0.61	1.00	0.22
G_2	0.22	0.05	0.20	-0.09	-0.02	0.22	1.00

(a) Blocks 1 through 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	0.75	0.92	0.98	0.99	0.94	0.97
B_3	0.75	1.00	0.79	0.75	0.77	0.72	0.79
C_3	0.92	0.79	1.00	0.86	0.95	0.80	0.95
D_3	0.98	0.75	0.86	1.00	0.97	0.97	0.95
E_3	0.99	0.77	0.95	0.97	1.00	0.94	0.98
F_3	0.94	0.72	0.80	0.97	0.94	1.00	0.94
G_3	0.97	0.79	0.95	0.95	0.98	0.94	1.00

(a) Blocks 1 through 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	0.92	0.97	0.97	0.99	0.94	0.98
B_3	0.92	1.00	0.89	0.82	0.89	0.84	0.95
C_3	0.97	0.89	1.00	0.92	0.98	0.94	0.98
D_3	0.97	0.82	0.92	1.00	0.96	0.87	0.92
E_3	0.99	0.89	0.98	0.96	1.00	0.94	0.98
F_3	0.94	0.84	0.94	0.87	0.94	1.00	0.94
G_3	0.98	0.95	0.98	0.92	0.98	0.94	1.00

(a) Blocks 1 through 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 eight F-fractiles which are significant and one which approaches significance. In the column headed "Block" there are ten F-fractiles which are significant. 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, three of the six F-fractiles for laboratory and two 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, all of the six F-fractiles for laboratory and all 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 Angeles 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 between blocks include the natural changes in the ambient sulfur dioxide level with time; an effect which is not significant in evaluating the Test Method.

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

Data Set		F-fractile, percent[(a)]		
Blocks	Sample Type	Laboratory	Block	Outlet
1,3,5,7	Unspiked	86	(99)	93
	Spiked	84	44	7
2,4,6,8	Unspiked	(98)	(99.9)	84
	Spiked	12	80	59
9,11,13,15	Unspiked	(99.4)	(99.8)	62
	Spiked	(99.9)	(99.8)	59
10,12,14,16	Unspiked	(99.6)	(99.98)	16
	Spiked	(99.8)	(99.98)	89
17,19,21,23	Unspiked	(99.4)	(99.99)	91
	Spiked	(99.6)	(99.99)	90
18,20,22,24	Unspiked	(99.3)	(99.97)	6
	Spiked	94	(99.9)	48

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

TABLE 25. F-FRACTILES OBTAINED FROM LATIN SQUARE ANALYSIS OF SULFUR 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	(98.8)	23	86
	Spiked	(99.5)	94	(97)
9,11,13,15	Unspiked	94	(99.3)	87
	Spiked	(96)	(98.8)	81
10,12,14,16	Unspiked	(b)	(b)	(b)
	Spiked	(b)	(b)	(b)
17,19,21,23	Unspiked	(b)	(b)	(b)
	Spiked	(b)	(b)	(b)
18,20,22,24	Unspiked	46	77	78
	Spiked	72	8	59

(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 SULFUR 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	(99.8)	(99.99)	25
	Spiked	(99.98)	(99.99)	82
9,11,13,15	Unspiked	(99.98)	(99.99)	84
	Spiked	(99.6)	(99.8)	50
10,12,14,16	Unspiked	(b)	(b)	(b)
	Spiked	(b)	(b)	(b)
17,19,21,23	Unspiked	(b)	(b)	(b)
	Spiked	(b)	(b)	(b)
18,20,22,24	Unspiked	(98)	(99.8)	73
	Spiked	(99.5)	(99.97)	71

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

Due to a change in the statistical design, beginning with Block 1 at Bloomington all seven laboratories sampled concurrently, and each pair of blocks in the same time period were combined into a single block. 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 1 through 24 at Bloomington as a two-way table in which the rows represent laboratories and the columns represent time periods; 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 requires 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]

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

where, E = estimated value
ℓ = 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, listing the degrees of freedom, indicates the number of independent comparisons that can be made between pairs of laboratory averages, pairs of time period averages, and pairs of laboratory-by-time period interaction effects. The third column of each table gives the mean square, or variance, associated with each source of 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.

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

Source	Degrees of Freedom	Mean Square	Variance Ratio	F-fractile
Laboratory	5.	216.40	10.2	>99.9
Time Period	11.	378.36	17.8	>99.9
Interaction	55.	21.25	-	

(a) Based on Blocks 1 through 24 of design, ignoring outlet position. All laboratory D_2 data excluded from analysis.

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

Source	Degrees of Freedom	Mean Square	Variance Ratio	F-fractile
Laboratory	5.	732.98	8.40	>99.9
Time Period	11.	403.39	4.62	>99.9
Interaction	55.	87.22	-	

(a) Based on Blocks 1 through 24 of design, ignoring outlet position. All laboratory D_2 data excluded from analysis.

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

Source	Degrees of Freedom	Mean Square	Variance Ratio	F-fractile
Laboratory	6.	5474.50	29.4	>99.9
Time Period	11.	8940.48	48.1	>99.9
Interaction	66.	185.98	-	

(a) Based on Blocks 1 through 24 of design, ignoring outlet position. Data obtained by laboratory B_3 for Blocks 4 and 11 were excluded from analysis.

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

	Degrees of Freedom	Mean Square	Variance Ratio	F-fractile
Laboratory	6.	7759.45	41.1	>99.9
Time Period	11.	10660.96	56.4	>99.9
Interaction	66.	188.94	-	

(a) Based on Blocks 1 through 24 of design, ignoring outlet position.

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, time period, and interaction in Tables 27 through 30 are composed of variations from the following sources.

Laboratory

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

Time Period

(a) Time variations in the ambient sulfur dioxide level
(b) Repeatability
(c) Laboratory-time period interaction
(d) Unidentified sources

Interaction

(a) Repeatability
(b) Laboratory-time period interaction
(c) Unidentified sources

Reproducibility and repeatability have been defined and discussed previously in this report. The laboratory-time period 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-time period 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 were 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 D 2914 for measuring sulfur 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:

$$s_b = 1.61 \sqrt{m},$$

where, s_b and, m, the mean concentration of sulfur 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:

$$s_w = 0.701 \sqrt{m},$$

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

(3) Based on data at three different geographic sites, measurements may, on the average, underestimate the true sulfur dioxide concentration by 11 percent. The most significant bias (-22 percent) was noted in measurements made at Los Angeles.

Bias in the measurements at Bloomington and Manhattan was -6 and -4 percent, respectively. The bias does not appear to be dependent on concentration over the range which was studied.

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

The results of the interlaboratory study validate that ASTM Method D 2914, as tested, is a sensitive, accurate, and precise technique for measurement of sulfur dioxide content in the atmosphere. The study of accuracy suggests that the method, as tested, may slightly underestimate sulfur dioxide levels. A similar effect has been noted by Blacker, et al.[10] who attribute the phenomenon to the calibration procedure. Blacker's work suggests that the negative bias can be eliminated by calibration with a permeation tube system in place of sulfite solutions. Other possible explanations for the negative bias are that the collection efficiency may be significantly less than 100 percent under some sampling conditions or that some substance in the atmosphere acts as an interference.

The precision of the method based on the measurements of its between-laboratory variability (reproducibility) and with-laboratory variability (repeatability) appears good. The results obtained for these measures of precision are within the ranges which have been reported previously.[11] The establishment of these statistical parameters by this study should enhance the acceptance of ASTM Method D 2914 as a reference technique for measurement of laboratory performance, evaluation of other sulfur dioxide measurement methods, and assessment of air quality relative to established standards.

RECOMMENDATIONS

Based on the results of this study, it is the general recommendation that no substantial changes are necessary in ASTM Method D 2914 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 options used should be specifically stated for any revision of the Test Method which reports the statistical characterization of the Method carried out in this study. In particular,

   (a) The midget impinger was selected for use by consensus, even though interpretations of published information (Reference 8 of the Method) indicated to some participants that the bubbler was more efficient. It appears that the choice between a bubbler or impinger should not affect the experimental results providing a limitation is placed on sampling rate and sample size.

   (b) The flexible TFE fluorocarbon tubing was used as a probe by all participants. This was a necessity for the sampling procedure. This option is given equal status with stainless steel and glass probes in the Method, but there was no opportunity to permit free choice of probe material.

(2) The Method states in Paragraph 6.3 that the pH of the absorbing reagent should not be less than 5.2 when prepared according to instructions. Experience of the laboratories showed that the pH is actually 3.8. Adjustment was made with dilute caustic as the instructions indicate. According to the information gathered from the participating laboratories neither of the two reasons for low pH was valid. This section should be checked experimentally and revised if necessary.

(3) It was reported, by two participants, that the constant K, in Paragraph 6.9.2 describing the assay procedure, should have the value 42.6 (instead of 21.3) when 0.2 g of dye is used in the formula for "grams taken" as the amount required in making up the stock solution. When a prepared 0.2 percent dye solution is used, as permitted by the Method, the instructions for assay become ambiguous, because "grams taken" would presumably refer to the amount of dye in 1 ml of stock solution used for the assay. These observations should be checked experimentally and both the ambiguity and factor-of-2 difference resolved when the Method is revised.

(4) Reference 9 in the Method should read "Volume 9, 1965" for the journal reported.

(5) The blank referred to in Paragraph 8 should consist of 10 ml of unexposed absorbing reagent, as specified, plus the approximately 5 ml of water specified for use in rinsing the absorbent solution from the collection vessel.

(6) A recommended sampling train arrangement, incorporating a dry test meter, should be shown in a figure in the Test Method.

(7) 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.

(8) Additional study is recommended to determine if the cause of the negative bias which was observed is due to the calibration procedure, the impinger collection efficiency, or atmospheric interferences.

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

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APPENDIX

REPRINT OF ASTM

TENTATIVE METHOD OF TEST FOR SULFUR DIOXIDE CONTENT OF THE ATMOSPHERE (WEST-GAEKE METHOD)

Designation: D 2914 - 70 T

Tentative Method of Test for SULFUR DIOXIDE CONTENT OF THE ATMOSPHERE (WEST-GAEKE METHOD)[1]

This Tentative Method has been approved by the sponsoring committee and accepted by the Society in accordance with established procedures for use pending adoption as standard. Suggestions for revisions should be addressed to the Society at 1916 Race St., Philadelphia, Pa. 19103.

1. Scope

1.1 This method covers the colorimetric determination of concentrations of 0.003 to 5.0 ppm of sulfur dioxide (SO_2) in the atmosphere. The method is selective, sensitive, reproducible, and suitable for field use. It is based on the Schiff Reaction (**1**).[2] The effects of the principal known interferences of oxides of nitrogen, ozone, and heavy metals (for example, iron, manganese, and chromium) have been minimized or eliminated.

1.2 The lower limit of detection of sulfur dioxide in 10 ml of potassium or sodium tetrachloromercurate is 0.3 μl (based on twice the standard deviation) representing a concentration of 0.01 ppm (26 $\mu g/m^3$) of SO_2 in an air sample of 30 liters.

1.3 Beer's law is followed through the working range from 0.005 to 1.0 absorbance units (0.2 to 35.0 μg in 25 ml of final solution).

1.4 One cannot extrapolate beyond these ranges by changing volumes of atmosphere sampled, unless the absorption efficiency of the particular system is known or determined at the volumes and concentrations under study.

2. Summary of Method

2.1 Sulfur dioxide is absorbed by aspirating a measured air sample through a solution of potassium or sodium tetrachloromercurate (TCM). This procedure results in the formation of a dichlorosulfitomercurate complex, which resists oxidation by the oxygen in the air (**2, 3**). Ethylenediaminetetraacetic acid disodium salt (EDTA) is added to this solution to complex heavy metals that can interfere by oxidation of the sulfur dioxide before formation of the dichlorosulfitomercurate (**4**). This compound, once formed, is stable to strong oxidents (for example, ozone and oxides of nitrogen). After the absorption is completed, any ozone in the solution is allowed to decay (**5**). The liquid is treated first with a solution of sulfamic acid to destroy the nitrite anion formed from the absorption of oxides of nitrogen present in the atmosphere (**6**). It is treated next with solutions of formaldehyde and specially purified acid - bleached pararosaniline containing phosphoric acid to control pH. Pararosaniline, formaldehyde, and the bisulfite anion react to form the intensely colored pararosaniline methyl sulfonic acid which behaves as a two-color pH indicator (λ 548 nm max at pH 1.6 $\pm$ 0.1 ϵ/(molar absorptivity) = 47.7×10^3). The pH of the final solution is adjusted to 1.6 $\pm$ 0.1 by the addition of prescribed amounts of 3 *M* phosphoric acid to the pararosaniline reagent (**5**).

2.1.1 Two variations are given; they differ only in the pH of the final solution. The variation described above is designated Variation A and is the method of choice. It gives the highest sensitivity. In Variation B, a larger quantity of phosphoric acid is added to yield a pH in the final solution of 1.2 $\pm$ 0.1. The wavelength of maximum absorbance under

[1] This method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres.
Effective Oct. 15, 1970.

[2] The boldface numbers in parentheses refer to the references listed at the end of this method.

these conditions is 575 nm, and the compound has a molar absorptivity of 37.0×10^3. Variation B is less sensitive, but has the advantage of a lower blank. It is pH-dependent, but may be more suitable with less expensive spectrophotometers.

2.2 Atmospheric sulfur dioxide concentrations of interest usually range from a few pphm to a few ppm. Higher concentrations (5 to 500 ppm) employed in special studies, must be analyzed by using smaller gas samples. A rapid redox reaction occurs between Hg(II) and the sulfito ion, if concentrations of the latter exceed a certain limit, 500 μg/ml (**7**).

2.3 Collection efficiency falls off rapidly below 0.01 ppm and varies with the geometry of the absorber, the size of the gas bubbles, and the contact time with the solution (**8,9,10**)

3. Definitions

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

4. Interferences

4.1 The interferences by oxides of nitrogen are eliminated by sulfamic acid (**5,6**), the ozone by time delay (**5**), and the heavy metals by EDTA and phosphoric acid (**4,5**). At least 60 μg of Fe(III), 10 μg of Mn(II), and 10 μg of Cr(III) in 10 ml of absorbing reagent can be tolerated in the procedure. No significant interference was found with 10 μg of Cu(II) and 22 μg of V(V).

5. Apparatus

5.1 *Absorber*—Satisfactory absorbers are (*a*) the midget or standard fritted bubbler; (*b*) the midget impinger; (*c*) the Greenberg-Smith impinger; and (*d*) the multiple-jet bubbler (**11**)

5.2 *Air Volume Measurement*—The air meter equipped with a standard odometer must be capable of measuring the air flow within ±2 percent. A wet or dry gasmeter with contacts on the 1-ft^3 or 10-liter dial to record air volume, or a specifically calibrated rotameter is satisfactory. Instead of these, critical orifices such as calibrated hypodermic needles may be used if the pump is capable of maintaining greater than 0.5 atmospheric differential across the needle (**12**).

5.3 *Manometer*—Mercury manometer accurate to 5 mm.

5.4 *Spectrophotometer or Colorimeter*—The instrument must be suitable for measurement of color at 548 nm or 575 nm. With Variation A, reagent blank problems may result with spectrophotometers or colorimeters having greater spectral band width than 16 nm. The wavelength calibration of the spectrophotometer should be verified.

5.5 *Sampling Probe*—If a sampling probe is used, it shall consist of a stainless steel, glass, or TFE-fluorocarbon tube. If a prefilter is used, it should consist of a material that has been shown to pass SO_2 (**13**).[4] Accumulated particulate on the prefilter may absorb SO_2 and must be checked.

6. Reagents

6.1 *Purity of Reagents*—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.[5] 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be distilled water in accordance with ASTM Specifications D 1193, for Reagent Water.[3] Water must be free from oxidants. It should preferably be double-distilled from all glass apparatus.

6.3 *Absorbing Reagent, 0.04 M Potassium Tetrachloromercurate (TCM)* K_2HgCl_4—Dissolve 10.86 g of mercuric chloride ($HgCl_2$) (**Caution**—Highly poisonous. If spilled on skin, flush off with water immediately), 5.96 g of potassium chloride (KCl), 0.066 g of EDTA in water, and bring to mark in a 1-liter volumetric flask. Sodium chloride (NaCl, 4.68 g) may be substituted for the KCl, but KCl is usually obtained in purer form. The pH of this reagent should not be less than 5.2. Low pH

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

[4] Nuclepore filters have been found to be satisfactory, and are available from the General Electric Co.

[5] "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."

values of the absorbing reagent reduce the collection efficiency of this reagent for SO_2. There are two reasons for obtaining low pH values. One, the incorrect ratio or concentrations of $HgCl_2$ and KCl. This can be adjusted by addition of a dilute solution of KCl if the ratio is not correct. The other occurs when the EDTA is not the disodium salt. If the latter is the cause of low pH value adjust to the correct value by the dropwise addition of dilute alkali. The absorbing reagent is normally stable for 6 months, but if a precipitate forms, discard the solution.

6.4 *Sulfamic Acid (0.6 percent)*—Dissolve 0.6 g of sulfamic acid in 100 ml of water. This reagent can be kept for a few days if protected from air.

6.5 *1-Butanol*—Certain batches of 1-butanol contain oxidants that create an SO_2 demand. Check by shaking 20 ml of 1-butanol with 5 ml of 15 percent potassium iodide (KI solution). If a yellow color appears in the alcohol phase redistill the 1-butanol from silver oxide.

6.6 *Buffer Stock Solution (pH 4.69)*—In a 100-ml volumetric flask, dissolve 13.61 g of sodium acetate trihydrate in water. Add 5.7 ml of glacial acetic acid and dilute to volume with water.

6.7 *Hydrochloric Acid (1 M)*—Dilute 86 ml of concentrated hydrochloric acid (HCl, sp gr 1.19) to 1 liter.

6.8 *Phosphoric Acid (3 M)*—Dilute 205 ml of concentrated phosphoric acid (H_3PO_4, sp gr 1.69) to 1 liter.

6.9 *Purified Pararosaniline (0.2 Percent (Nominal) Stock Solution)*—The pararosaniline dye needed to prepare this reagent must meet the following performance specifications: The dye must have a wavelength of maximum absorbance of 540 nm, when assayed in a buffered solution of 0.1 *M* solution acetate acetic acid; the absorbance of the reagent blank (8.1) which is temperature sensitive (0.015 absorbance units/deg C) should not exceed 0.170 absorbance unit at 22 C when prepared in accordance with the prescribed analytical procedure and to the specified concentration of the dye; and the reagents should give a calibration curve with a slope of 0.746 ± 0.040 absorbance units/μg/ml for a 1-cm cell, when the dye is pure and the sulfite solution is properly standardized. If specifically purified pararosaniline dye[6] 99.0 percent is available, weigh 0.200 g and completely dissolve the dye by shaking with 100 ml of 1 *M* HCl in a 100-ml graduated cylinder that is glass-stoppered. If the pararosaniline dye is obtained in solution, assay the concentration in accordance with 6.9.2, and proceed to 6.9.3. When the dye does not meet these specifications, it normally can be purified satisfactorily by following the procedure in 6.9.1.

6.9.1 *Purification Procedure*—In a large separatory funnel (250 ml), equilibrate 100 ml each of 1-butanol and 1 *M* HCl. Weigh 0.1 g of pararosaniline hydrochloride (PRA) in a beaker. Add 50 ml of the equilibrated acid and let stand for several minutes. To a 125-ml separatory funnel add 50 ml of the equilibrated 1-butanol. Transfer the acid solution containing the dye to the funnel and extract. The violet impurity will transfer to the organic phase. Transfer the lower (aqueous) phase into another separatory funnel and add 20-ml portions of 1-butanol. This is usually sufficient to remove almost all the violet impurity which contributes to the reagent blank. If violet impurity still appears in 1-butanol phase after five extractions, discard this lot of dye. After the final extraction, filter the aqueous phase through a cotton plug into a 50-ml volumetric flask and bring to volume with 1 *N* HCl. This stock reagent will be yellowish red.

6.9.2 *Assay Procedure*—The actual concentration of PRA need be assayed only once for each lot of dye in the following manner: Dilute 1 ml of the stock reagent to the mark in a 100-ml volumetric flask with water. Transfer a 5-ml aliquot to a 50-ml volumetric flask. Add 5 ml of 1 *M* sodium acetate-acetic acid buffer, and dilute the mixture to 50-ml volume with water. After 1 h, determine the absorbance at 540 nm with a spectrophotometer. Determine the percent of nominal concentration of PRA as follows:

$$\text{PRA, percent} = (\text{absorbance} \times K)/\text{grams taken}$$

For 1-cm cells and 0.04-mm slit width in a Beckman DU Spectrophotometer K = 21.3 (mean value after extensive purification of

[6] Specially purfied dye in the form of pararosaniline hydrochloride (PRA) is available from a number of reagent supply sources.

dye).

6.10 *Pararosaniline Reagent*—To a 250-ml volumetric flask add 20 ml of stock pararosaniline reagent. Add an additional 0.2 ml of stock for each percent the stock assays below 100 percent. For Variation A, add 25 ml of 3 *M* H_3PO_4 and dilute to volume with water. These reagents are stable for at least 9 months. For Variation B add 200 ml of 3 *M* H_3PO_4 and dilute to volume.

6.11 *Formaldehyde (0.2 Percent)*—Dilute 5 ml of 36 to 38 percent formaldehyde to 1 liter with water. Prepare this solution daily.

6.12 *Reagents for Standardization*

6.12.1 *Stock Iodine Solution (0.1 N)*—Place 12.7 g of iodine in a 250-ml beaker, add 40 g of KI and 25 ml of water. Stir until all is dissolved, then dilute to 1 liter with water.

6.12.1.1 *Working Iodine Solution, 0.01 N*—Prepare approximately 0.01 *N* iodine solution by diluting 50 ml of the stock solution to 500 ml with distilled water.

6.12.1.2 *Starch Indicator Solution*—Triturate 0.4 g of soluble starch and 0.002 g of mercuric iodide (preservative) with a little water, and add the paste slowly to 200 ml of boiling water. Continue boiling until clear; cool and transfer to a glass stoppered bottle.

6.12.3 *Sodium Thiosulfate, Standard Solution (0.1 N)*—Dissolve 25 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 1 liter of freshly boiled, cooled distilled water and add 0.1 g of sodium carbonate to the solution. Allow the solution to stand for 1 day before standardizing. To standardize, weigh 1.5 g of potassium iodate, primary standard grade, that was dried at 180 C and dilute to volume in a 500-ml volumetric flask. To a 500-ml iodine flask, pipet 50 ml of the iodate solution. Add 2 g of potassium iodide and 10 ml of a 1+10 dilution of concentrated hydrochloric acid. Stopper the flask. After 5 min, titrate with thiosulfate to a pale yellow color. Add 5 ml of starch indicator and complete the titration. Calculate the normality of sodium thiosulfate, *N*, as follows:

$$N = \frac{[\text{weight (g } KIO_3) \times 10^3 \times 0.1]}{(\text{ml of titer} \times 35.67)}$$

6.12.3.1 *Standard .01 N Sodium Thiosulfate*—Dilute 50.0 ml of standard 0.1 *N* sodium thiosulfate to 500 ml with distilled water and mix. This .01 *N* solution is *not* stable, and must be prepared fresh on the day it is used by diluting the standard 0.1 *N* sodium thiosulfate.

6.12.4 *Standard Sulfite Solution*—Dissolve 0.4 g of sodium sulfite (Na_2SO_3) or 0.3 g of sodium metabisulfite ($Na_2S_2O_5$) in 500 ml of recently boiled and cooled distilled water. (Double-distilled water that has been dearerated is preferred.) This solution contains from 320 to 400 μg/ml as SO_2. The actual concentration in the standard solution is determined by adding excess iodine and back titrating with sodium thiosulfate that has been standardized against potassium iodate or dichromate (primary standard). Sulfite solution is unstable.

6.12.4.1 Back titration is performed in the following manner: Add 25 ml of distilled water to a 500-ml iodine flask and pipet 50 ml of the 0.01 *N* iodine solution into the flask designated flask A (blank). Pipet 25 ml of the standard sulfite solution to a second 500-ml iodine flask and pipet 50 ml of the 0.01 *N* iodine into this flask designated B (sample). Stopper the flasks and allow to react for 5 min. By means of a buret containing standard 0.01 *N* thiosulfate solution, titrate each flask in turn to a pale yellow color. Then add 5 ml of starch solution and continue the titration to the disappearance of the blue color. Calculate the concentration of SO_2 in the standard solution as follows:

$$SO_2, \mu g/ml = [(A - B)NK]/V$$

where:

A = milliliters of thiosulfate solution required for titration of the blank,
B = milliliters of thiosulfate solution required for titration of the sample,
N = normality of the thiosulfate solution,
K = micro equivalent weight for SO_2 = 32,030, and
V = milliliters of sample taken.

6.12.5 *Dilute Sulfite Solution*—Immediately after standardization of the sulfite solution, pipet 2 ml of the freshly standardized solution into a 100-ml volumetric flask and bring to mark with 0.04 *M* TCM. This solution is stable for 30 days if stored at 5 C.

7. Sampling

7.1 *Collection of Sample*—Place 10 ml of 0.04 *M* TCM (20 ml for sampling of long duration) absorbing solution in a midget impinger, or 75 to 100 ml in one of the larger ab-

sorbers. Connect the sampling probe upstream of the absorber with glass, stainless steel or TFE-fluorocarbon.[7] Rigid tubing may be joined with butted joints under polyethylene tubing. Downstream, a trap and calibrated air flow meter or a gas meter or both provided with thermometer and manometer lead to the pump. (Alternatively, a hypodermic needle in parallel with a manometer can be used as a critical orifice in a thermostrated box, if the pump can maintain a differential pressure of at least 0.5 atmosphere across the needle.) The duration and rate of aspiration depend on the concentration of sulfur dioxide. With midget impingers, rates of 0.5 to 2.5 liters/min are satisfactory; with large absorbers, the rate can be 5 to 15 liters/min. The minimum quantity of atmosphere aspirated into the Greenburg-Smith impinger has been found to be 25 liters to produce satisfactory results. Rates of sampling within the above ranges generally have an efficiency of absorption of 98 percent or greater. For best results, rates and sampling time should be chosen to absorb 0.5 to 3.0 μg (0.2 to 1.3 μl at 760 mm Hg 25 C) of SO_2/ml of sampling solution. Shield the absorbing reagent from direct sunlight during and after sampling by covering the absorber with a suitable wrapping, such as aluminum foil, to prevent deterioration. If the sample must be stored for more than 1 day before analysis, keep it at 5 C in a refrigerator (see Section 11). Record atmospheric temperature and pressure.

7.2 *Centrifugation*—If a precipitate is observed, remove it by centrifugation.

8. Procedure

8.1 After collection, transfer the sample quantitatively to a 25-ml volumetric flask, using about 5 ml of water for rinsing. Aliquots may be taken at this point if the concentration or volume of reagent is large. If the presence of ozone is suspected, delay analysis for 20 min after sampling to allow the ozone to decompose. For each set of determinations, prepare a reagent blank by adding 10 ml of the unexposed absorbing reagent to a 25-ml volumetric flask. To each flask add 1 ml of 0.6 percent sulfamic acid and allow to react for 10 min to destroy the nitrite from oxides of nitrogen. Accurately pipet in 2 ml of the 0.2 percent formaldehyde, then 5 ml of pararosaniline reagent prescribed for Variation A or Variation B. Start a laboratory timer that has been set for 30 min. Bring all flasks to volume with freshly boiled distilled water. After 30 min, determine the absorbances of the sample and of the blank at the wavelength of maximum absorbance 548 nm for Variation A or 575 nm for Variation B. Use water (not the reagent blank) in the reference cell. Do not allow the colored solution to stand in absorbance cell; a film of dye will be deposited thereon.

8.1.1 If the absorbance of the sample solution ranges between 1.0 and 2.0, the sample can be diluted 1+1 with a portion of the reagent blank and read within a few minutes. Solutions with high absorbance can be diluted up to sixfold with the reagent blank in order to obtain on-scale readings within 10 percent of the true absorbance value.

9. Calibration and Standards

9.1 Pipet graduated amounts of the diluted sulfite solution (such as 0, 1, 2, 3, 4, and 5 ml) into a series of 25-ml volumetric flasks. Add sufficient 0.04 *M* TCM to each flask to bring the volume of its contents to approximately 10 ml. Then add the remaining reagents as described in the procedure, (see 8.1). For greater precision, a constant-temperature bath is preferred. The temperature of calibration should not differ from the temperature of analysis by more than a few degrees.

9.2 Plot total absorbance of these solutions (as ordinates) against the total micrograms of SO_2. A linear relationship is obtained. The absorbance should be read on the samples and standards in the same cell; or if more than one cell is used, the cells should be spectrophotometrically matched. The intercept with the vertical axis of the line best fitting the points is usually within 0.2 absorbance units of the blank (zero standard) reading. Under these conditions the plot need be determined only once to evaluate the calibration factor (reciprocal of the slope of the line). This calibration factor can be used for calculating results provided there are no radical changes in temperature or pH. At least one control sample is recommended per series of determinations to ensure the reliability of this factor.

[7] TFE-fluorocarbon tubes are available from Analytical Instrument Development, Inc., 230 S. Franklin St., West Chester, Pa. 19380, and Metronics, Inc., 3201 Porter Drive, Palo Alto, Calif. 94304.

9.3 *Alternative Calibration Procedure*—Calibrate permeation tubes that contain liquefied SO_2 gravimetrically and use to prepare standard concentrations of SO_2 in air (**14,15,16**). Analyses of these known concentrations give calibration curves that simulate all the operational conditions performed during the sampling and chemical procedures. This calibration curve includes the important correction for collection efficiency at various concentrations of SO_2.

9.3.1 Prepare or obtain[7] a TFE fluorocarbon permeation tube that emits at a rate of 0.1 to 0.2 μg/min (0.04 to 0.08 μl/min at standard conditions of 25 C and 1 atmosphere). A permeation tube with an effective length of 10 to 20 mm and a wall thickness of 0.76 mm (0.030 in.) will yield the desired permeation rate if held at a constant temperature of 20 C.

9.3.1.1 Permeation tubes containing SO_2 are calibrated under a stream of dry nitrogen to prevent the formation of blisters in the walls and sulfuric acid inside the tube.

9.3.2 To prepare standard concentrations of SO_2, select either the system designed for laboratory or field use (see Fig. 1 and Fig. 2, respectively). Assemble the apparatus, as shown in one of these systems, consisting of a water-cooled condenser; constant-temperature water bath maintained at 20 C; cylinders containing pure, dry nitrogen and pure, dry air with appropriate pressure regulators; needle valves and flow meters for the nitrogen and dry air, diluent gas streams. The diluent gases are brought to temperature by passage through a 2-m long copper coil immersed in the water bath. Insert a calibrated permeation tube (**15**) into the central tube of the condenser maintained at 20 C by circulating water from the constant-temperature bath and pass a stream of nitrogen over the tube at a fixed rate of approximately 50 ml/min. Dilute this gas stream to the desired concentration by varying the flow rate of the "clean dry air".[8] This flow rate can normally be varied from 0.2 to 15 liters/min. The flow rate of the sampling system determines the lower limit for the flow rate of the diluent gases. The flow rates of the nitrogen and the diluent air must be measured to an accuracy of 1 to 2 percent. With a tube permeating SO_2 at a rate of 0.1 μl/min (0.26 μg/min), the range of concentration of SO_2 will be between 0.007 to 0.04 ppm (18 to 1047 $\mu g/m^3$), a generally satisfactory range for ambient air conditions. When higher concentrations are desired, calibrate and use longer permeation tubes.

9.3.3 *Procedure for Preparing Simulated Calibration Curves*—Obviously, one can prepare a multitude of curves by selecting different combinations of sampling rate and sampling time. The following description represents a typical procedure for ambient air sampling of short duration, with a brief mention of a modification for 24-h sampling. The system is designed to provide an accurate measure of SO_2 in the 0.01 to 0.5 ppm range. It can be easily modified to meet special needs.

9.3.3.1 The dynamic range of the colorimetric procedure fixes the total volume of the sample at 30 liters; then, to obtain linearity between the absorbance of the solution and the concentration of SO_2 in parts per million, select a constant sampling time. This fixing of sampling time is also desirable from a practical standpoint. In this case, select a sampling time of 30 min. Then to obtain a 30-liter sample requires a flow rate of 1 liter/min. A 22-gage hypodermic needle operating as a critical orifice will control air flow at this approximate desired rate. Calculate the concentration of standard SO_2 in air as follows:

$$C = (P \times M)/(R + r)$$

where:

C = concentration of SO_2, ppm,
P = permeation rate, μg/min,
M = reciprocal of vapor density = 0.382 μl/μg,
R = flow rate of diluent air, liters/min, and
r = flow rate of diluent nitrogen, liters/min.

Data for a typical calibration curve are listed in Table 1.

9.3.3.2 A plot of the concentration of SO_2 in ppm (x axis) against absorbance of the final solution (y axis) will yield a straight line, the slope of which is the factor for conversion of absorbance to ppm. This factor includes the correction for collection efficiency. Any deviation from linearity at the lower concentration

[8] "Clean dry air" may also be prepared by passing ambient air from a relatively uncontaminated outside source through absorption tubes packed with activiated carbon and soda lime followed by an efficient fiber glass filter in series.

range indicates a change in collection efficiency of the sampling system. Actually, the standard concentration of 0.01 ppm is slightly below the dynamic range of the method. If this is the range of interest, the total volume of air collected should be increased to obtain sufficient color within the dynamic range of the colorimetric procedure. Also, once the calibration factor has been established under simulated conditions, the conditions can be modified so that the concentration of SO_2 is a simple multiple of the absorbance of the colored solution.

9.3.3.3 For long-term sampling of 24-h duration, the conditions can be fixed to collect 300 liters of sample in a larger volume of tetrachloromercurate. For example, for 24 h at 0.2 liter/min, approximately 288 liters of air are collected. An aliquot representing 0.1 of the entire amount of the sample is taken for the analysis. The remainder of the analytical procedure is the same as described in 8.1.

10. Calculations

10.1 Calculate the concentration of SO_2 in the sample as follows:

$$SO_2, \text{ ppm} = (A - A^1)\, 0.382 B/V$$

where:

A = sample absorbance,
A^1 = reagent blank absorbance,
0.382 = volume (μl) of 1 μg of SO_2 at 25 C, 760 mm Hg,
B = calibration factor, μg/absorbance unit, and
V = sample volume in liters corrected to 25 C, 760 mm Hg by $PV = nRT$.

11. Effects of Storage

11.1 Sampling solutions of dichlorosulfitomercurate are relatively stable. When stored at 5 C for 30 days no detectable losses of SO_2 occur. At 25 C losses of SO_2 in solution occur at a rate of 1.5 percent/day. These losses of SO_2 follow a first order reaction and the reaction rate is independent of concentration. Actual field samples containing EDTA have similar decay curves, and when analysis of the samples is delayed for any appreciable time, the results must be corrected for these losses.

12. Precision and Accuracy

12.1 The precision at the 95 percent confidence level is 4.6 percent (4). The accuracy of the method has not yet been determined to any degree of certainty over a variety of concentrations of SO_2, nor is the absolute collection efficiency known for the wide variety of possible systems of sampling and testing.

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TABLE 1 Typical Calibration Data

Concentrations of SO_2, ppm	Amount of SO_2 for 30 liters, μl	Absorbance of Sample
0.005	0.15	0.01
0.01	0.30	0.02
0.05	1.50	0.117
0.10	3.00	0.234
0.20	6.00	0.468
0.30	9.00	0.703
0.40	12.00	0.937

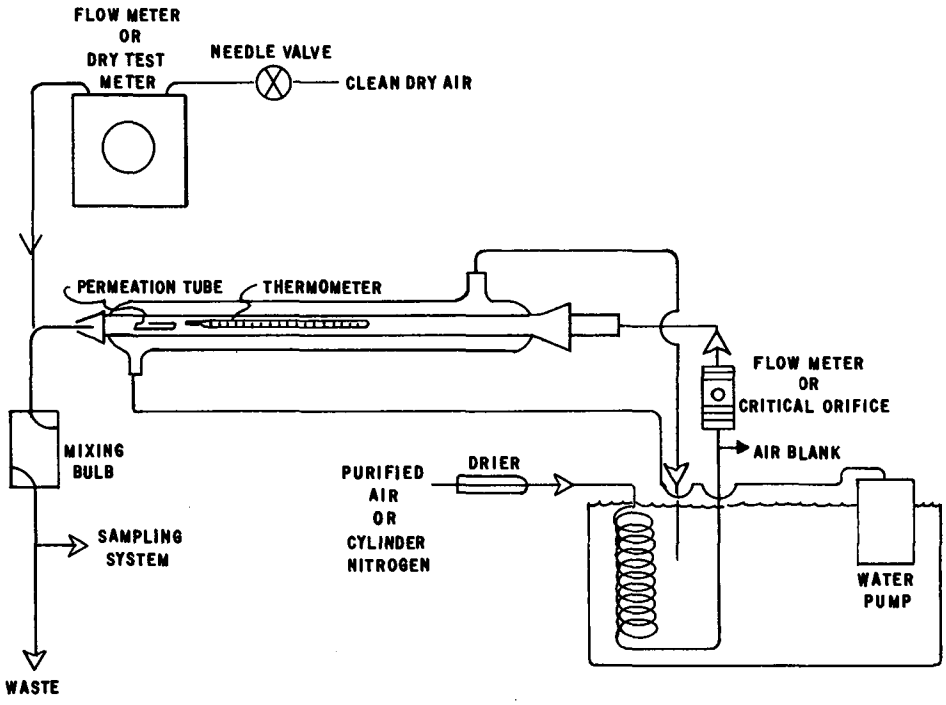

FIG. 1 Gas Dilution System for Preparation of Standard Concentrations of Sulfur Dioxide for Laboratory Use by the Permeation Tube Method.

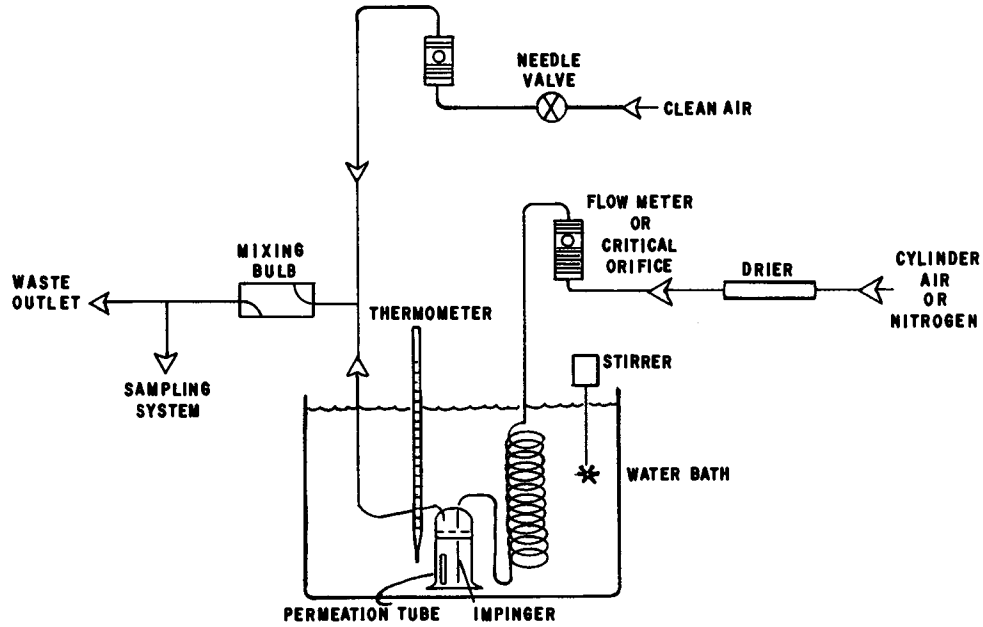

FIG. 2 Gas Dilution System for Preparation of Standard Concentrations of Sulfur Dioxide for Field Use by the Permeation Tube Method.

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