



**Interlaboratory Cooperative Study of
the Precision and Accuracy
of the Determination**

**SULFUR OXIDES
IN GASEOUS COMBUSTION PRODUCTS
(Barium Chloranilate Method)**

**using
ASTM Method D 3226-73T**

DS 55-S9



AMERICAN SOCIETY FOR TESTING AND MATERIALS



FINAL REPORT

on

INTERLABORATORY COOPERATIVE STUDY OF THE PRECISION AND ACCURACY OF THE DETERMINATION OF SULFUR OXIDES IN GASEOUS COMBUSTION PRODUCTS

(Barium Chloranilate Method)

USING ASTM METHOD D 3226-73T

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INTERLABORATORY COOPERATIVE STUDY OF THE PRECISION
AND ACCURACY OF THE DETERMINATION OF SULFUR OXIDES
IN GASEOUS COMBUSTION PRODUCTS (BARIUM CHLORANILATE METHOD)
USING ASTM METHOD D3226-73T

by

J. E. Howes, Jr., R. N. Pesut, and J. F. Foster

INTRODUCTION

In 1971 in recognition of the important relationship between the measurement and the effective control of air pollution, Committee D-22 of American Society for Testing and Materials (ASTM) initiated a pioneering program, designated Project Threshold, to validate methods for measuring contaminants in the ambient atmosphere and in emissions from individual sources. The first phase of the program was devoted to evaluation of methods for measuring the content of nitrogen dioxide (D 1607-69), sulfur dioxide (D 2914-70T), dustfall (D 1739-70), total sulfation (D 2010-65), particulate matter (D 1704-61), and lead (D 3112) in

the atmosphere (1-6)*.

Methods for the measurement of the relative density of black smoke (D 3211-73T)⁽⁷⁾, oxides of nitrogen (D 1608-60)⁽⁸⁾, sulfur oxides (D 3226-73T), and particulates and collected residue⁽⁹⁾ in source emissions have been evaluated in Phase 2 of Project Threshold. Evaluation of a pitot tube method (D 3154-72)⁽¹⁰⁾ for determining the average velocity in a duct was performed in conjunction with the particulates and collected residue tests.

The interlaboratory "round-robin" approach where separate teams sample the same source simultaneously has been applied to Project Threshold by bringing together groups of competent laboratories for concurrent performance of the test procedures under actual field conditions. Each participating laboratory was responsible for providing personnel and equipment, assembling apparatus, sampling, and analyzing collected samples either on-site or at its own facility. The coordination of the testing program, statistical analysis of the data, and evaluation of the measurement methods based on the experimental results has been performed by Battelle's Columbus Laboratories.

This report describes test procedures and presents the results obtained from an experimental study of the accuracy and precision of determinations of sulfur oxides (commonly called SO_x) in pilot plant and actual source emissions using ASTM Method D 3226-73T⁽¹¹⁾.

SUMMARY OF RESULTS

Statistical analysis of 277 SO₂ determinations and 342 SO₃ determinations in flue gas from a pilot plant furnace and determinations in industrial combustion source emissions using ASTM D 3226-73T produced the following results;

- The between-laboratory component of variance (reproducibility) of SO₂ determinations over the concentration range of about 300 to 2500 ppm SO₂, as estimated from the pilot plant tests, may be expressed by the equation

$$\hat{S}_B = 12.48 \sqrt{m} - 96.70,$$

where \hat{S}_B , the between-laboratory component of variance, and m , the mean SO₂ concentration, are given in ppm SO₂.

* References are given on page 83.

- The between-laboratory component of variance (reproducibility) of SO_3 determinations over the concentration range of about 5 to 50 ppm SO_3 , as estimated from the pilot plant tests, may be expressed by the equation

$$\hat{S}_B = 0.26 \sqrt{m} + 5.33,$$

where \hat{S}_B , the between-laboratory component of variance, and m , the mean SO_3 concentration, are given in ppm SO_3 .

- The within-laboratory component of variance (repeatability) of SO_2 determinations over the concentration range of about 300 to 2500 ppm SO_2 , as estimated from the pilot plant tests, may be expressed by the equation

$$\hat{S}_W = 5.32 \sqrt{m} - 53.92,$$

where \hat{S}_W , the within-laboratory component of variance, and m , the mean SO_2 concentration, are given in ppm SO_2 .

- The within-laboratory component of variance (repeatability) of SO_3 determinations over the concentration range of about 5 to 50 ppm SO_3 , as estimated from the pilot plant tests, may be expressed by the equation

$$\hat{S}_W = 2.43 \sqrt{m} - 4.76,$$

where \hat{S}_W , the within-laboratory component of variance, and m , the mean SO_3 concentration, are given in ppm SO_3 .

- The mean coefficient of variation of concurrent SO_x measurements by four laboratories at three field sites are as follows:

Site	Mean Coefficient of Variation, Percent	
	SO_2	SO_3
Oil-fired Power Plant	20	85
Coal-fired Power Plant	94	174
Cement Plant	45	93

- Pilot plant tests in which known spikes over the range of about 350 to 1100 ppm SO_2 were added to the flue gas samples produced experimentally determined spike concentrations, the average of which was not significantly different from the true value. Statistically significant biases were not detected when the data were divided into three spike concentration ranges (less than 400 ppm, between 400 and 850 ppm, and greater than 850 ppm) for the purpose of testing for bias as a function of SO_x concentration. Accuracy results were not obtained for SO_3 measures since SO_3 spiking was not performed.
- Solutions containing known quantities of sulfate were supplied to each laboratory for analysis with the samples obtained from the pilot plant and field tests. The measure of between-laboratory standard deviation of the D 3226-73T analytical procedure, expressed as the coefficient of variation, ranged from 1.7 to 37.0 percent, based on standard solutions containing 14.6 to 58.4 mg SO_2 . The measure of within-laboratory standard deviation, expressed as the coefficient of variation, ranged from 2.8 to 21.3 percent. The mean differences between the experimentally determined and actual values of the standards did not show a statistical significant bias in sulfate determinations over a concentrations range equivalent to 14.6 to 131.5 mg SO_2 .

EXPERIMENTAL PROGRAM

ASTM Test Method D3226-73T

ASTM Method D3226-73T describes equipment and procedures for the determination of the concentration of sulfur oxides combustion source emissions. Sulfur trioxide (SO_3) is condensed in the sample gas stream when passed through a glass coil held at a temperature below the dew point of SO_3 . The condensed mist is collected on the condenser coils and a glass-frit filter at a temperature above the water dew point. The filtered gas stream passes through two midget impingers in series containing hydrogen peroxide solution to absorb the SO_2 and oxidize it to H_2SO_4 for analysis. The sulfate concentrations of the SO_3 and SO_2 samples are determined separately by reacting with barium chloranilate to form a colored acid chloranilate whose concentration is measured by comparison to sulfate standards using a spectrophotometer. A copy of the version of ASTM D 3226-73T which was evaluated is presented in an Appendix to this report.

Apparatus

A close-up view of the glass condenser showing the coil and glass-frit filter, as they are enclosed in a glass water jacket, is shown in Figure 1. A dimensioned drawing of the coil is presented in Figure 2. The two ends are equipped with spherical ground glass connectors for coupling directly to a heated probe on one end and to midget impingers on the end with the glass frit. Figure 3 shows the mounted coil and filter assembled with the two midget impingers on a portable carrier that was used in field tests. The temperature of the condensation coil and filter is controlled by circulating water through the water jacket from a heated thermostatically controlled water bath. A drawing showing the components of the water heating and circulating system is given in Figure 4.

Other components of the apparatus include a heated probe, a pump with a flow control and flow rate measuring device to withdraw the sample while maintaining a constant rate of sampling and pressure and temperature indicators inserted into the sample stream at the intake to a calibrated dry gas meter, which registers the volume of each sample. The components of a typical system as assembled for source sampling is shown in Figure 5.

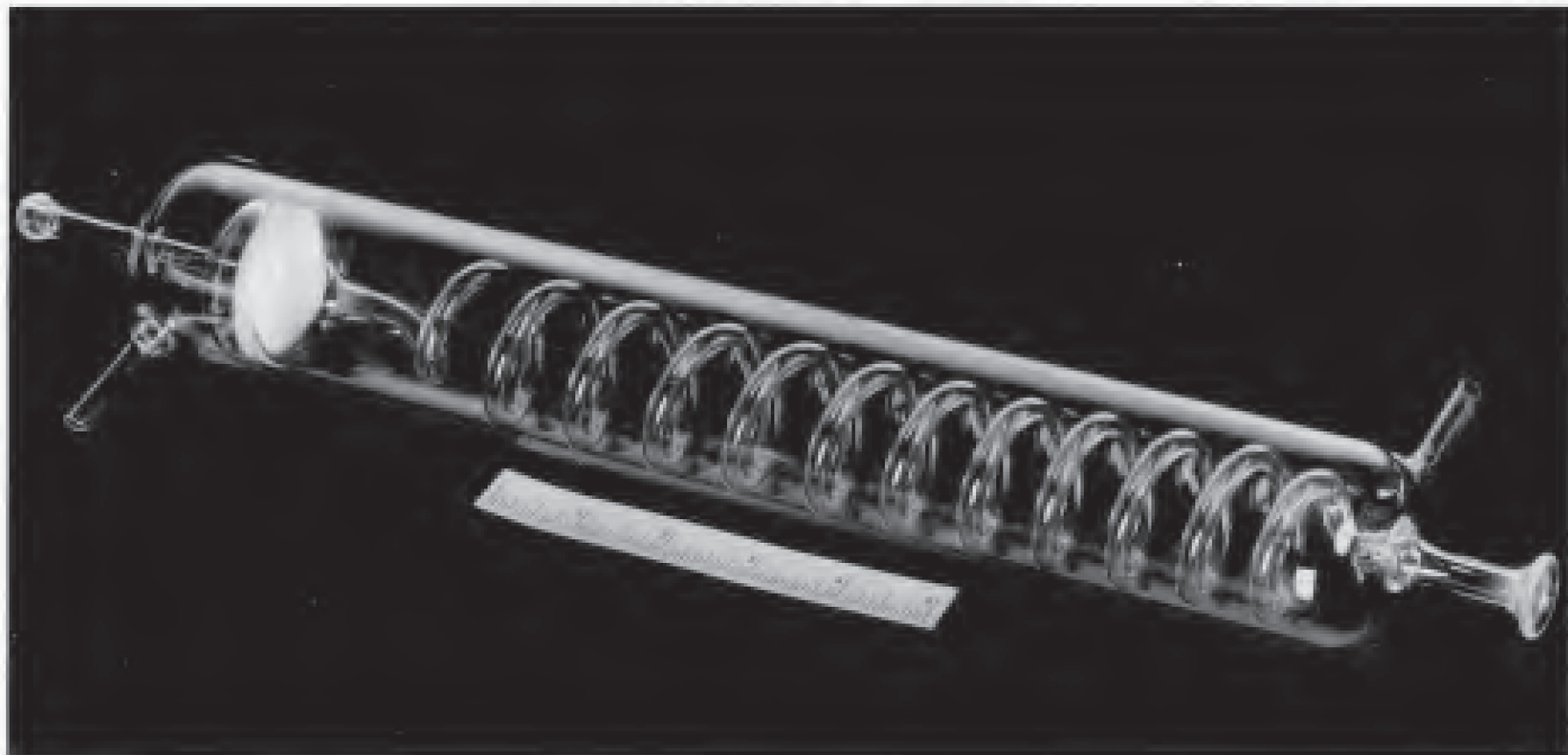


FIGURE 1. CONDENSER COIL FOR COLLECTING $\text{SO}_3/\text{H}_2\text{SO}_4$

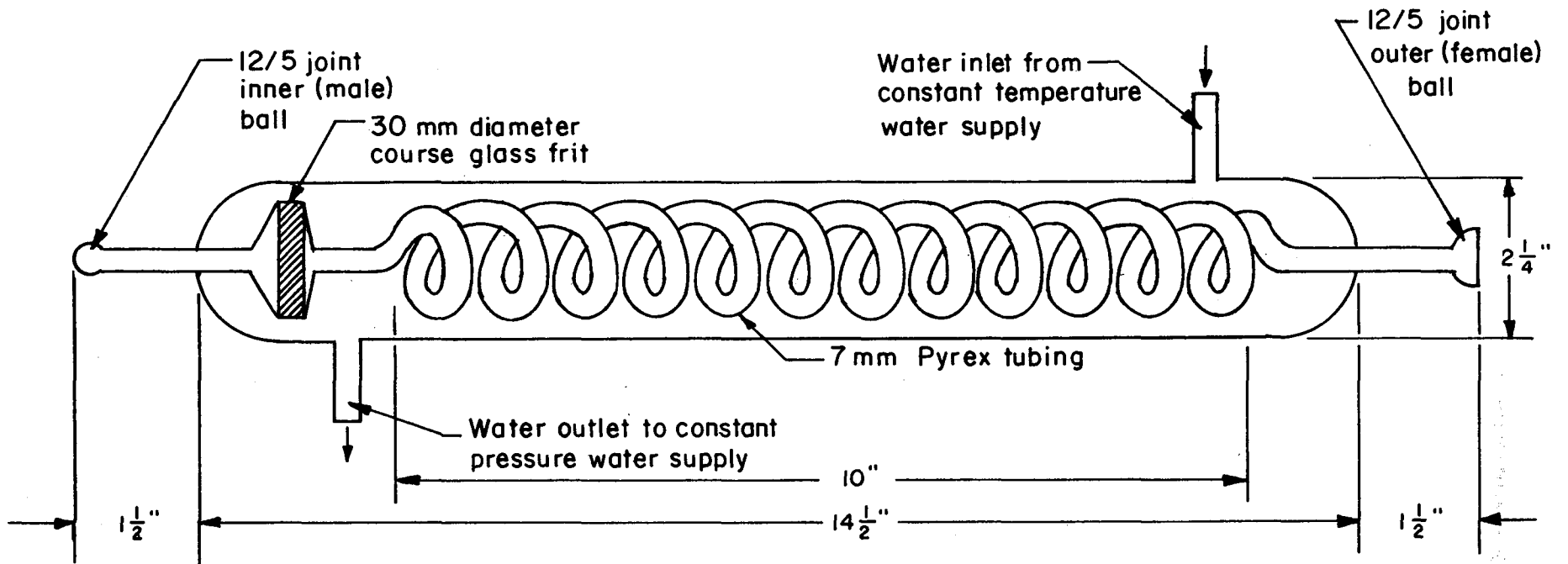


FIGURE 2. DIMENSIONED DRAWING OF SO₃ CONDENSATION COIL USED FOR TESTS OF D 3226-73T

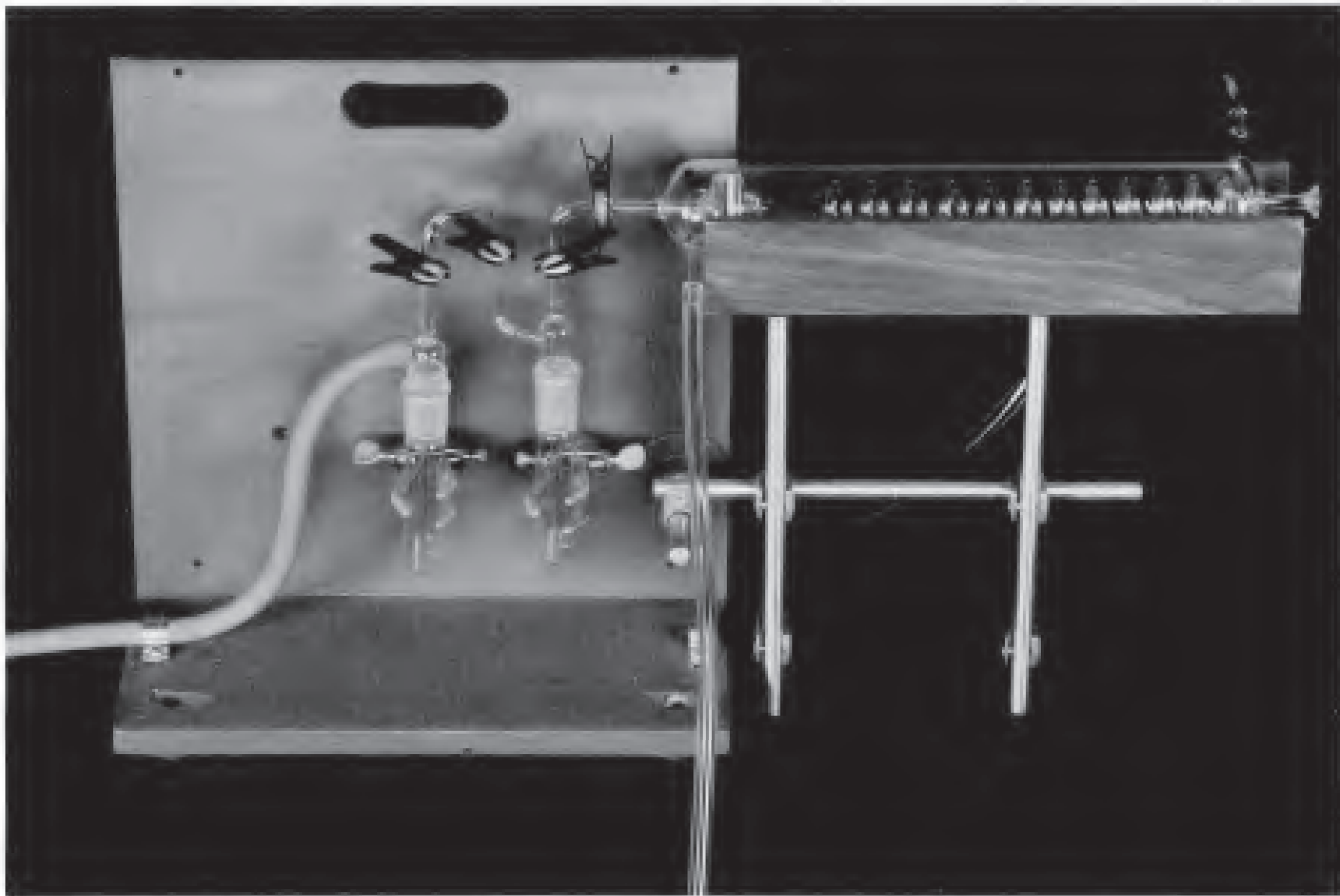


FIGURE 3. MOUNTED COLLECTION SYSTEM WITH SO_3 CONDENSER AND SO_2 ABSORBERS

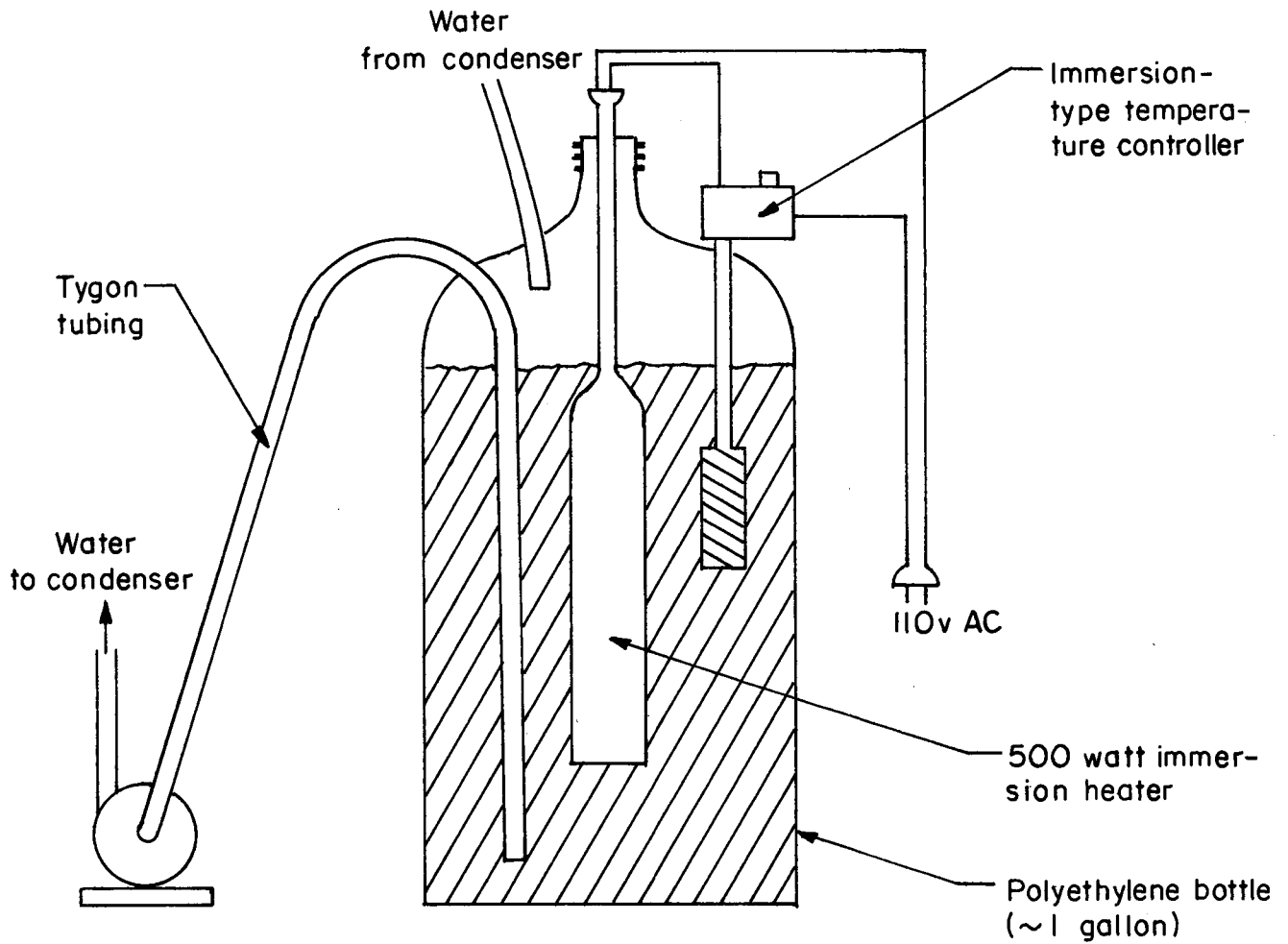


FIGURE 4. HEATED WATER SUPPLY SYSTEM FOR SO_3 CONDENSATION COILS

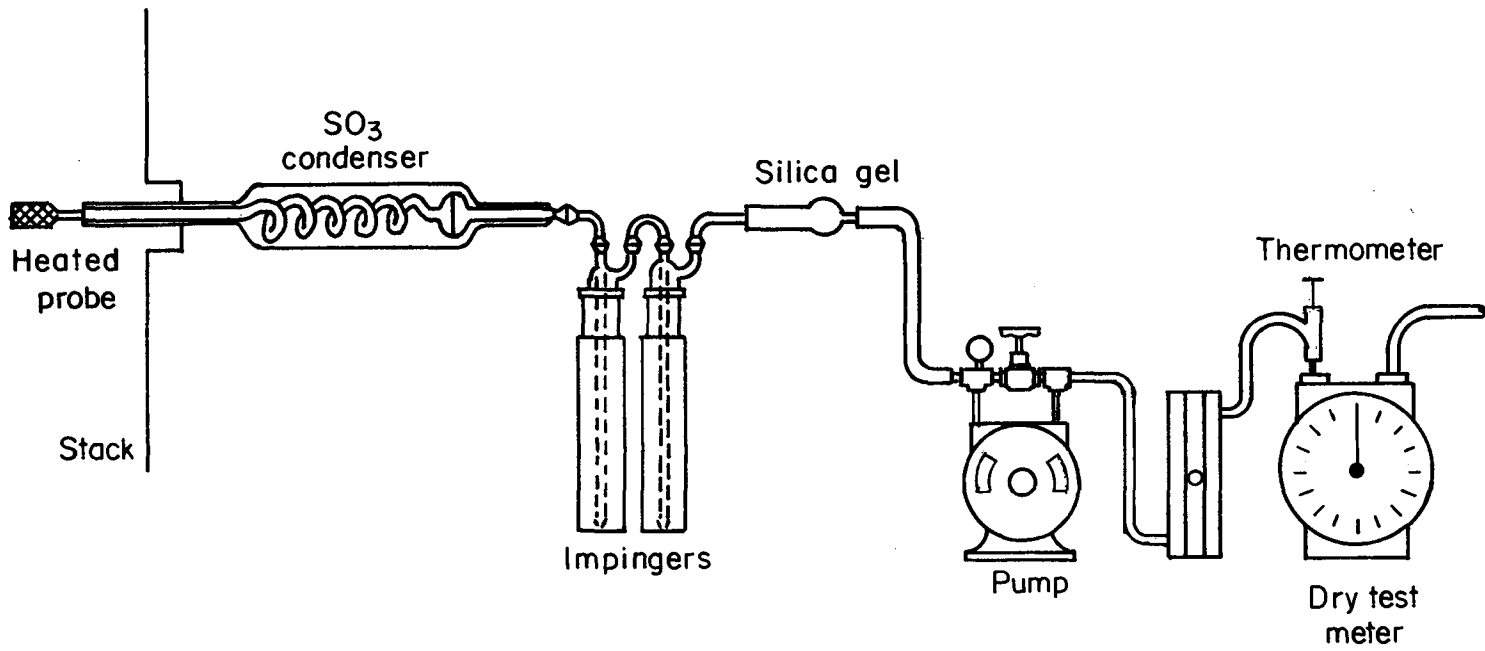


FIGURE 5. TYPICAL SO_x SAMPLING TRAIN

Pilot Plant Tests

Tests of the sulfur oxides content of flue gases from the Battelle multifuel furnace using ASTM D3226-73T were performed by ten cooperating laboratories during two two-day periods in consecutive weeks, with six laboratories sampling in the first test week and four sampling in the second test week. The furnace was operated on fuel oil with burner settings, furnace temperatures, and fuel sulfur additions selected to produce a range of SO_x concentrations in the flue gases.

The flue gases were cooled to permit handling in a sampling system that separated the total sample stream from the furnace flue into two parallel streams, one of which was spiked by addition of a known concentration of sulfur dioxide. Spiking increased the level of sulfur oxides above that of the unspiked stream, so that measurements of the difference in concentration between simultaneous samples from the two streams, when compared with the known concentration increase from the added sulfur dioxide, permitted estimation of the accuracy of the method of measurement. The following sections present detailed descriptions of the test site, the sample generating system, the spiking procedure, the sampling procedure, and the statistical design of the experiments.

Test Site Description

A test area in Building 9 pilot plant of the Columbus Laboratories of Battelle houses the Battelle multifuel furnace and its auxiliary equipment, and the sample generating system with two loops for spiked and unspiked sample streams. Each loop had a single sampling manifold with 12 sampling positions and flow control valves. Areas were available for each laboratory crew to process the samples in preparation for transporting them to their home site for completing the analyses.

Multifuel Furnace. The multifuel furnace was used for firing No. 2 fuel oil to generate the flue gas stream for sampling. It has a refractory lined cylindrical combustion chamber about 15 inches in diameter and 90 inches long which is enclosed by a steel airtight outer shell. Versatile air controls and a special burner design permit simulation of conditions which obtain in firing fuel oil in a full-scale combustion furnace. Figure 6 is a schematic drawing of the setup for firing fuel oil.

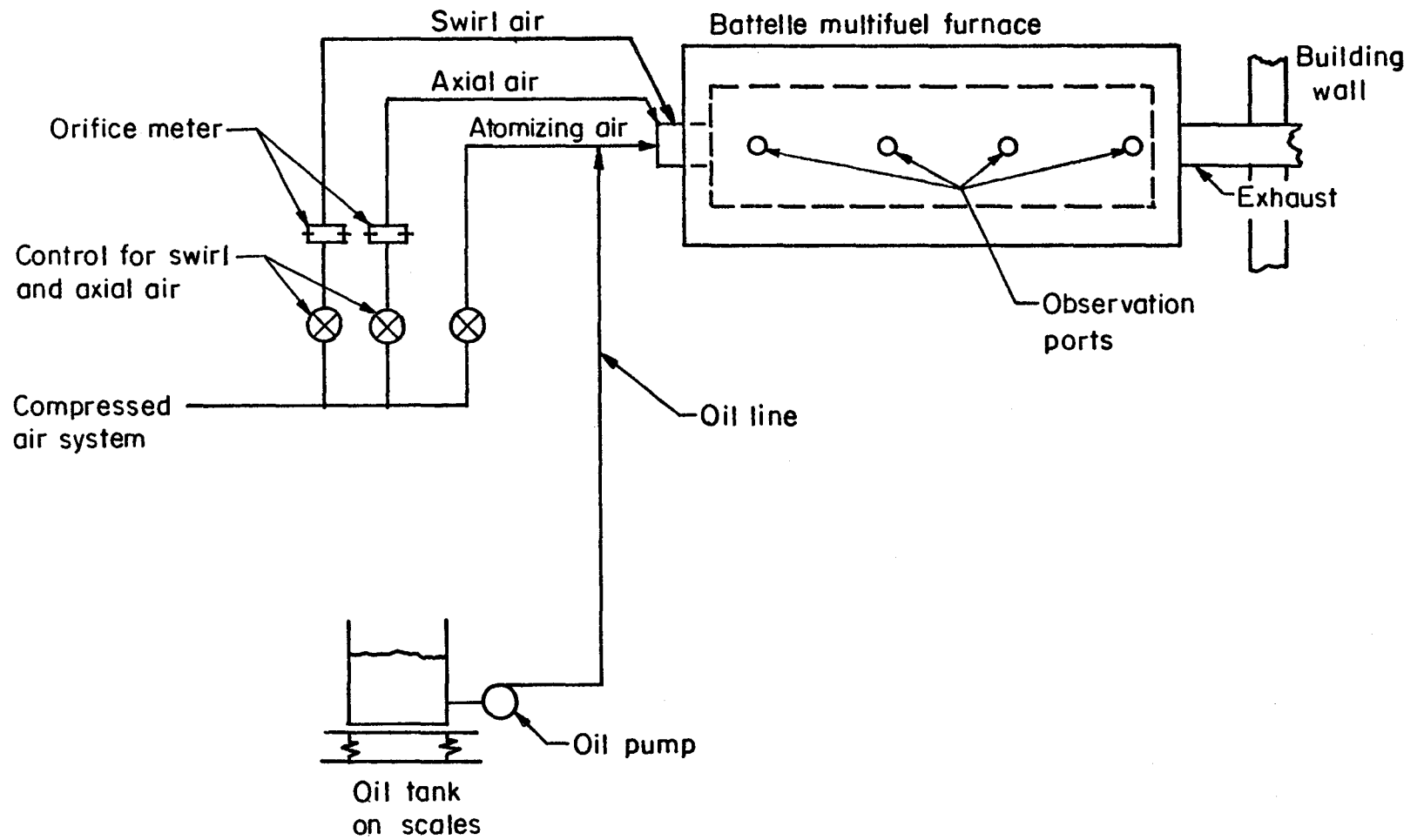


FIGURE 6. SCHEMATIC DIAGRAM OF THE BATTELLE MULTIFUEL FURNACE ARRANGED FOR FIRING WITH FUEL OIL

Figure 7 is a view of the multifuel furnace from the burner end. The exhaust passes out the other end through the building wall into the main stack except for a portion that is diverted into an exhaust cooling loop which reenters the building wall to the sampling system inside the pilot plant area.

The range of operating conditions of the multifuel furnace during the test series is given in Table 1.

TABLE 1. RANGE OF MULTIFUEL FURNACE OPERATING CONDITIONS FOR SO_x TESTS

Fuel	Firing Rate, GPH	Flue Gas Comp., %		Max Furnace Temp, F	Flue Gas Temp, F ^(a)	
		CO ₂	O ₂		U	S
#2 Fuel Oil	1.5-3.0	10-15	1.2-7.8	2580-2730	370-500	400-470

(a) U-unspiked sampling line temperature
S-spiked sampling line temperature

Sampling System. The sampling system was assembled from 3-inch anodized aluminum pipe for the main loop carrying unspiked flue gas, and from 2-inch anodized aluminum pipe for the branch loop in which an accurately measured flow of spiked flue gas was prepared and sampled. The spike was a precisely metered flow of sulfur dioxide (Matheson, C.P.) which produced a known concentration increase of SO₂ in the flue gas taken from the spiked loop.

Figure 8 is an overhead view of the sampling system and Figure 9 is a dimensioned sketch from approximately the same aspect as Figure 8. The flue gas stream enters near the bottom of the wooden panel in the outside wall of the area, as shown in the left center of the photograph. The entering line branches into two insulated legs, one of which proceeds along the wall to feed the spiked loop and the main stream of flue gas is carried away from the wall to beneath the round sampling table for unspiked gas at the bottom center of the picture. A vertical riser of the sampling line turns upward and passes upward through the center of the table to the 12-port sample manifold. Flexible insulated Teflon connectors are attached to some of these ports in the picture with their exits resting on the table surface. These carry the individual samples to the sampling systems of each of the participating laboratories during the tests.

The vertical portion of the return leg in the loop above the sample manifold is also thermally insulated to prevent condensation and flow of condensate into the sampling ports. The uninsulated 3-inch return line

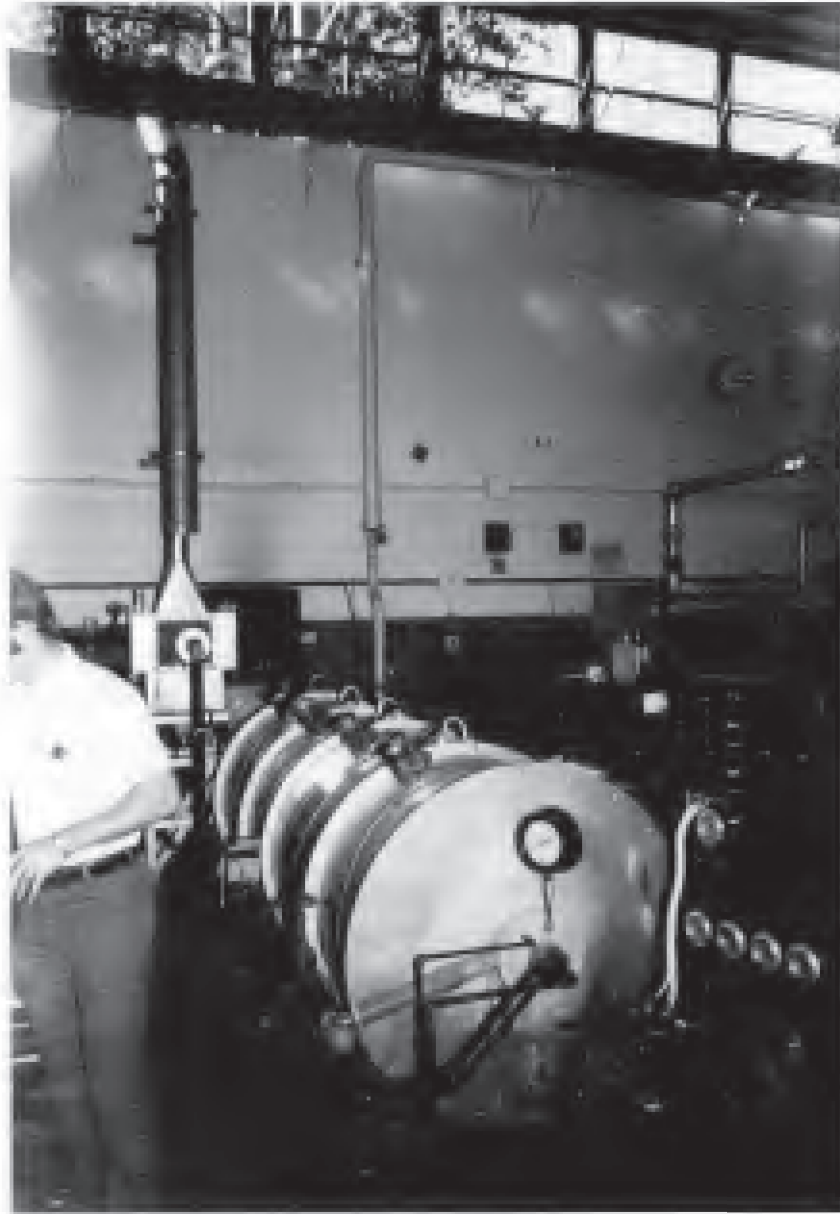
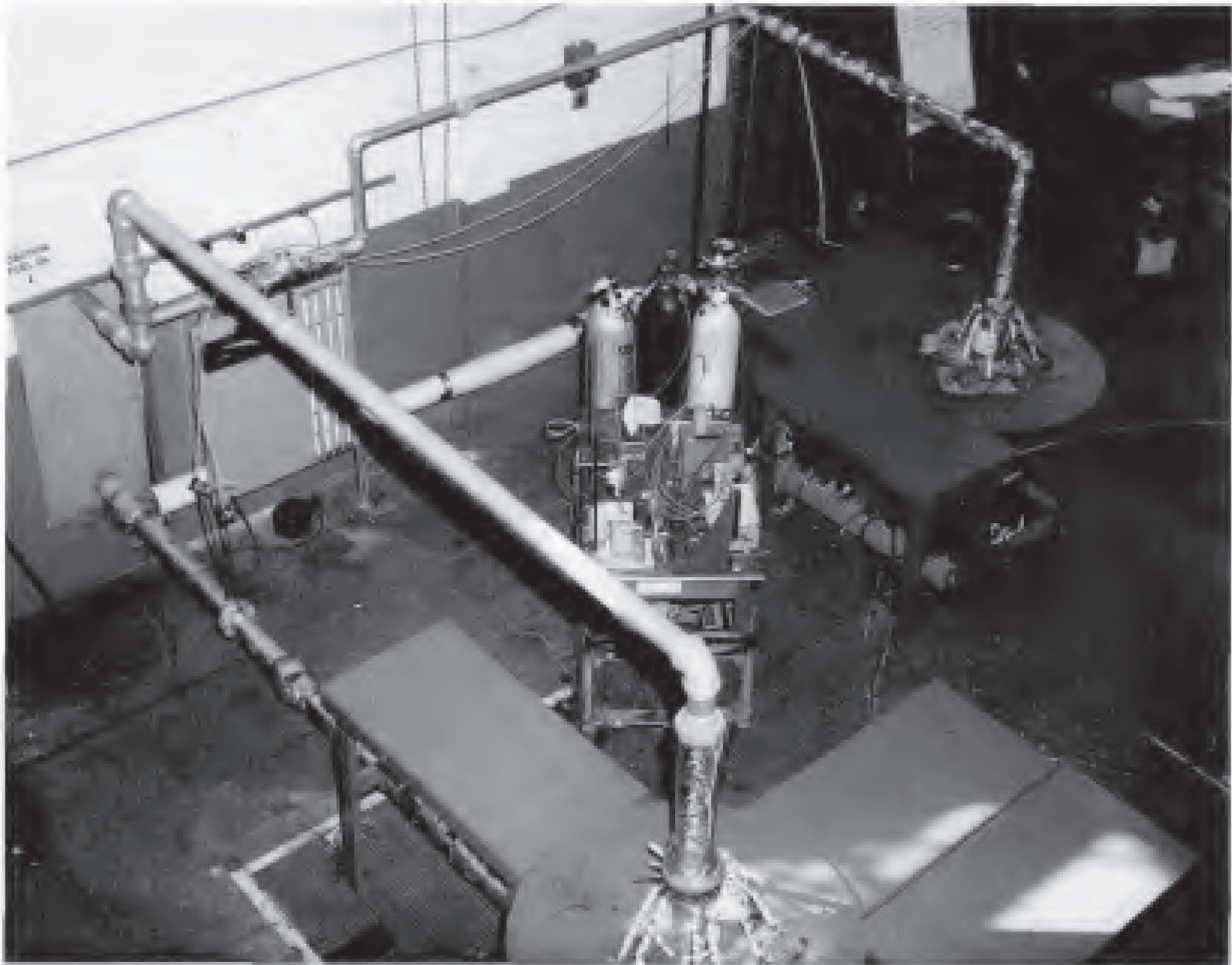


FIGURE 7. MULTIFUEL FURNACE SETUP FOR GENERATING FLUE GASES FROM COMBUSTION OF NATURAL GAS OR FUEL OIL



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FIGURE 8. OVERHEAD VIEW OF SAMPLING SYSTEM

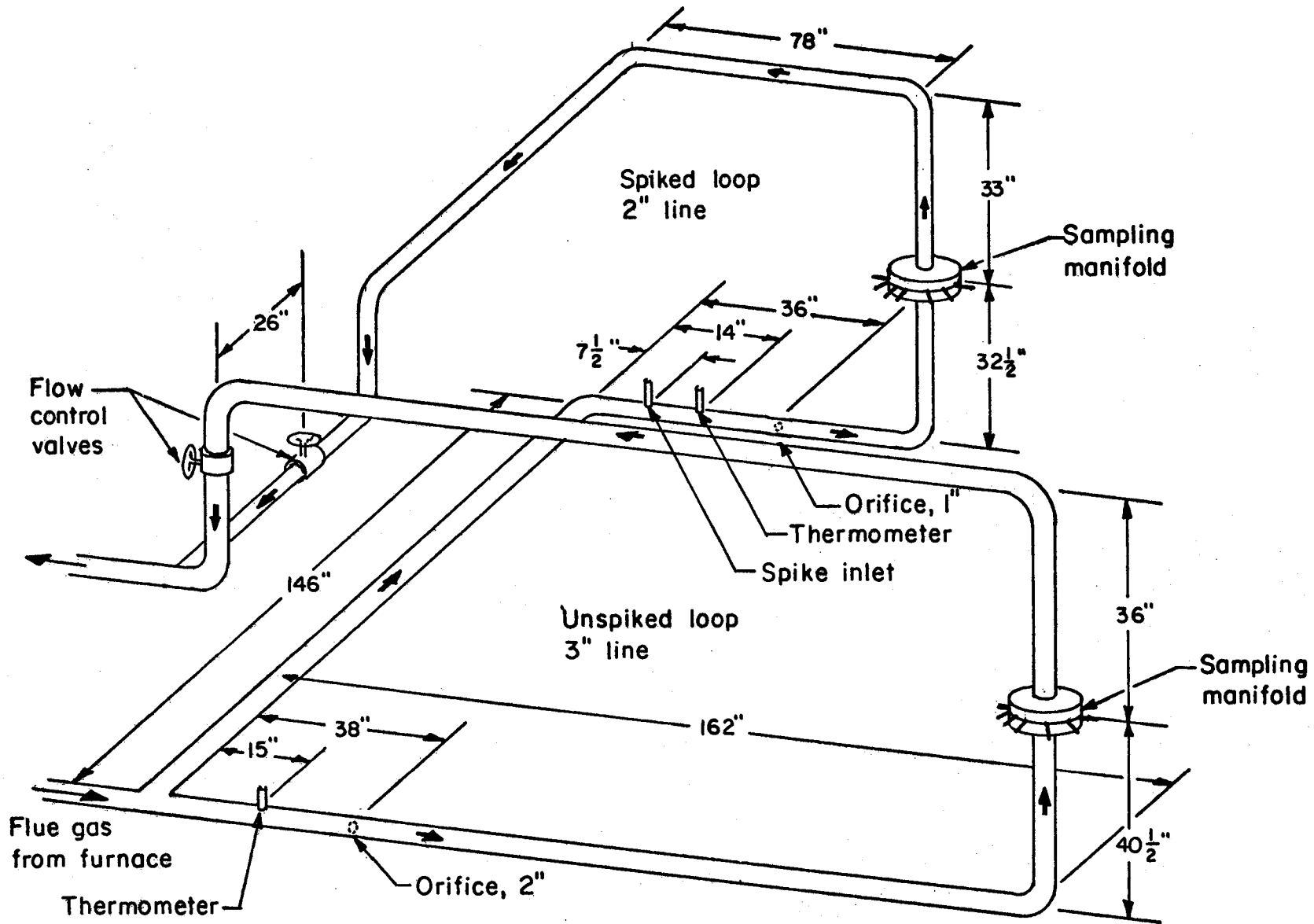


FIGURE 9. DIMENSIONED SKETCH OF SAMPLING SYSTEM

then proceeds back to the building wall where it connects with the return portion of the spiked gas loop for discharge of the combined flows of the two loops through the pipe passing outside the building through the top of the wall panel.

Similarly the incoming leg of the branch loop turns away from the wall and then upward through the center of the round table in the background of the picture to the spiked-sample manifold with its flexible connectors resting on the table surface. The return loop is also insulated part way to prevent condensate from flowing back to sample ports.

It was found advisable to add electric heating by thermal tapes inside the insulating cover of both incoming legs of the two loops to control the temperature of both gas streams well above the condensation temperature at the tips of the connectors. Initially condensate formed at these tips until insulation was added and the sample streams were allowed to flow continuously to keep the flexible tubing hot between samples. Figure 10 shows laboratories using the sampling apparatuses in concurrent sampling during the pilot plant tests.

Figure 11 is a closeup view of the spiked-sample loop with sampling table and flexible connectors in the foreground; a cylinder of the spiking gas with associated metering equipment stands on the floor inside the turn of the pipe carrying the incoming stream. Details of the spike measuring apparatus are given below. In the background behind the sampling table is a partial view of the monitoring instruments which were used to measure the concentrations of in both loops during the sampling sessions to be certain that the furnace was generating approximately the desired amount of sulfur oxides, and that the gas streams were properly equilibrated before sampling proceeded.

Spiking Procedure

A gaseous spike of sulfur dioxide was injected into the flow stream of flue gas from a cylinder of the gas which assayed 99.80 percent SO_2 . The impurities were determined in the Battelle analytical laboratory by mass spectrometry as follows: carbon dioxide, 0.16 percent; nitrogen, 0.04 percent. The flow rate of spiking gas was controlled by a critical flow orifice with a constant upstream pressure measured by a precision pressure gauge. The temperature of the spiking gas was equilibrated at ambient and the flow rates were so small that no appreciable cooling occurred during expansion through the pressure control and the orifice.

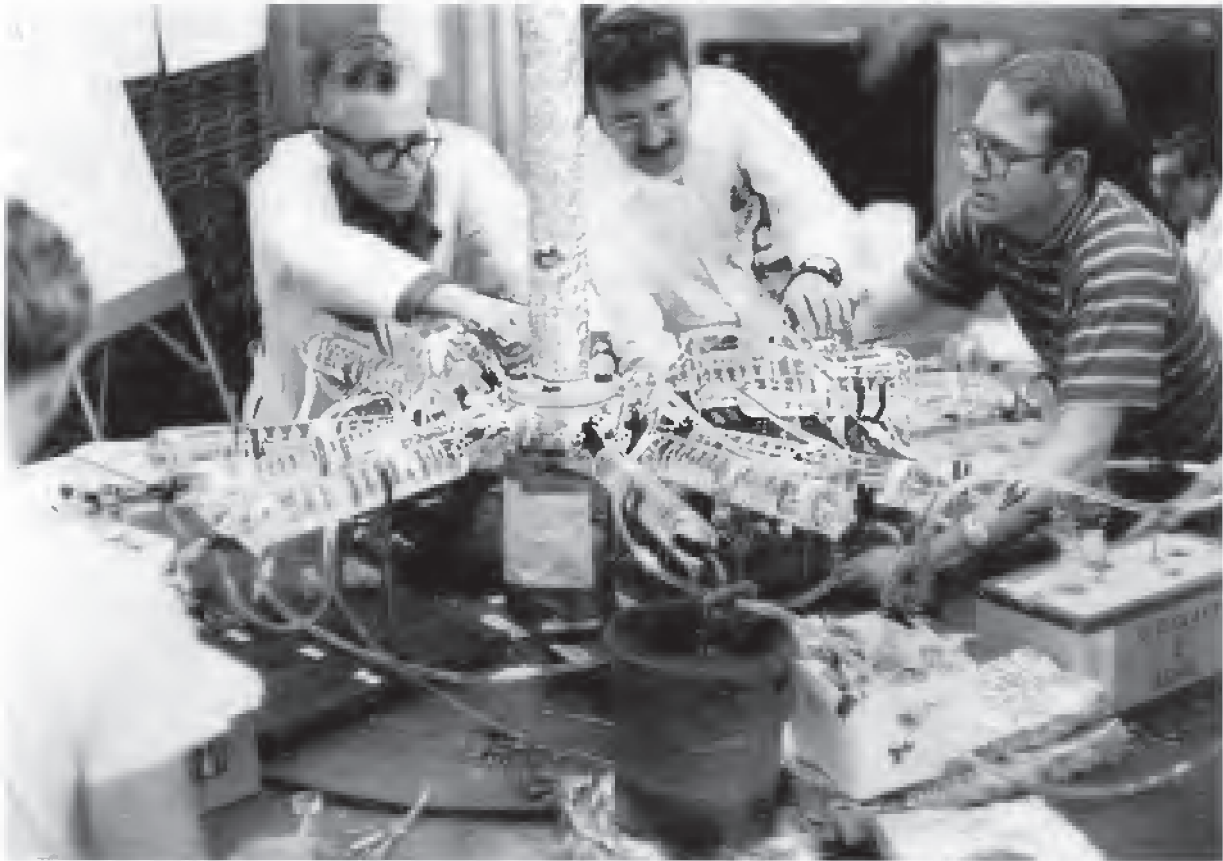
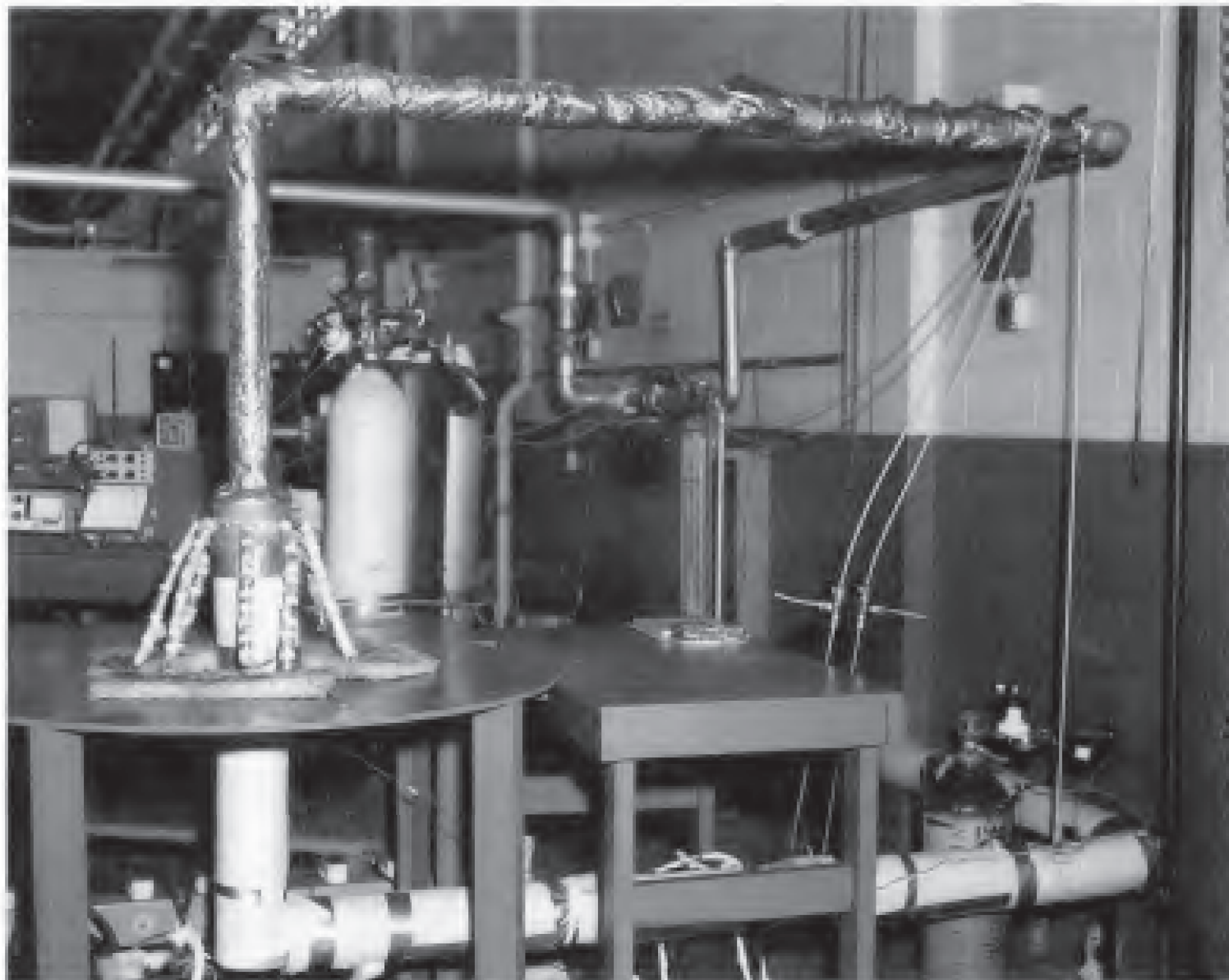


FIGURE 10. COOPERATION LABORATORIES PERFORMING CONCURRENT SAMPLING IN PILOI PLANI TESTS OF ASTM D 3226-73I



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FIGURE 11. CLOSE-UP VIEW OF SPIKED SAMPLE LOOP

A 1/16-inch flexible polyethylene tube attached to the orifice housing and to the injection fitting in the pipe wall by leak-proof connectors carried the spike into the flue gas stream. A photo showing details of the spiking system is presented in Figure 12. The precision gauge had a mirror background to avoid parallax errors in reading the needle and a scale divided into tenths of a pound.

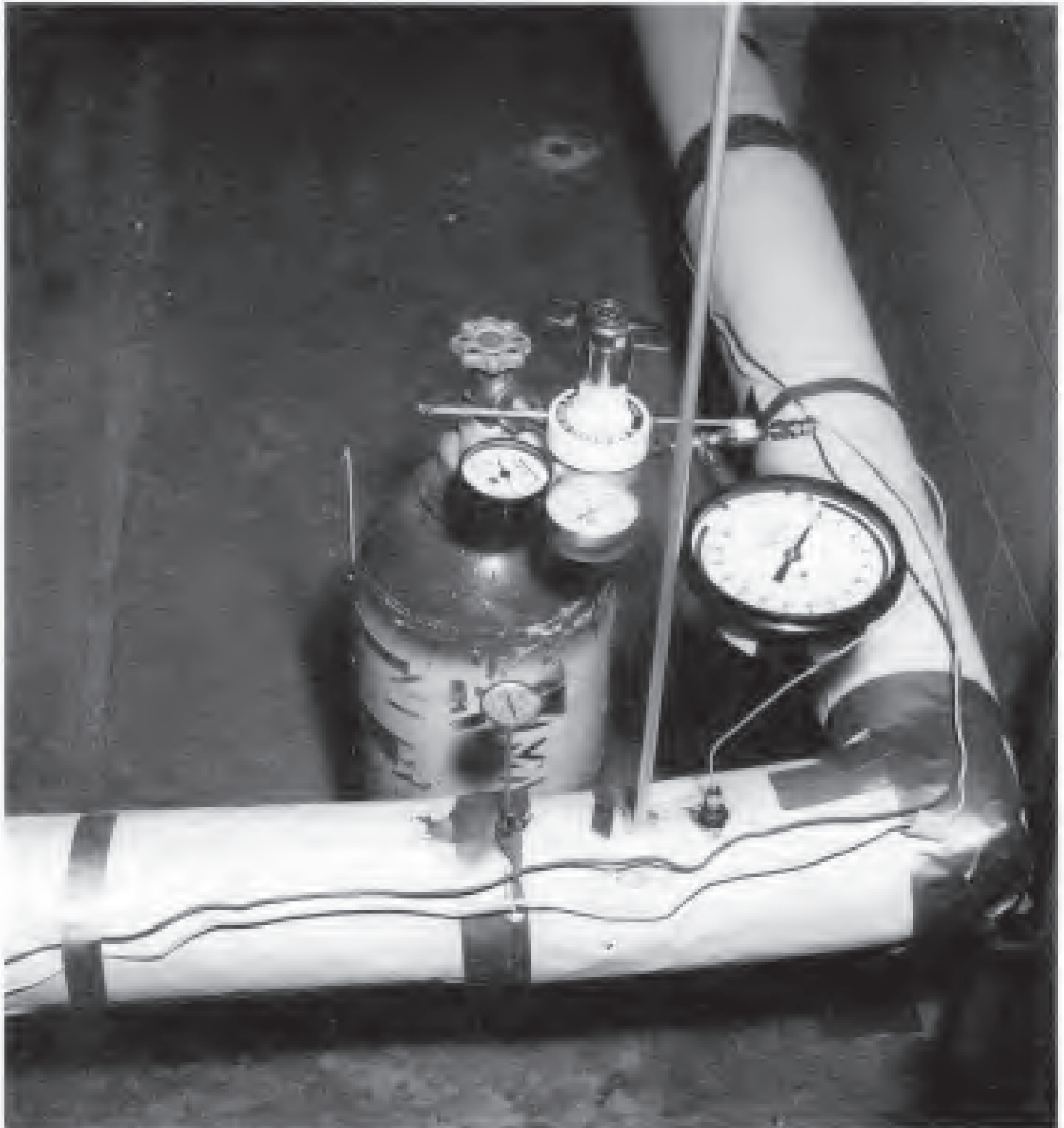
Three critical flow orifices available for use over a range of flows were specially fabricated from watch jewels having bore diameters of 0.08 to 0.14 mm which covered the range from about 75 to 217 ml of SO₂ per minute from a 15-psig source. These metering orifices were calibrated by a gravimetric procedure. A small cylinder of the pure spiking gas was fitted with a regulator, the precision pressure gauge, and the orifice undergoing calibration in the same manner as the operating system shown in Figure 9. Gas pressure was adjusted to 15 psig and the entire assembly was placed on a 10-kg top loading balance. A balance reading device was devised to reduce parallax error. The weight loss of the assembly was monitored over a period of several hours and the resulting data were used to determine a gravimetric rate for each orifice, using a least squares fit.

In a separate experiment it was determined that the orifice rates were unaffected by a downstream back pressure of 12 inches of water, which was several times the pressure of the sampling loop. A subsequent experiment demonstrated that the rates were independent of ambient temperatures over the range 15 to 30°C.

The calibration of the spiking system equipment and addition of the known quantities of sulfur dioxide during the tests was performed by Dr. R. H. Johns, ASTM Fellow at the National Bureau of Standards.

Sampling Procedure

The sampling procedure followed the instructions prescribed by the the printed method (see Appendix), although the coordinating laboratory selected certain options which are left to the choice of the analyst by the method. Each laboratory brought their own components for two sampling trains except the glass condensing coil which was supplied by Battelle. Battelle also provided the thermostated water baths and operated them during the tests. The SO₃ condenser and SO₂ absorbers were connected to the pumping system with appropriate devices for measuring pressure, temperature, flow, and cumulative volume of each



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FIGURE 12. DETAIL OF SPIKE INJECTION SYSTEM

sample. Flow rate was set at 1 liter per minute for all samples and was maintained within 5 percent variation from the nominal value throughout the sampling periods. Samples were taken for periods of 15 or 30 minutes, depending upon the concentration level of SO_2 expected. Sampling was started and stopped simultaneously on signal. Each crew followed the specified procedure for transferring the collected sulfates derived from SO_3 and SO_2 separately and quantitatively to containers for transport to the home laboratory and subsequent analysis. The condensers and impingers were rinsed with sulfate-free water and methanol prior to use in subsequent tests.

A few variations from normal procedure occurred and were handled as best judgment would dictate. When a connection was faulty on a single train, for example, the remaining samples were continued, and the faulty one discarded. In one instance a sampling period was shortened by equipment failure, but all samples were comparable and were accepted as valid.

Test Pattern

The test pattern was selected with the objectives of providing comparisons that would deduce the within-laboratory component of variance (repeatability), the between-laboratory component of variance (reproducibility), and the accuracy of the method for determination of SO_x in actual samples over a wide range of SO_x concentrations derived from natural combustion of sulfur compounds in the fuel and by the spiking process of adding sulfur dioxide to the flue gas. Table 2 shows the target pattern of operating that was developed in planning the statistical pattern. Four operating variables were used in controlling the amount of SO_2 between about 500 ppm and 3000 ppm. These variables included two fuel rates to vary the furnace temperature, appropriate amounts of excess air for each fuel, low-sulfur fuel oil and the same oil doped with sulfur-containing carbon disulfide and appropriate spiking rates with sulfur dioxide to cover the approximate range for which the test method was expected to be valid. The test pattern outlined in the first column of Table 2 shows 14 daily blocks. Each block constituted a pair of samples taken by each laboratory during one sampling period which extended for 15 to 30 minutes. Table 3 shows the actual sequence of sampling achieved during Thursday and Friday of each test week. It was found convenient to alter the order of the daily blocks in order to minimize the

DAILY BLOCKS				THURS (4)	FRI (5)		
No.	Positions			High Fuel Rate	Low Fuel Rate		
1	Each lab: Two spiked samples	Lo Spike	Undoped Fuel Oil	Sulfur Oxides Tests			
2	Each lab: One spiked, one unspiked			Lo Spike	Undoped Fuel Oil	Blocks 1-14 3 GPH No. 2 oil 20% excess air	Blocks 1-14 1-1/2 GPH No. 2 oil 5% excess air
3	Each lab: One spiked, one unspiked						
4	Each lab: Two unspiked						
5	Each lab: One spiked, one unspiked	Hi Spike	Undoped Fuel Oil				
6	Each lab: One spiked, one unspiked						
7	Each lab: Two spiked samples			Blocks 1-3 SO ₂ spike 400 ppm Target total = 900 ppm	Blocks 1-3 SO ₂ spike 400 ppm Target total = 900 ppm		
8	Each lab: Two spiked samples	Lo Spike	Undoped Fuel Oil (N or S)	Blocks 5-7 SO ₂ spike 760 ppm Target total SO ₂ 1260 ppm	Blocks 5-7 SO ₂ spike 760 ppm Target total SO ₂ 1260 ppm		
9	Each lab: One spiked, one unspiked						
10	Each lab: One spiked, one unspiked			Blocks 8-14 Doped fuel 3% S as CS ₂ Targets 1800 SO ₂ 30 ppm SO ₃	Blocks 8-14 Doped fuel 3% S as CS ₂ Targets 1800 SO ₂ 10 ppm SO ₃		
11	Each lab: Two unspiked	Hi Spike	Doped Fuel Oil (N or S)	Blocks 8-10 SO ₂ spike 760 ppm Target total 2560 30 ppm SO ₃	Blocks 8-10 SO ₂ spike 760 ppm Target total 2560 10 ppm SO ₃		
12	Each lab: One spiked, one unspiked						
13	Each lab: One spiked, one unspiked						
14	Each lab: Two spiked samples			Blocks 12-14 SO ₂ spike 1410 ppm Target total 3210 30 ppm SO ₃	Blocks 12-14 SO ₂ spike 1410 ppm Target total 3210 10 ppm SO ₃		

TABLE 2. TARGET PATTERN OF SO₂ SPIKE CONCENTRATIONS FOR PILOT PLANT TESTS AT BATTELLE

TABLES 3. SO_x SAMPLES TAKEN DURING PILOT PLANT TESTS

Date, 1972	Hours	Week No.	Day No.	Sequence of Samples by Block Number
Oct. 12	p.m.	1	4	8, 11, 14, 12, 13, 9
Oct. 13	a.m.	1	5	1, 4, 7, 5, 2
Oct. 13	p.m.	1	5	8, 11, 14, 12, 9, 10
Oct. 19	a.m.	2	4	1, 4, 7, 6, 2
Oct. 19	p.m.	2	4	8, 11, 14, 13, 9, 10, 12
Oct. 20	a.m.	2	5	11, 8, 14, 4, 1, 7
Oct. 20	p.m.	2	5	13, 12, 9, 10, 2, 3

number of changes of apparatus to another sampling location or for convenience in equilibrating the furnace and sampling system after a change in operating conditions. An acceptably large part of the planned series was completed successfully to permit statistical analysis of the data obtained.

During each test block, the SO_2 concentration was monitored with an Environmetrics Model NS-200 Faristor unit to verify flue gas concentrations and spike values were being achieved. The Faristor detector is a liquid-state device in which the pollutant being measured is absorbed by catalytic action on an activated surface. A change in oxidation state occurs resulting in a surface charge the magnitude of which is proportional to the pollutant concentration. The unit used in these tests is also capable of measuring NO_x in addition to SO_2 .

Field Tests

Measurement of sulfur oxides in flue gas were performed in field tests at three sites; an oil-fired power plant, a coal-fired power plant, and a cement plant. Descriptions of the emission sources and the field test procedures are given in the following sections.

Test Site Descriptions

The characteristics of the three test sites at which the test method was evaluated are summarized in Table 4.

Site I

Tests at Site I were performed on a 120 MW oil-fired unit of an electrical generating station. During the testing period the unit was fired with a low-sulfur fuel and was operated under steady-state conditions at full load capacity.

Sulfur oxides measurements were made in four ports located in a vertical run of the rectangular duct which is one of a pair that conducts the flue gas from the induction fan to the stack. The flow is approximately uniform between the two ducts. Curvature in the duct causes some irregularities in the flow pattern at the test location.

The SO_2 and SO_3 concentrations during the test series were on the order

TABLE 4. SUMMARY OF TEST SITE CHARACTERISTICS

Site Characteristic	Site I	Site II	Site III
Type of Operation	Electrical generation (120 MW Unit)	Electrical generation (two -800 MW Units)	Portland Cement Mfg. (dry process)
Emission Source	Oil-fired boiler	Coal-fired boilers	Coal-fired kiln
Emission Control Equipment	Electrostatic precipitator	Electrostatic precipitator	Electrostatic precipitator
Fuel Data			
Feed Rate	63,000 lb/hr	500 ton/hr	5500 lb/hr
Excess Air	30% (b)	50% (b)	
Composition - C (wt. percent)	86.5	(fixed, dry) 50.6	(fixed, dry) 52.9
- H	12.6	--	--
- N	0.25	--	--
- S	0.43	3 - 4	2.8
		Volatiles 33.5	Volatiles 36.0
Flue Gas Data			
Average Velocity, fps	60	120	72-97
Average Gas Temperature, F	280	330	340-370
Composition - CO ₂ Volume Percent	11.6	12.0	10.0
- O ₂ Volume Percent	5.4	6.8	13.4
- H ₂ O Volume Percent	8-10	5-7	4-6
- SO ₂ ppm	225	2200	800-1500
- NO _x ppm (as NO ₂)	140-220	~300-400	100-250
Stack Data			
Size	4.67 ft x 12 ft	30 ft diameter	4 ft diameter
Height	(duct prior to stack)	1200 ft	50 ft

(a) NA - not applicable.

(b) Based on Orsat analysis at test port location.

of 225 and 2 ppm, respectively.

Site II

Site II is a large coal-fired electrical generating station which has two units with a total production capacity of about 1600 MW. During most of the tests, the units operated at an output of about 1400 MW. During Tests 12 and 13, one of the units was operated at reduced load capacity.

The sulfur oxides measurements were performed in the stack which handles the combustion products for both units. The four test ports, which are spaced at 90 degrees around the stack, are located at the 300-ft stack level. The port location is at least eight stack diameters above the inlets at the base of the stack. SO₂ concentrations during the test series were in the range of about 2000 ppm.

Site III

Test Site III is a dry process portland cement manufacturing plant. At the site, tests were conducted using two different stacks carrying emissions from 10-ft diameter by 154-ft long cement kilns.

Tests 1 through 12 and 13 through 24 were performed on different stacks. Test ports in both stacks are located at 90 degree angles at a stack height of about 28 feet (about seven stack diameters) above the induction fan. The SO₂ and SO₃ concentrations were about 1200 and 7 ppm, respectively.

Sampling Procedure

Sampling at each field site was performed as prescribed in the Test Method using the apparatus described previously. Borosilicate glass probes about four feet in length were used to withdraw the stack gas samples. The probes were heated to 320 F to prevent condensation of moisture and SO₃/H₂SO₄. A glass or quartz wool plug was inserted in the probe at the inlet end to remove particulates.

The sampling period at each test site was 15 minutes. Sampling was performed at a nominal rate of one liter per minute at standard conditions.

Test Patterns

A total of 32 SO_x measurements were made at Site I by four different laboratories. Each laboratory performed sampling at a different sampling port and port assignments were the same for all tests. All tests were performed on the same day.

Site II tests included four different laboratories, each of which performed 16 SO_x measurements for a total of 64 measurements. Port assignments were varied during the test in accordance with the pattern shown in Table 5. Tests 1 through 8 were performed during the first test day and Tests 9 through 16 were completed on the following day.

Six different laboratories participated in the Site III test. Concurrent sampling was performed by groups of four laboratories in the pattern shown in Table 6. Forty-eight measurements, Tests 1 through 12 were performed during the first day of the first test week. Tests 13 through 24, also 48 measurements, were made during the first test day of the following week. At Site III the SO₃/H₂SO₄ condensers were exchanged among the cooperating laboratories in a selected pattern.

Analysis of Standard Sulfate Solutions

A series of solutions containing known quantities of sulfate were supplied to each participating laboratory following the pilot plant tests and field tests at Sites II and III. These standard solutions were to be analyzed along with collected samples to obtain data on the accuracy and precision of the analytical portion of the Test Method.

The solutions were prepared and distributed by Dr. R. H. Johns.

Participating Laboratories

A total of ten laboratories participated in the pilot plant and field tests in which the sulfur oxide method was evaluated. The participants were teams from the following organizations:

George D. Clayton and Associates

The Detroit Edison Company

General Motors Corporation

Huron Cement Division of National Gypsum Company

Marquette Cement Manufacturing Company

TABLE 5. SAMPLING PATTERN FOR SO_x TESTS AT
FIELD SITE II

Test Number	Port Number			
	1	2	3	4
1 & 2	B	A	D	C
3 & 4	C	B	A	D
5 & 6	D	C	B	A
7 & 8	A	D	C	B
9 & 10	B	A	D	C
11 & 12	C	B	A	D
13 & 14	D	C	B	A
15 & 16	A	D	C	B

TABLE 6. SAMPLING PATTERN FOR SO_x TESTS AT
FIELD SITE III

Test Number	Port Number			
	1	2	3	4
1 through 4	A	C	B	D
5 through 8	D	A	C	B
9 through 12	B	D	A	C
13 through 16	F	E	C	A
17 through 20	A	F	E	C
21 through 24	C	A	F	E

Public Service Electric and Gas Company (New Jersey)

Research Triangle Institute

TRW

Western Electric Company

York Research Corporation.

Throughout this report the data generated by the various laboratories are concealed by using a set of code letters. The code letters designate different laboratories at each test site.

STATISTICAL ANALYSIS OF SULFUR OXIDE TESTSStatistical Measures

The experimental program was designed and conducted to provide measures of the precision and accuracy of the sulfur oxides method.

Measure of Precision

ASTM Method D 2906-70T⁽¹²⁾ defines precision as "the degree of agreement within a set of observations or test results obtained when using a method". The document further defines specific sources of variability in measuring precision, namely

Single-operator precision - the precision of a set of statistically independent observations, all obtained as directed in the method and obtained over the shortest practical time interval in one laboratory by a single operator using one apparatus and randomized specimens from one sample of the material being tested.

Within-laboratory precision - the precision of a set of statistically independent test results all obtained by one laboratory using a single sample of material and with each test result obtained by a different operator with each operator using one apparatus to obtain the same number of observations by testing randomized specimens over the shortest practical time interval.

Between-laboratory precision - the precision of a set of statistically independent test results all of which are obtained by testing the same sample of material and each of which is obtained in a different laboratory by one operator using one apparatus to obtain the same number of observations by testing randomized specimens over the shortest practical time interval.

The estimates of these measures of precision are formed by combining components of variance which are typically derived from an analysis of variance. In section 5.4 of ASTM Method D 2906-70T, the components of variance obtained from an analysis of variance table are given the following notations:

S_S^2 = the single operator component of variance, or the residual error component of variance.

S_W^2 = the within-laboratory component of variance

S_B^2 = the between-laboratory component of variance

With the above components of variance, the standard errors (S_T) of specific types of averages are calculated as follows:

$$\text{Single-operator standard error} \\ S_T \text{ (single-operator)} = (S_S^2/n)^{1/2}$$

$$\text{Within-laboratory standard error} \\ S_T \text{ (within-laboratory)} = [S_W^2 + (S_S^2/n)]^{1/2}$$

$$\text{Between-laboratory standard error} \\ S_T \text{ (between-laboratory)} = [S_B^2 + S_W^2 + (S_S^2/n)]^{1/2},$$

where n is the number of observations by a single operator averaged into a determination. (If S_S^2 is not determined separately from S_W^2 in the equations above, it is understood to be part of S_W^2 and should be deleted from the expressions).

The pilot plant tests provide data for the estimate of between-laboratory and within-laboratory precision. The testing pattern was not designed to determine the operator component of variance. Thus, variance due to operators within a laboratory, S_S^2 , is combined in the estimate of within-laboratory variance S_W^2 .

The cooperating laboratories concurrently performed duplicate determinations of SO_x in the pilot plant study. Differences among the concurrent measurements provided a means of estimating the variability among laboratories, while differences between duplicate measurements provided a measure of variability within laboratories. Using the analysis of variance procedure, components of variance within-laboratories and between-laboratories were estimated. The within-laboratory component of variance, S_W^2 , estimates the variance of duplicate (or more generally, replicate) measurements made on the same material in a single laboratory. The square root of this component of variance is referred to as the within-laboratory precision, or repeatability in this report, and is denoted by the symbol S_W .

The other component of variance estimated by the analysis, S_B^2 , can be understood in terms of a "population of populations". Each laboratory's results can be assumed to represent sampling from a population of results for that laboratory, where the population has a variance, S_W^2 . This variance is assumed to be the same for all laboratories. However the mean of each laboratory's population of results is a quantity which is assumed to vary from laboratory to laboratory. Considering a large number of laboratories, the mean becomes a

random variable itself. The estimated component of variance, S_B^2 , estimates the variance of this population of means. The square root of this estimated component of variance is referred to as the between-laboratory precision, or reproducibility, in this report, and is denoted by the symbol, S_B .

The estimates of repeatability and reproducibility, as defined above, allow for the calculation of standard errors (S_T) of specific types of averages, e.g. the between-laboratory standard error, S_T (between-laboratory). More general calculations also follow. Suppose, for example, that a number of laboratories collect samples from which each laboratory submits an average determination of SO_x concentration based upon 2 measurements. The amount of variability to be expected in these averages of 2 measurements, from laboratory to laboratory, is $S_B^2 + S_W^2/2$, since each average contains two sources of variation - variability between the means, measured by S_B^2 , and variability within each laboratory, which is reduced by averaging 2 measurements from each laboratory, i.e. $S_W^2/2$. Details of the procedures used to calculate S_W^2 and S_B^2 are presented in the data analysis section of this report.

It should be noted that the usage of the terms "reproducibility" and "repeatability" varies in the literature. Some sources relate the terms to maximum values which will be exceeded by the absolute difference of two randomly selected test results only about 5 percent of the time in repeated experiments, e.g. Mandel⁽¹³⁾. Others use less quantitatively oriented definitions, e.g. Davies⁽¹⁴⁾. The usage in this report can be directly applied to statements of precision, as outlined in ASTM Method D 2906-60T and E 177⁽¹⁵⁾, and is consistent with the usage in other Project Threshold reports.

The field site tests of D 3226-73T provide an estimate of between-laboratory standard error, S_T (between-laboratory), for the determination of SO_x in flue gas. The relationship of between laboratory standard error to the components of variance discussed previously is expressed by Equation (5), ASTM D 2906-70T, as S_T (between-laboratory) = $[S_B^2 + S_W^2 + (S_S^2/n)]^{1/2}$ where n is the number of observations by a single operator averaged into a determination. Field testing limitations did not permit conduct of the testing pattern in such a manner that the individual components of variance, S_B^2 , S_W^2 , and S_S^2 , could be computed. At each site, groups of four laboratories performed SO_x determinations with each laboratory making one determination per test. For this situation the between-laboratory standard error, S_T (between-laboratory), is the same as the standard deviation of the four concurrent SO_x determinations. It should be noted from the above definition that S_T (between-laboratory) includes

the individual components of variance, but it should not to be confused with either repeatability or reproducibility, as defined and used in this or previous Project Threshold reports.

Measure of Accuracy

Accuracy is defined in D 2906-70T as "the degree of agreement between the true value of the property being tested (or an accepted standard value) and the average of many observations made according to the test method, preferably by many observers". Disagreement between the true value and test results may occur as a systematic difference or error which is called bias.

The accuracy of SO₂ measurements by D 3226-73T is estimated from the pilot plant tests in which the cooperating laboratories performed duplicate determinations in which one of the flue gas samples was spiked with a known concentration (true value) of sulfur dioxide. The difference between a laboratory's determinations for such a sample pair is an estimated measure of the true value of the spike. Differences between this experimentally determined quantity and the true value of the spike provide a measure of the accuracy of the test method.

The data are reported as the percentage between the measured and true concentration of the spike, relative to the true concentration. The estimate of accuracy is derived from the average of these differences.

Experimental Results

Pilot Plant Tests

The results obtained from the pilot plant tests of ASTM Method D 3226-73T in accordance with the pattern given in Table 2 are summarized in Tables 7 through 12. All values are reported as parts per million of SO₂ or SO₃.

The data in Tables 7 through 12 contain results of tests where spiked and unspiked samples of SO₂ were taken. Since spiking of SO₃ was not performed, all results presented for SO₃ represent duplicate determinations of unspiked samples. For SO₂, the results shown in Table 7 through 10 represent duplicate determinations, either spiked or unspiked. Tables 11 and 12 represent results for tests in which both a spiked and an unspiked determination of SO₂ were made. Table 7, 9, and 11 present results obtained by six cooperating laboratories (coded A through F) during the first week of tests, and Tables 8, 10, and 12 contain the second week's test data for four

TABLE 7. RESULTS OF PILOT PLANT SO_x DETERMINATIONS FOR BLOCKS IN WHICH LABORATORIES OBTAINED DUPLICATE SO₂-SPIKED SAMPLES (FIRST WEEK)

(Results in ppm SO₂ or SO₃)

Week	Day	Block	Lab	SO ₂		SO ₃	
				Sample 1	Sample 2	Sample 1	Sample 2
1	4	1	A	880	878	2	9
			B	684	691	28	42 (a)
			C	643	698	11	3
			D	647	663	18	14
			E	1590	1550	104 (a)	110 (a)
			F	719	640	23	24
1	4	7	A	1038	1059	10	16
			B	481	943	37	36
			C	1013	1032	8	6
			D	981	972	9	9
			E	(b)	(b)	(b)	(b)
			F	1091	1124	23	15
1	4	8	A	2165	2250	25	19
			B	714	710	38	32
			C	1851	(c)	33	(c)
			D	1900	1910	68	58
			E	2370	(c)	92 (a)	(c)
			F	1926	1935	35	25
1	4	14	A	2058	1548	11	25
			B	436	659	40	35
			C	2108	2320	19	9
			D	2430	2470	20	15
			E	2320	1010	58 (a)	53
			F	2458	2414	25	26
1	5	8	A	(d)	1656	(d)	27
			B	246	332	48	38
			C	1715	2307	10	6
			D	2260	2270	36	64 (a)
			E	2200	2140	24	25
			F	2264	2174	37	12
1	5	14	A	2817	(d)	9	(d)
			B	233 (a)	384 (a)	95 (a)	34
			C	1864	2698	12	8
			D	2620	2660	11	10
			E	2710	2710	12	9
			F	2663	2689	18	17

(a) Outlying value based on statistical tests.

(b) Samples were not taken concurrently with other laboratories.

(c) Condenser frit plugged during sampling.

(d) Leak developed in sampling system.

TABLE 8. RESULTS OF PILOT PLANT SO_x DETERMINATIONS FOR BLOCKS IN WHICH LABORATORIES OBTAINED DUPLICATE SO₂-SPIKED SAMPLES (SECOND WEEK)
(Results in ppm SO₂ or SO₃)

Week	Day	Block	Lab	SO ₂		SO ₃	
				Sample 1	Sample 2	Sample 1	Sample 2
2	4	1	G	816	867	34	25
			H	944	906	18	21
			I	753	(a)	18	49
			J	726	731	17	17
2	4	7	G	936	940	11	12
			H	1012	1207	12	10
			I	1039	1028	19	28
			J	819	909	11	15
2	4	8	G	1684	(b)	42	(b)
			H	1795	1791	37	36
			I	1662	1796	56	15
			J	1735	1181	37	36
2	4	14	G	3319	2363	35	50
			H	2328	1957	51	56
			I	2173	2193	48	78
			J	2150	2230	44	48
2	5	1	G	838	836	5	7
			H	914	914	1	(c)
			I	874	945	11	15
			J	848	828	(c)	(c)
2	5	7	G	1217	1233	6	8
			H	1407	1296	7	(c)
			I	1252	1285	10	13
			J	1235	1239	(c)	(c)
2	5	8	G	1838	1816	12	16
			H	1989	1960	16	13
			I	1901	1980	18	16
			J	1796	1772	13	12
2	5	14	G	2452	2320	23	27
			H	2231	2613	32	26
			I	2527	2443	32	28
			J	2359	2481	21	17

(a) Low sampling rate.

(b) Equipment malfunction during sampling.

(c) SO₃ not detected.

TABLE 9. RESULTS OF PILOT PLANT SO_x DETERMINATIONS FOR BLOCKS IN WHICH LABORATORIES OBTAINED DUPLICATE UNSPIKED SAMPLES (FIRST WEEK)

(Results in ppm SO₂ or SO₃)

Week	Day	Block	Lab	SO ₂		SO ₃	
				Sample 1	Sample 2	Sample 1	Sample 2
1	4	4	A	123(a)	0(a)	5	1
			B	274	330	36(a)	32
			C	309	320	8	4
			D	274	268	7	4
			E	(b)	668(a)	(b)	14
			F	325	320	17	17
1	4	11	A	1716	1152	12	29
			B	750	871	39	47
			C	1156	1294	20	27
			D	1330	1350	36	35
			E	(c)	(c)	(c)	(c)
			F	1363	1395	30	17
1	5	11	A	1736	1593	28	14
			B	211	263	26	103(a)
			C	1129	1529	14	9
			D	1470	1490	26	13
			E	1430	1450	16	16
			F	1579	1544	24	24

- (a) Outlying value based on statistical tests.
 (b) Leak developed in sampling system.
 (c) Condenser frit plugged during test.

TABLE 10. RESULTS OF PILOT PLANT SO_x DETERMINATIONS FOR BLOCKS IN WHICH LABORATORIES OBTAINED DUPLICATE UNSPIKED SAMPLES (SECOND WEEK)

(Results in ppm SO_2 or SO_3)

Week	Day	Block	Lab	SO_2		SO_3	
				Sample 1	Sample 2	Sample 1	Sample 2
2	4	4	G	274	400	11	15
			H	334	297	12	23
			I	328	(a)	13	86(b)
			J	298	270	11	11
2	4	11	G	1016	1021	34	34
			H	1225	1274	47	43
			I	1033	1075	36	88(b)
			J	1319	986	42	37
2	5	4	G	456	466	10	6
			H	502	549	(c)	2
			I	414	577	10	13
			J	376	467	(c)	(c)
2	5	11	G	1142	1142	19	16
			H	1303	1147	25	24
			I	1168	1597	20	25
			J	1173	1177	12	14

(a) Low sampling rate

(b) Outlying value based on statistical tests.

(c) SO_3 not detected.

TABLE 11. RESULTS OF PILOT PLANT SO_x DETERMINATIONS FOR BLOCKS IN WHICH LABORATORIES OBTAINED CONCURRENT SO₂- SPIKED AND UNSPIKED SAMPLES (FIRST WEEK)

(Results in ppm SO₂ or SO₃)

Week	Day	Block	Lab	SO ₂		SO ₃		Estimated SO ₂ Spike Conc.	True SO ₂ Spike Conc.	Difference, % of True SO ₂ Conc.
				Spiked Sample	Unspiked Sample	Unspiked Sample 1	Unspiked Sample 2			
1	4	2	A	897	407	16	11	490	357	37.3
			B	643	398	32	54	245	357	-31.4
			C	705	366	10	17	339	357	-5.0
			D	739	381	55(d)	15	358	357	0.3
			E	686	216	36	22	470	357	31.7
			F	(a)	(a)	(a)	(a)	--	--	--
1	4	5	A	1154	321	9	(b)	833	808	3.1
			B	396	410	32	42	--	--	--
			C	1116	370	10	24	746	808	-7.7
			D	1160	379	19	103(d)	781	808	-3.3
			E	937	298	22	12	639	808	-20.9
			F	1286	547	7	23	739	808	-8.5
1	4	9	A	(c)	(c)	(c)	(c)	--	--	--
			B	619	406	39	84(d)	213	751	-71.6
			C	1936	1268	44	51	668	751	-11.1
			D	2000	1100	35	36	900	751	19.8
			E	5500	1100	60	12	4400	751	485.9
			F	2080	1317	28	41	763	751	1.6
1	4	12	A	1787	900	22	32	887	947	-6.3
			B	431	504	39	71(d)	--	--	--
			C	2291	1254	34	42	1037	947	9.5
			D	2320	1280	34	30	1040	947	9.8
			E	(a)	(a)	(a)	(a)	--	--	--
			F	(a)	(a)	(a)	(a)	--	--	--
1	4	13	A	(c)	(c)	(c)	(c)	--	--	--
			B	521	901	43	130(d)	--	--	--
			C	2440	1272	45	52	1168	1080	8.1
			D	2500	1240	39	42	1260	1080	16.7
			E	2300	913	82	42	1387	1080	28.4
			F	2870	1317	23	60	1553	1080	43.8

TABLE 11. (Continued)

Week	Day	Block	Lab	SO ₂		SO ₃		Estimated SO ₂ Spike Conc.	True SO ₂ Spike Conc.	Difference, % of True SO ₂ Conc.
				Spiked Sample	Unspiked Sample	Unspiked Sample 1	Unspiked Sample 2			
1	5	9	A	2279	1415	23	16	864	781	10.6
			B	179	526	29	31	--	--	--
			C	2187	1456	5	9	731	781	-6.4
			D	2100	1420	11	15	680	781	-12.9
			E	2250	1210	19	8	1040	781	33.2
			F	2425	1505	25	24	920	781	17.8
1	5	10	A	2150	1567	10	36	583	764	-23.7
			B	374	276	29	26	98	764	-87.2
			C	2161	1443	64(d)	18	718	764	-6.0
			D	2160	1320	12	12	840	764	9.9
			E	2150	1390	21	10	760	764	-0.5
			F	2224	1545	32	32	679	764	-11.1
1	5	12	A	2936	1531	30	7	1405	1101	27.6
			B	330	201	39(d)	28	129	1101	-88.3
			C	2757	1513	5	8	1244	1101	33.0
			D	2775	1280	11	6	1495	1101	35.8
			E	2700	1350	4	2	1350	1101	22.6
			F	2710	1464	6	29	1246	1101	13.2

- (a) Spiked and unspiked samples were not obtained concurrently.
- (b) Sample lost during analysis.
- (c) Samples mixed up.
- (d) Outlying value based upon statistical tests.

TABLE 12. RESULTS OF PILOT PLANT SO_x DETERMINATIONS FOR BLOCKS IN WHICH LABORATORIES OBTAINED CONCURRENT SO₂-SPIKED AND UNSPIKED SAMPLES (SECOND WEEK)

(Results in ppm SO₂ or SO₃)

Week	Day	Block	Lab	SO ₂		SO ₃		Estimated SO ₂ Spike Conc.	True SO ₂ Spike Conc.	Difference, % of True Conc.
				Spiked Sample	Unspiked Sample	Unspiked Sample 1	Unspiked Sample 2			
2	4	2	G	729	323	11	17	406	392	3.6
			H	693	195	16	17	498	392	27.0
			I	873	370	24	24	503	392	28.3
			J	760	319	17	23	441	392	12.5
2	4	6	G	980	325	11	22	655	777	-15.7
			H	1116	349	17	21	767	777	-1.3
			I	1099	346	26	26	753	777	-3.1
			J	958	323	15	19	635	777	-18.3
2	4	9	G	1856	1226	29	52	630	809	-22.1
			H	(a)	1225	(a)	54	--	809	--
			I	1649	1104	48	45	545	809	-32.6
			J	1727	1079	47	50	648	809	-19.9
2	4	10	G	1530	880	29	53	650	822	-20.9
			H	1521	818	26	56	703	822	-14.5
			I	1724	1018	55	42	706	822	-14.1
			J	1419	862	29	56	557	822	-32.2
2	4	12	G	2326	1044	30	39	1282	1088	17.8
			H	1841	1191	33	39	650	1088	-40.3
			I	2416	1070	54	50	1346	1088	23.7
			J	2220	1006	34	52	1214	1088	11.6
2	4	13	G	2248	919	32	49	1329	1122	18.4
			H	2121	918	45	58	1203	1122	7.2
			I	2190	904	57	42	1286	1122	14.6
			J	2177	922	39	56	1255	1122	11.9
2	5	2	G	857	449	16	34	408	369	10.6
			H	572	387	18	39	185	369	-49.9
			I	966	301	42	41	665	369	80.2
			J	846	454	(b)	(b)	392	369	6.2

TABLE 12. (Continued)

Week	Day	Block	Lab	SO ₂		SO ₃		Estimated SO ₂ Spike Conc.	True SO ₂ Spike Conc.	Difference, % of True Conc.
				Spiked Sample	Unspiked Sample	Unspiked Sample 1	Unspiked Sample 2			
2	5	3	G	867	442	14	73 (c)	425	369	15.2
			H	871	612	11	18	259	369	-29.8
			I	885	323	23	24	562	369	52.5
			J	843	456	(b)	(b)	387	369	4.9
2	5	9	G	2426	1630	36	46	796	759	4.9
			H	2436	1649	34	38	787	759	3.7
			I	2578	1623	47	32	955	759	25.8
			J	1703	1250	14	34	453	759	-40.3
2	5	10	G	2186	1592	31	54	594	759	-21.7
			H	2375	1523	32	63	852	759	12.3
			I	2463	1584	52	76	879	759	15.8
			J	2348	1546	29	40	802	759	5.7
2	5	12	G	2972	1740	24	32	1232	1061	16.1
			H	3145	1671	18	17	1474	1061	38.9
			I	3196	1641	32	32	1555	1061	46.6
			J	3235	1734	28	28	1501	1061	41.5
2	5	13	G	3246	1949	26	20	1297	1052	23.3
			H	3267	1838	24	17	1429	1052	35.8
			I	3340	1984	25	43	1356	1052	28.9
			J	3258	1938	18	18	1320	1052	25.5

(a) Low Sampling rate.

(b) SO₃ not detected.

(c) Outlying values based upon statistical test.

additional laboratories (coded G through J). The data from Table 7 through 10, with duplicate determinations, were used to generate estimates of between-laboratory and within-laboratory precision of SO₂ measurements using D 3226-73T, while the data from Tables 7 through 12 were used for similar precision estimates of SO₃ measurements.

For the SO₂ measurements, the data in Tables 11 and 12 represent results of determinations in which the cooperating laboratories concurrently obtained one unspiked flue gas sample and a duplicate flue gas sample spiked with a known quantity of sulfur dioxide. The laboratories' estimates of the SO₂ spike concentration, determined by subtracting the unspiked sample value from the spike sample result, are given along with the "true" spike concentration. The last column of the tables reports the percentage difference between the laboratory estimate and the "true" value based on the "true value". These data in Tables 11 and 12 provide the basis for the estimate of the accuracy of the Test Method with respect to measurement of SO₂.

The data in Tables 7 through 12, which were used for estimates of between- and within-laboratory variance were examined for outliers using statistical criteria. In particular, the Studentized range test was used in which the ratio of the range of observations to the estimated standard deviation of the observations within a group (defined by block, week, and day) was compared with tabulated critical values of the Studentized range at a 99% significance level. Significantly high ratios indicated a group of observations containing a suspected outlier. The suspected outlier was easily identified by examination of the observations within the group.

Field Tests

Tables 13, 14 and 15 present the results obtained from field tests at an oil-fired power plant (Site I), coal-fired power plant (Site II) and a cement plant (Site III), respectively. The data were obtained from tests series in which concurrent measurements were made by four laboratories.

In general, the field test data exhibit considerable variation in the concurrent SO₂ and SO₃ measurements. The variations are most highly correlated with differences among laboratories rather than sampling port or SO₃/H₂SO₄ condenser used. For example, Laboratory C at Site II obtained results which were consistently higher than the other laboratories. At Site III, Laboratory A obtained consistently lower values during the second test week. However, the same laboratory obtained results more nearly comparable to the

TABLE 13. RESULTS OF SULFUR OXIDE MEASUREMENTS AT FIELD
TEST SITE I

Test Number	Laboratory	Port Number	Condenser Number	SO ₂ Concentration, ppm	SO ₃ Concentration ppm
1	A	7	(a)	247	3.8
	B	9		249	1.8
	C	5		153	(b)
	D	3		74	(c)
2	A	7	(a)	219	10.5
	B	9		260	1.4
	C	5		161	(b)
	D	3		96	(c)
3	A	7	(a)	222	8.6
	B	9		258	1.4
	C	5		223	(b)
	D	3		222	(c)
4	A	7	(a)	229	10.5
	B	9		253	1.7
	C	5		194	(b)
	D	3		222	(c)
5	A	7	(a)	225	6.8
	B	9		259	1.4
	C	5		189	(b)
	D	3		216	(c)
6	A	7	(a)	195	1.7
	B	9		254	1.8
	C	5		152	(b)
	D	3		216	(c)

TABLE 13. (Continued)

Test Number	Laboratory	Port Number	Condenser Number	SO ₂ Concentration, ppm	SO ₃ Concentration ppm
7	A	7	(a)	194	9.9
	B	9		253	1.2
	C	5		214	(b)
	D	3		212	(c)
8	A	7	(a)	220	6.9
	B	9		258	0.9
	C	5		205	(b)
	D	3		210	(c)

- (a) Each laboratory used the same condenser for all tests.
 (b) Samples contaminated with sulfuric acid.
 (c) SO₃ was not detected.

TABLE 14. RESULTS OF SULFUR OXIDE MEASUREMENTS AT FIELD TEST SITE II

Test Number	Laboratory	Port Number	Condenser Number	SO ₂ Concentration, ppm	SO ₃ Concentration ppm
1	A	2	2	21	0
	B	1	1	(a)	(a)
	C	4	4	2596	144.2
	D	3	3	0	5.5
2	A	2	2	0	1.0
	B	1	1	1081	2.5
	C	4	4	2222	133.0
	D	3	3	0	2.2
3	A	3	2	20	0
	B	2	1	(b)	(b)
	C	1	4	2240	166.2
	D	4	3	1699	2.0
4	A	3	2	31	1.0
	B	2	1	1538	16.7
	C	1	4	2205	179.0
	D	4	3	1870	0
5	A	4	2	(c)	(c)
	B	3	1	65	0
	C	2	4	2225	139.2
	D	1	3	921	0
6	A	4	2	1379	13.3
	B	3	1	44	0
	C	2	4	2137	142.5
	D	1	3	859	3.0
7	A	1	2	861	4.0
	B	4	1	805	56.7
	C	3	4	2231	137.1
	D	2	3	1950	5.2

TABLE 14. (Continued)

Test Number	Laboratory	Port Number	Condenser Number	SO ₂ Concentration, ppm	SO ₃ Concentration, ppm
8	A	1	2	827	1.0
	B	4	1	1327	2.0
	C	3	4	2230	127.4
	D	2	3	1972	6.7
9	A	1	2	288	0
	B	4	1	832	0.5
	C	3	4	2396	155.0
	D	2	3	1330	1.9
10	A	1	2	110	0
	B	4	1	939	4.0
	C	3	4	2247	147.7
	D	2	3	1331	1.9
11	A	4	2	1360	3.4
	B	3	1	107	2.6
	C	2	4	2807	154.7
	D	1	3	192	0
12	A	4	2	1112	4.4
	B	3	1	0	2.0
	C	2	4	2980	163.5
	D	1	3	182	1.9
13	A	3	2	25	1.3
	B	2	1	796	15.4
	C	1	4	2161	177.1
	D	4	3	1629	4.7
14	A	3	2	21	1.1
	B	2	1	853	62
	C	1	4	2556	186.2
	D	4	3	1667	4.6

TABLE 14. (Continued)

Test Number	Laboratory	Port Number	Condenser Number	SO ₂ Concentration, ppm	SO ₃ Concentration, ppm
15	A	2	2	1050	10.4
	B	1	1	(d)	5.2
	C	4	4	2493	155.3
	D	3	3	0	0.6
16	A	2	2	1403	7.5
	B	1	1	339	3.1
	C	4	4	2628	167.9
	D	3	3	0	4.6

- (a) Critical orifice plugged, did not obtain sample.
 (b) Probe heater burned out, melting hole in glass liner.
 (c) Sample was not obtained due to equipment malfunction.
 (d) Sample leaked from shipping container.

TABLE 15. RESULTS OF SULFUR OXIDE MEASUREMENTS AT FIELD TEST SITE III

Test Number	Laboratory	Port Number	Condenser Number	SO ₂ Concentration, ppm	SO ₃ Concentration, ppm
1	A	1	3	1244	6.7
	B	3	2	590	3.0
	C	2	1	1230	7.3
	D	4	4	1211	5.3
2	A	1	4	1195	6.0
	B	3	1	1057	2.8
	C	2	3	960	7.5
	D	4	2	563	(a)
3	A	1	2	1102	4.7
	B	3	3	945	5.6
	C	2	4	1002	12.2
	D	4	1	1149	12.4
4	A	1	1	925	0
	B	3	4	873	9.1
	C	2	2	883	8.6
	D	4	3	1559	10.9
5	A	2	2	1219	3.6
	B	4	4	1130	0
	C	3	3	1125	13.2
	D	1	1	1283	11.1

TABLE 15. (Continued)

Test Number	Laboratory	Port Number	Condenser Number	SO ₂ Concentration, ppm	SO ₃ Concentration, ppm
6	A	2	1	1422	16.6
	B	4	3	693 ^(b)	801 ^(b)
	C	3	2	764	3.7
	D	1	4	741	0
7	A	2	4	1000	7.7
	B	4	2	852	0.5
	C	3	1	816	12.2
	D	1	3	208	5.5
8	A	2	3	879	6.0
	B	4	1	(c)	(c)
	C	3	4	798	0
	D	1	2	230	5.7
9	A	3	3	1235	7.4
	B	1	1	1102	1.5
	C	4	4	988	0
	D	2	2	279	9.1
10	A	3	2	1063	8.6
	B	1	4	953	9.0
	C	4	3	989	17.7
	D	2	1	58	4.3
11	A	3	1	1062	5.1
	B	1	3	110	(d)
	C	4	2	1061	7.2
	D	2	4	99	3.7

TABLE 15. (Continued)

Test Number	Laboratory	Port Number	Condenser Number	SO ₂ , Concentration, ppm	SO ₃ Concentration, ppm
12	A	3	4	1017	4.2
	B	1	2	939	1.5
	C	4	1	959	0
	D	2	3	374	8.0
13	A	4	4	119	0
	E	2	2	1043	0.6
	C	3	3	775	0
	F	1	1	753	6.6
14	A	4	3	275	1.3
	E	2	1	1467	3.1
	C	3	2	1560	2.0
	F	1	4	1542	5.9
15	A	4	2	211	1.6
	E	2	4	1239	9.2
	C	3	1	1027	5.2
	F	1	3	1124	9.4
16	A	4	1	229	1.4
	E	2	3	1205	9.5
	C	3	4	1079	2.6
	F	1	2	1100	3.4
17	A	1	1	64	0
	E	3	3	1166	5.2
	C	4	4	1093	0
	F	2	2	1055	6.4
18	A	1	4	220	0
	E	3	2	999	0.5
	C	4	3	901	0
	F	2	1	537	2.5

TABLE 15. (Continued)

Test Number	Laboratory	Port Number	Condenser Number	SO ₂ Concentration, ppm	SO ₃ Concentration, ppm
19	A	1	3	121	0.4
	E	3	1	1041	21.5
	C	4	2	988	5.3
	F	2	4	689	5.1
20	A	1	2	167	2.8
	E	3	4	821	45.6
	C	4	1	738	3.7
	F	2	3	364	3.3
21	A	2	2	335	5.4
	E	4	4	922	28.8
	C	1	1	854	0
	F	3	3	796	10.6
22	A	2	1	384	5.2
	E	4	3	866	25.7
	C	1	4	1198	0
	F	3	2	1047	5.4
23	A	2	4	674	3.5
	E	4	2	1986	8.7
	C	1	3	1576	0
	F	3	1	1904	6.1
24	A	2	3	595	1.3
	E	4	1	1588	5.2
	C	1	2	1563	0
	F	3	4	1588	0.8

- (a) Sample contaminated.
 (b) Probe unheated.
 (c) Low flow rate.
 (d) Sample contaminated with methanol.

other laboratories during the first test week at Site III.

The SO_3 measurements show large variations between laboratories at all three test sites. At Site II, the variation is closely correlated with laboratory differences e.g. Laboratory C. At Site III, the variation is more random and does not appear to be strongly associated with laboratories, ports, nor condensers.

Due to the unexplainable, generally variable nature of the SO_x measurements, it is deemed inappropriate to apply outlier tests, therefore, all reported data with exception of determinations in which procedural errors were committed, were used in the statistical analysis.

Analysis of Between-Laboratory and Within-Laboratory Components of Variance of Pilot Plant Data

The data used for the estimate of between-laboratory variability (reproducibility) and within-laboratory variability (repeatability) of the SO_2 measurement method were the data collected in blocks 1, 4, 7, 8, 11, and 14 of the pilot plant tests. For the SO_3 measurement method, data from all blocks were used. The blocks used contain duplicate samples for which laboratories made separate determinations and thus provide estimates of both within-laboratory and between-laboratory variability. The total variation within a block of simultaneous determinations was partitioned into these two components of variation using the analysis of variance procedures.⁽¹⁶⁾ Basically, this method partitions the total sum of squares of deviations associated with the determination X_{ij} , where i identifies the laboratory making the determination, and j identifies the duplicate determination for the laboratory, into the "within" and "between" sum of squares of deviations, used to develop variance estimates. If the number of duplicates for the i^{th} laboratory is denoted by n_i , and k is the number of laboratories making simultaneous determinations, an Analysis of Variance Table can be constructed as shown in Table 16. From this table, it can be seen that an estimate of within-laboratory precision, S_w , is given by

TABLE 16. ANALYSIS OF VARIANCE TABLE

Source	Degrees of Freedom	Sum of Squares	Mean Square	Expected Mean Square
Between Labs	$k-1$	$\sum_{i=1}^k n_i (\bar{X}_{i.} - \bar{X}_{..})^2$	S_2^2	$\sigma_B^2 + c\sigma_W^2$
Within Lab	$\sum_{i=1}^k n_i - k$	$\sum_{i=1}^k \sum_{j=1}^{n_i} (X_{ij} - \bar{X}_{i.})^2$	S_1^2	σ_B^2
Total	$\sum_{i=1}^k n_i - 1$	$\sum_{i=1}^k \sum_{j=1}^{n_i} (X_{ij} - \bar{X}_{..})^2$		

$$S_W = S_1 = \sqrt{\frac{\sum_{i=1}^k \sum_{j=1}^{n_i} (X_{ij} - \bar{X}_{i.})^2}{\sum_{i=1}^k n_i - k}}$$

where $\bar{X}_{i.}$ is the mean of the determinations for laboratory i . Likewise, an estimate of between-laboratory precision, S_B , is given by

$$S_B = \sqrt{\frac{S_2^2 - S_1^2}{c}} = \sqrt{\frac{1}{c} \left[\frac{\sum_{i=1}^k n_i (\bar{X}_{i.} - \bar{X}_{..})^2}{k-1} - S_W^2 \right]}$$

where

$$c = \frac{1}{k-1} \left(\begin{array}{c} k \\ \sum_{i=1}^k n_i \end{array} - \frac{\begin{array}{c} k \\ \sum_{i=1}^k n_i^2 \end{array}}{\begin{array}{c} k \\ \sum_{i=1}^k n_i \end{array}} \right)$$

and $\bar{X}_{..}$ is the mean of all the simultaneous determinations in the block.

The results of this statistical analysis are presented in Tables 17, 18 and 19. Table 17 presents the estimates of between- and within-laboratory components of variance for each block of simultaneous determinations of duplicate spiked samples of SO_2 , Table 18 gives the corresponding data for duplicate unspiked samples of SO_2 , and Table 19 presents the analysis results for SO_3 . The statistical summaries presented in Tables 17, 18, and 19 do not include the data points which were rejected as outliers.

Figures 13 and 14 are scattergrams of the block statistics, presenting a plot of between-laboratory component of variance, \hat{S}_B , (reproducibility) versus the square root of the mean concentration, \sqrt{m} , of SO_2 and SO_3 respectively.

A least-squares regression equation of the form $\hat{S}_B = a + b\sqrt{m}$ was fitted to the data points in Figures 13 and 14 by the method of weighted least squares. Weights were assigned to the data points in order to compensate for the fact that two assumptions of the statistical method are being violated:

- (1) The coordinates of the data points are averages, which are not always computed from the same number of observations;
- (2) The variances along the regression curve are not equal.

The appropriate weighting formula is $W = f / (\beta\sqrt{m} + \alpha)^2$, where W represents the weight, f denotes the number of degrees of freedom associated with the computed standard deviation S_B , α and β denote constant terms in the true regression curve, and m is the mean concentration.* The parameters α and β are not known, nor are their least-squares estimates, a and b . An iterative approach is required, using successive estimates of a , b , and W which converge to a least-squares solution. By this procedure, the equation $\hat{S}_B = 12.48\sqrt{m} - 96.70$ is obtained as an estimate of the true regression curve, $s = \beta\sqrt{m} + \alpha$, for SO_2 measurements and $\hat{S}_B = 0.26\sqrt{m} + 5.33$ is obtained for SO_3 measurements. The standard deviation of the residuals about the regression line is found to be 177.2 ppm for SO_2 and 3.5 ppm for SO_3 . The regressions account for approximately 33 percent of the variability in reproducibility estimates for SO_2 and less than 1 percent of the variability in reproducibility for SO_3 . These curves summarize the estimates of the between-laboratory component of variance (reproducibility) over the concentration range of about 300 to 2,500 ppm SO_2 and 5 to 50 ppm SO_3 , obtained from the pilot plant tests.

* In order to assure that each pair of data points has weight of at least one, all weights were increased by multiplying by the square of an upper limit of the reproducibility estimate (1,000 ppm for SO_2 and 50 ppm for SO_3).

TABLE 17. BETWEEN-LABORATORY AND WITHIN-LABORATORY PRECISION FOR DETERMINATION OF DUPLICATE SPIKED SO₂ SAMPLES

Week	Day	Block	No. of Labs	No. of Measmts.	Mean SO ₂ Conc., ppm	Between-Lab Std. Dev(S _B), ppm	CV, %	Within-Lab Std. Dev.(S _w), ppm	CV %
1	4	1	6	12	856.9	358.4	41.8	30.5	3.6
		7	5	10	973.4	113.2	11.6	146.8	15.1
		8	6	10	1773.1	612.0	34.5	30.5	1.7
		14	6	12	1852.6	653.7	35.3	415.8	22.4
1	5	8	6	11	1778.6	780.9	43.9	192.3	10.8
		14	5	9	2603.4	(a)	(a)	295.4	11.3
2	4	1	4	7	820.4	90.6	11.0	26.0	3.2
		7	4	8	986.2	93.1	9.4	76.0	7.7
		8	4	7	1663.4	(a)	(a)	232.7	14.0
		14	4	8	2339.1	215.0	9.2	363.7	15.6
2	5	1	4	8	874.6	38.7	4.4	26.1	3.0
		7	4	8	1270.5	49.0	3.8	41.4	3.3
		8	4	8	1881.5	87.7	4.7	31.9	1.7
		14	4	8	2428.2	(a)	(a)	152.2	6.3

(a) Between-laboratory component of variance is not statistically distinguishable from zero.

TABLE 18. BETWEEN-LABORATORY AND WITHIN-LABORATORY PRECISION FOR DETERMINATION OF DUPLICATE UNSPIKED SO₂ SAMPLES

Week	Day	Block	No. of Labs	No. of Measmts.	Mean SO ₂ Conc., ppm	Between-Lab Std. Dev(S _B), ppm	CV %	Within-Lab Std. Dev(S _w), ppm	CV %
1	4	4	4	8	302.5	17.5	5.8	20.4	6.7
		11	5	10	1237.7	212.7	17.2	187.9	15.2
1	5	11	6	12	1285.3	518.5	40.3	124.2	9.7
2	4	4	4	7	314.4	(a)	(a)	54.8	17.4
		11	4	8	1118.6	60.3	5.4	119.9	10.7
2	5	4	4	8	475.9	(a)	(a)	68.2	14.3
		11	4	8	1231.1	(a)	(a)	161.4	13.1

(a) Between-laboratory component of variance is not statistically distinguishable from zero.

TABLE 19. BETWEEN-LABORATORY AND WITHIN-LABORATORY PRECISION FOR DETERMINATION OF DUPLICATE UNSPIKED SO₃ SAMPLES

Week	Day	Block	No. of Labs	No. of Measmts.	Mean SO ₃ Conc., ppm	Between-Lab Std. Dev(S _B), ppm	CV %	Within-Lab Std. Dev(S _B), ppm	CV %		
1	4	1	6	9	14.7	8.9	60.4	4.0	27.5		
		2	6	9	22.6	12.8	56.6	9.7	43.0		
		4	7	10	10.9	9.5	86.8	2.3	20.8		
		5	7	10	20.0	6.8	34.0	9.0	45.1		
		7	6	10	16.9	11.6	69.0	3.2	19.2		
		8	6	9	37.0	15.9	42.0	5.8	15.8		
		9	6	9	38.4	(a)	(a)	17.8	46.2		
		11	6	10	29.2	8.0	27.4	7.6	25.9		
		12	5	7	33.3	3.7	11.0	5.5	16.5		
		13	6	9	47.6	(a)	(a)	19.4	40.9		
		14	7	11	25.3	12.3	48.7	5.9	23.3		
		1	5	8	7	10	26.3	10.3	39.2	9.6	36.6
				9	7	12	17.9	7.9	44.1	4.2	23.2
				10	7	11	21.6	4.2	19.3	9.0	41.5
11	7			11	19.1	2.2	11.4	6.2	32.7		
12	7			11	12.4	3.3	26.6	10.5	84.7		
14	7			10	14.0	7.9	56.5	1.8	13.1		
2	4	1	5	8	24.9	(a)	(a)	11.5	46.1		
		2	5	8	18.6	3.8	20.3	3.0	16.2		
		4	5	7	13.7	(a)	(a)	4.8	34.8		
		6	5	8	19.6	3.1	15.8	4.4	22.3		
		7	5	8	14.8	5.3	36.1	3.6	24.2		
		8	5	7	37.0	(a)	(a)	16.8	45.3		
		9	5	7	46.4	(a)	(a)	9.6	20.6		
		10	5	8	43.2	(a)	(a)	17.2	39.8		
		11	5	7	39.0	4.6	11.9	2.6	6.7		
		12	5	8	41.4	5.9	14.4	7.6	18.3		
		13	5	8	47.2	(a)	(a)	11.0	23.3		
		14	5	8	51.2	3.1	6.0	12.1	23.6		
		2	5	1	4	5	7.8	5.5	70.5	2.2	14.0
				2	4	6	31.7	3.4	10.8	11.3	35.7
3	4			5	18.0	4.9	27.1	3.5	19.6		

TABLE 19. (Continued)

Week	Day	Block	No. of Labs	No. of Measmts.	Mean SO ₃ Conc., ppm	Between-Lab Std. Dev(S _B), ppm	CV %	Within-Lab Std. Dev(S _B), ppm	CV %
2	5	4	4	5	8.2	3.9	47.1	2.5	30.5
		7	4	5	8.8	2.4	26.8	1.8	20.5
		8	5	8	14.5	1.3	8.8	1.9	13.4
		9	5	8	35.1	3.6	10.3	9.6	27.4
		10	5	8	47.1	4.3	9.1	16.5	35.1
		11	5	8	19.4	4.9	25.4	2.2	11.4
		12	5	8	26.4	5.9	22.3	2.8	10.8
		13	5	8	23.9	4.9	20.6	7.2	30.0
		14	5	8	25.8	4.4	17.2	3.2	12.6

(a) Between-laboratory component of variance is not statistically distinguishable from zero.

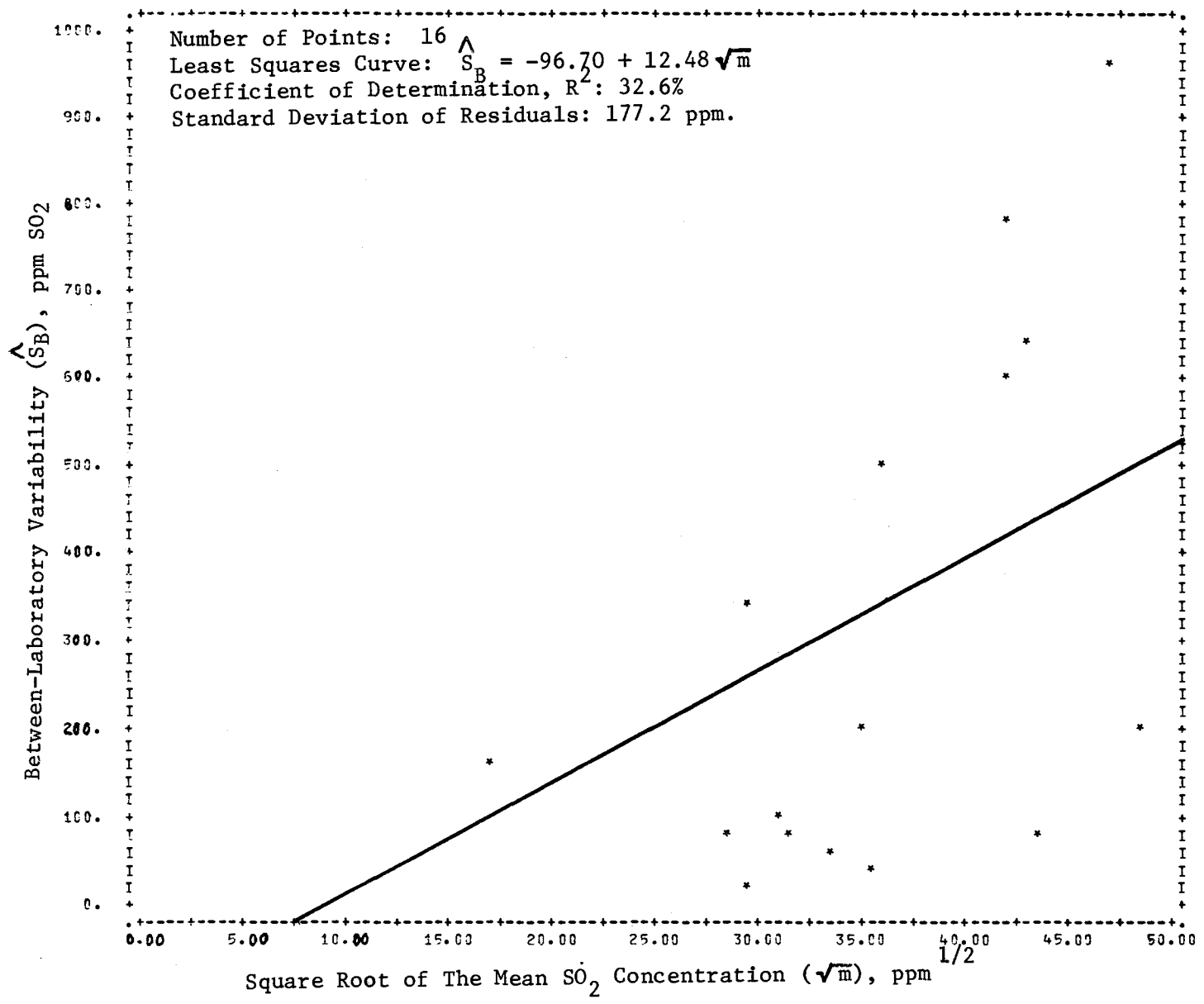


FIGURE 13. SCATTERGRAM AND LEAST-SQUARES CURVE RELATING BETWEEN-LABORATORY STANDARD DEVIATION (REPRODUCIBILITY) TO THE SQUARE ROOT OF THE MEAN SO₂ CONCENTRATION FOR PILOT PLANT DATA

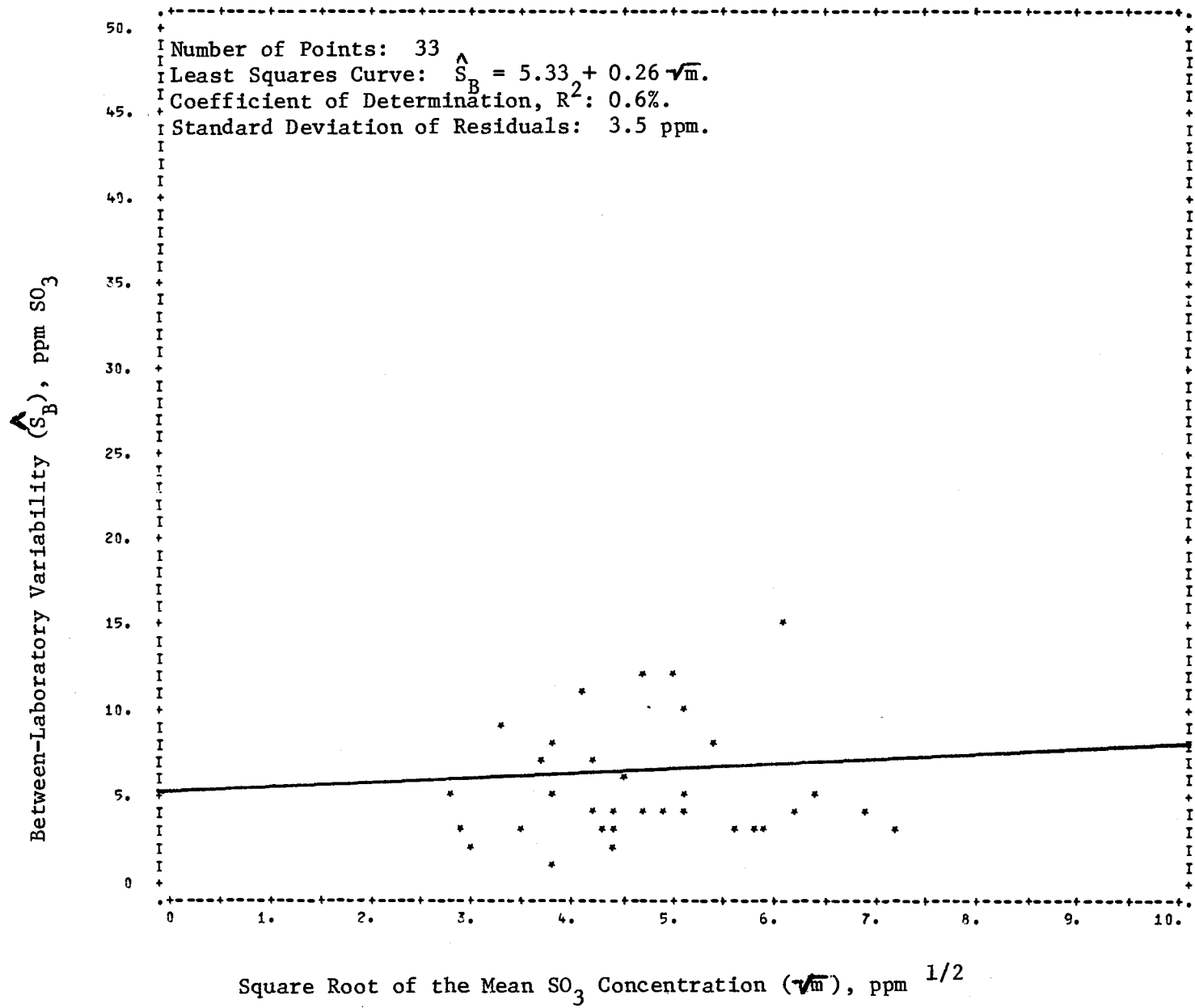


FIGURE 14. SCATTERGRAM AND LEAST-SQUARES CURVE RELATING BETWEEN-LABORATORY STANDARD DEVIATION (REPRODUCIBILITY) TO THE SQUARE ROOT OF THE MEAN SO_3 CONCENTRATION FOR PILOT PLANT DATA

In Figures 15 and 16, scattergrams of the block estimates of within-laboratory variability (repeatability), \hat{S}_W , versus the square root of the mean SO_2 and SO_3 concentration are presented. A curve of the form $s = a + b \sqrt{m}$ was fitted to these data points by the method of weighted least squares, using a similar weighting* procedure used for the reproducibility analysis. The iterative approach which is required, results in the equations, $\hat{S}_W = 5.32 \sqrt{m} - 53.92$ for SO_2 measurements and $\hat{S}_W = 2.43 \sqrt{m} - 4.76$ for SO_3 measurements. The standard deviation of residuals equals 54.4 ppm for the SO_2 data and 2.81 ppm for the SO_3 data. The regressions account for approximately 45 percent of the variability in repeatability estimates of SO_2 and 43 percent of the variability in repeatability estimates of SO_3 . The curves in Figures 15 and 16 summarize the estimates of within-laboratory variability (repeatability) over the concentration range of about 300 to 2,500 ppm SO_2 and 5 to 50 ppm SO_3 , based on the pilot plant test data.

Statistical Analysis of Field Test Data

The results of the statistical analysis of the field test data from Sites I, II and III are presented in Table 20. The table presents, for the SO_2 and SO_3 measurements, the number of measurements per test, n ; the mean value of the SO_2 or SO_3 measurements, m ; the between laboratory variation, S_T (between-laboratory); and the coefficient of variation (CV) for the tests at each field site. The between laboratory variation is calculated as the standard deviation of measurements from each test, using the equation

$$S_T(\text{between laboratory}) = \sqrt{\frac{\sum_{i=1}^n (X_i - m)^2}{n-1}}$$

where m is the test mean, X_i is the SO_2 or SO_3 value determined by the i^{th} laboratory, and n is the number of SO_2 or SO_3 measurements per test. The coefficient of variation, expressed in percent, is calculated from the test mean (m) and the standard error, S_T (between-laboratory), using the equation,

$$CV, \% = \frac{100 S_T(\text{between-laboratory})}{m}$$

The overall scatter in the field data is illustrated in Figures 17 and 18 which show the coefficients of variation for the SO_2 and SO_3 measurements plotted versus the mean SO_2 and SO_3 concentrations. Taken by site, the mean

* To assure that each pair of data points has weight of at least one, all weights were increased by multiplying by the square of an upper limit of the repeatability estimate (500 ppm for SO_2 and 50 ppm for SO_3).

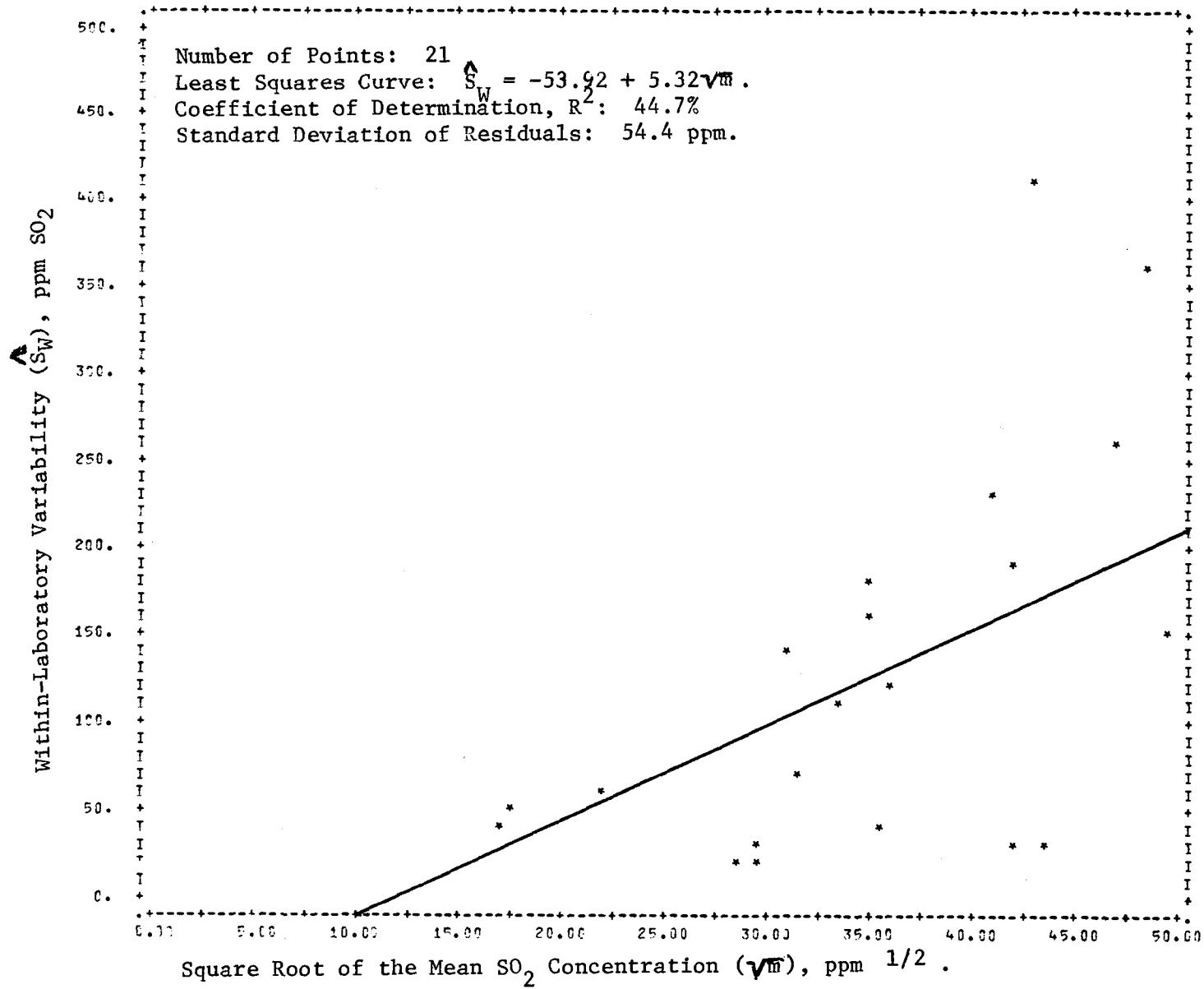


FIGURE 15. SCATTERGRAM AND LEAST-SQUARES CURVE RELATING WITHIN-LABORATORY STANDARD DEVIATION (REPEATABILITY) TO THE SQUARE ROOT OF THE MEAN SO₂ CONCENTRATION FOR PILOT PLANT DATA

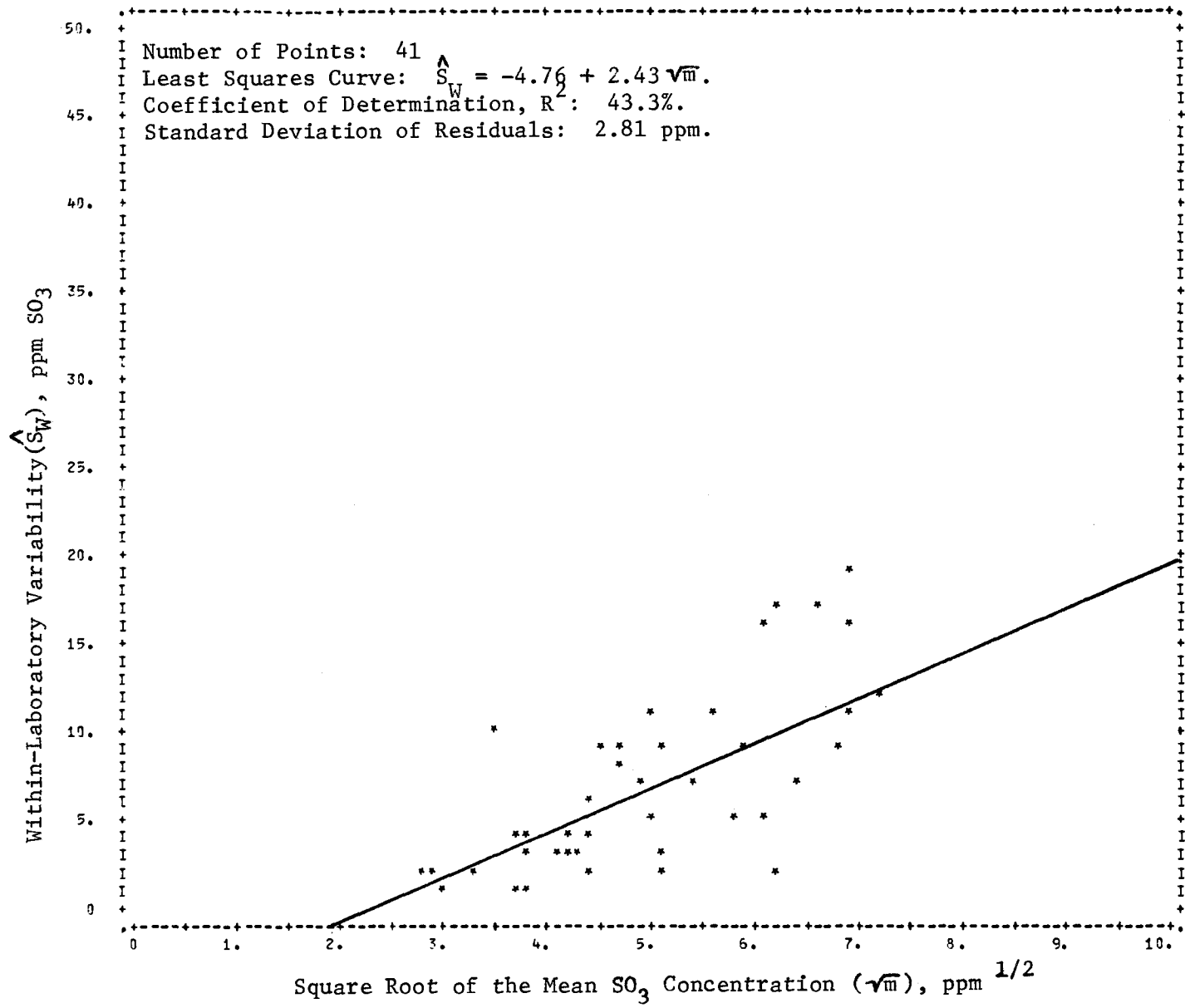


FIGURE 16. SCATTERGRAM AND LEAST-SQUARES CURVE RELATING WITHIN-LABORATORY STANDARD DEVIATION (REPEATABILITY) TO THE SQUARE ROOT OF THE MEAN SO₃ CONCENTRATION FOR PILOT PLANT DATA.

TABLE 20. STATISTICAL ANALYSIS OF SO_x MEASUREMENTS PERFORMED AT FIELD TEST SITES

Site	Test Number	SO ₂ Data				SO ₃ Data			
		Determinations	Mean Conc., ppm SO ₂	S _T , ppm SO ₂	CV, %	Determinations	Mean Conc., ppm SO ₃	S _T , ppm SO ₃	CV, %
I	1	4	181	84	46	2	2.8	1.4	50
	2	4	184	71	39	2	6.0	6.4	107
	3	4	231	18	8	2	5.0	5.1	102
	4	4	225	24	11	2	6.1	6.2	102
	5	4	222	29	13	2	4.1	3.8	93
	6	4	204	43	21	2	1.8	0.1	6
	7	4	218	25	12	2	5.6	6.2	111
	8	4	223	24	11	2	3.9	4.2	108
II	1	3	872	1493	171	3	49.9	81.7	164
	2	4	826	1061	128	4	34.7	65.6	189
	3	3	1320	1158	88	3	56.1	95.4	170
	4	4	1411	959	68	4	49.2	86.9	177
	5	3	1070	1088	102	3	46.4	80.4	173
	6	4	1105	881	80	4	39.7	68.8	173
	7	4	1462	735	50	4	50.8	62.6	123
	8	4	1589	634	40	4	34.3	62.1	181
	9	4	1211	897	74	4	39.4	77.1	196
	10	4	1157	887	77	4	38.4	72.9	190
	11	4	1117	1264	113	4	40.2	76.4	190
	12	4	1069	1364	128	4	35.3	71.4	202
	13	4	1153	939	81	4	49.3	85.2	172
	14	4	1274	1087	85	4	63.5	86.5	136
	15	3	1181	1252	106	4	42.9	75.1	175
	16	4	1093	1185	108	4	45.8	81.4	178
III	1	4	1069	319	30	4	5.6	1.9	34
	2	4	943	272	29	3	5.4	2.4	44
	3	4	1050	93	9	4	8.7	4.1	47
	4	4	1060	333	31	4	7.2	4.9	68
	5	4	1189	76	6	4	7.0	6.2	89
	6	3	976	387	40	3	6.8	8.7	128
	7	4	719	350	49	4	6.5	4.9	75
	8	3	636	354	56	3	3.9	3.4	87

TABLE 20. (Continued)

Site	Test Number	SO ₂ Data				SO ₃ Data			
		Determinations	Mean Conc., ppm SO ₂	S _T , ppm SO ₂	CV, %	Determinations	Mean Conc., ppm SO ₃	S _T , ppm SO ₃	CV, %
III	9	4	901	427	47	4	4.5	4.4	98
	10	4	766	474	62	4	9.9	5.6	57
	11	4	583	553	95	3	5.3	1.8	34
	12	4	822	301	37	4	3.4	3.5	103
	13	4	673	392	58	4	1.8	3.2	178
	14	4	1211	625	52	4	3.1	2.0	65
	15	4	900	468	52	4	6.4	3.7	58
	16	4	903	453	50	4	4.2	3.6	86
	17	4	845	522	62	4	2.9	3.4	117
	18	4	664	357	54	4	0.8	1.2	150
	19	4	710	422	59	4	8.1	9.2	114
	20	4	523	309	59	4	13.9	21.2	153
	21	4	727	266	37	4	11.2	12.5	112
	22	4	874	354	41	4	9.1	11.4	125
	23	4	1535	601	39	4	4.6	3.7	80
	24	4	1334	492	37	4	1.8	2.3	128

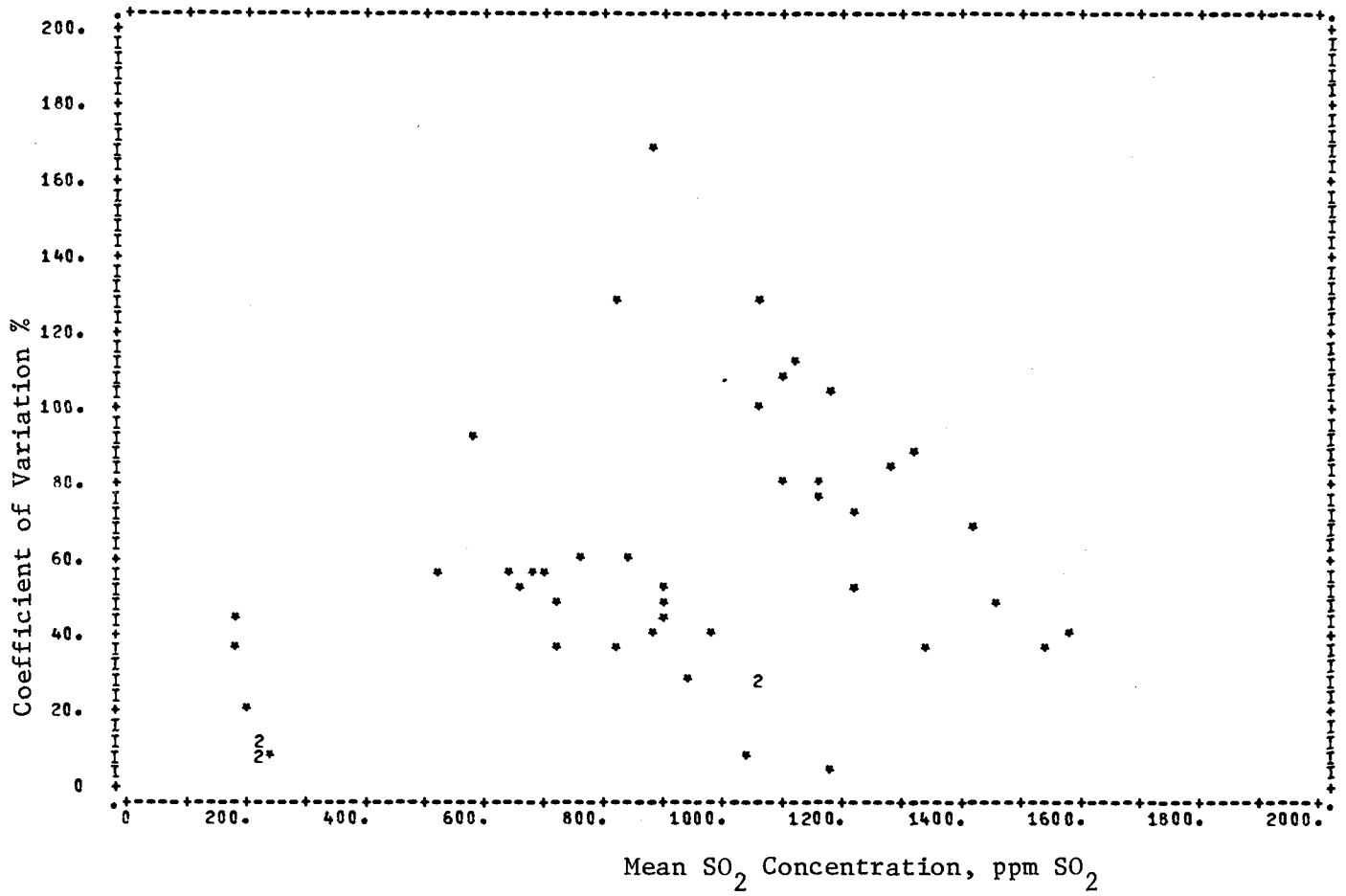


FIGURE 17. SCATTERGRAM SHOWING RELATIONSHIP OF THE COEFFICIENT OF VARIATION TO MEAN SO₂ CONCENTRATION FOR FIELD TEST DATA

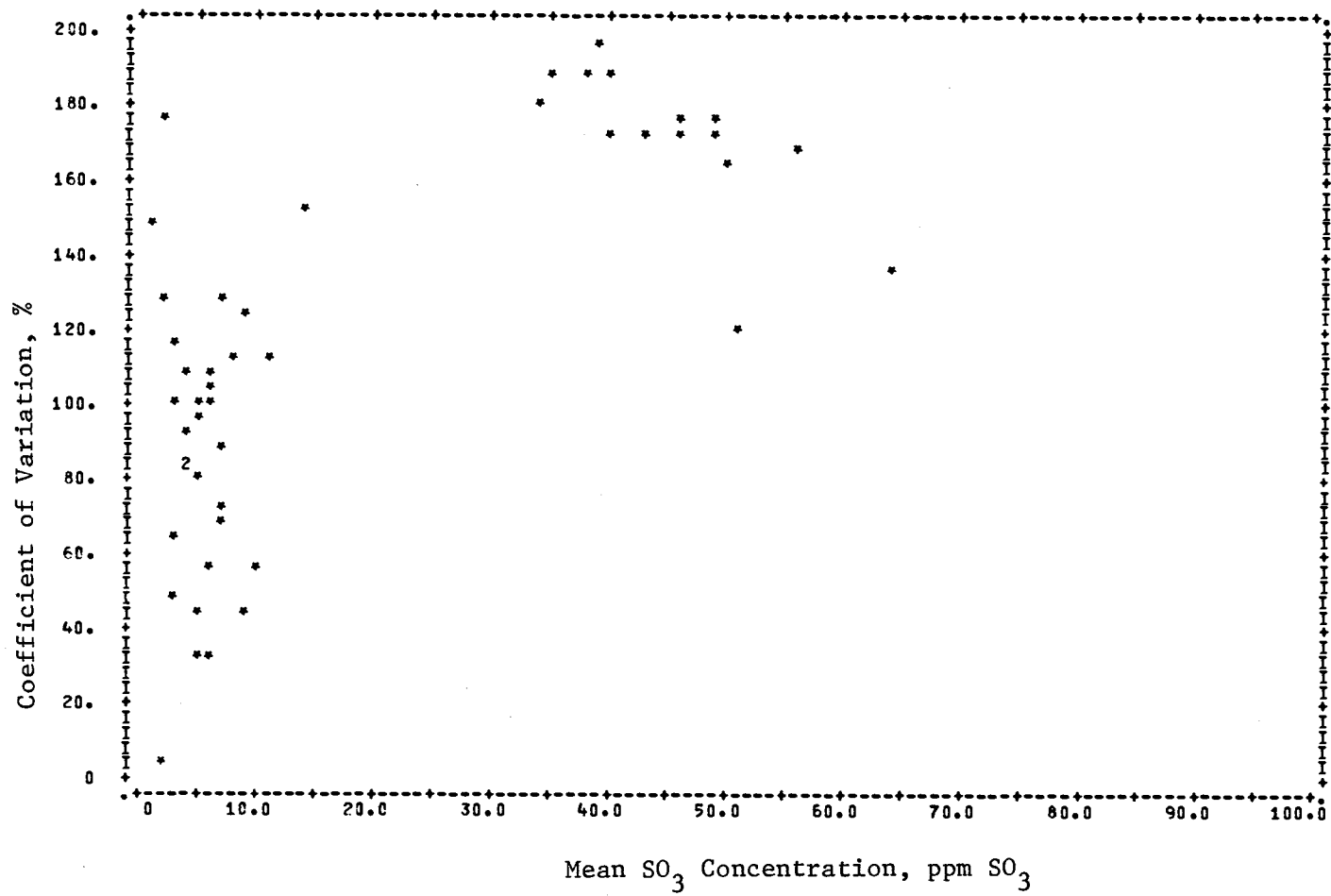


FIGURE 18. SCATTERGRAM SHOWING RELATIONSHIP OF THE COEFFICIENT OF VARIATION TO MEAN SO₃ CONCENTRATION FOR FIELD TEST DATA

coefficient of variation for the SO₂ measurements are 20, 94, and 45 percent, respectively for Sites I, II, and III. For Sites I, II, and III, the respective mean coefficient of variation for the SO₃ measurements are 85,174, and 93 percent.

Analysis of Accuracy

Data from the Blocks in which both spiked and unspiked SO₂ sample determinations were performed were used to estimate the accuracy of D 3226-73T. The difference 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 test samples. These differences, obtained by each laboratory are the basis for the analysis of accuracy. Since no spiking of SO₃ was performed, no accuracy analysis for SO₃ was conducted.

The accuracy of SO₂ measurements is determined as a percentage difference from the true value, calculated by the equation

$$\begin{array}{l} \text{Percentage difference} \\ \text{from true concentration} \end{array} = \frac{(\text{Estimated spike conc.} - \text{True spike conc.})100}{\text{True spike conc.}}$$

The estimated spike concentration is the difference between the laboratories determinations of the spiked and unspiked samples.

Figure 19 presents a histogram of percentage differences for data at all spike concentrations. The distribution appears normal with a mean of 3.14 percent and a standard deviation of 64.02, based upon 90 observations. 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:

$$t = x \sqrt{n}/s = 3.14 \sqrt{90}/64.02 = 0.465$$

For n-1 = 89 degrees of freedom, the value for t is not statistically significant at the 99 percent level. Therefore, the test hypothesis is accepted and it is concluded that the true bias is probably zero.

A breakdown of accuracy estimates as a function of spike concentration level is given in Table 21. These data permit an investigation of bias in the Test Method at three concentration ranges. The results indicate that there is

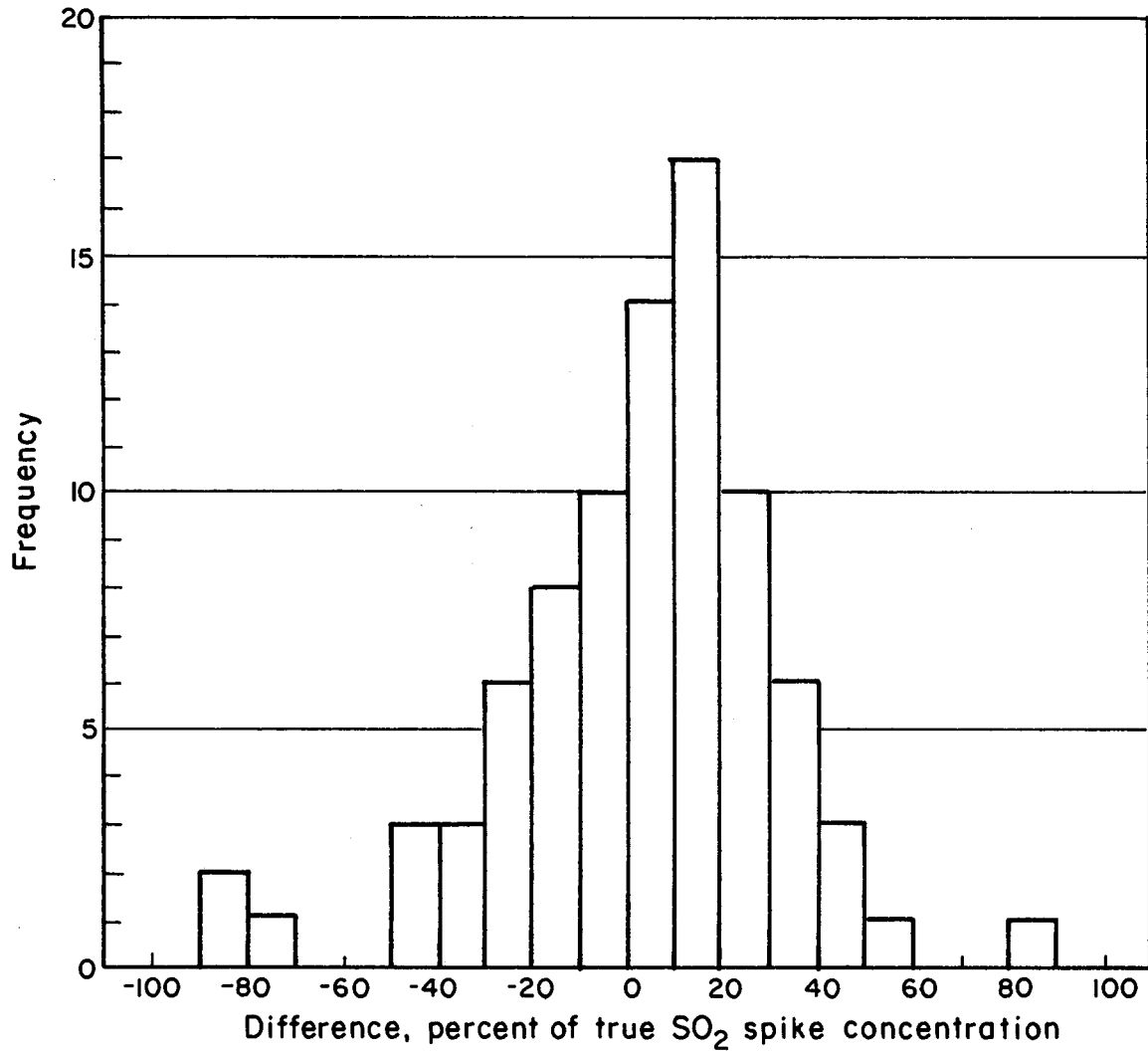


FIGURE 19. DISTRIBUTION OF PERCENTAGE DIFFERENCES BETWEEN ESTIMATED AND TRUE SO₂ SPIKE CONCENTRATIONS

TABLE 21. SUMMARY OF ACCURACY OF SO₂ DETERMINATIONS
AS A FUNCTION OF SPIKE CONCENTRATION

Spike Concentration, ppm SO ₂	Number of Observations	Mean Percent Difference	Standard Deviation	Student's t	Conclusion ^(a)
$X \leq 400$	17	11.41	31.46	1.50	N
$400 < X \leq 850$	42	-2.95	84.24	-0.23	N
$850 < X$	31	6.86	42.72	0.89	N
Total	90	3.14	64.02	0.46	N

(a) N = t is not statistically significant at the 99 percent level and the test hypothesis that the true bias is zero is not rejected.

no statistically significant bias present in any of the concentration ranges examined.

A summary of the accuracy of the SO_x determinations by laboratory is given in Table 22. Because of the small sample sizes and large standard deviations, the biases, estimated as mean percent difference, in most cases do not yield statistically significant test results. With one exception, we can conclude that the average bias of each laboratory is probably zero.

Analysis of Standard Sulfate Solutions

Series of standard sulfate solutions were supplied to each cooperating laboratory to be analyzed along with the pilot plant and Site II and III test samples.

Three standards containing the equivalent of 39.4, 78.9, and 131.5mg SO_2 were provided following the pilot plant tests. The results of the analysis of these samples by the various laboratories are given in Table 23. The laboratory code designations for the standard data are the same as those used for the pilot plant test results. Three laboratories, A, E, and F appeared to have problems with the analysis procedure.

The means and standard deviations of the quantity found by the various laboratories are shown at the bottom of the table. The standard deviations about the measured values provide an estimate of the between-laboratory standard error for determination of sulfate using the D 3226-73T analytical procedure.

The mean and standard deviations of the differences, in percent, between the actual value and the quantity found (based on the actual value) are also given at the bottom of the table. The analysis of the differences using Student's test indicates that the bias is not statistically significant at any of the three concentration levels.

A set of nine standard sulfate solutions were sent to each cooperating laboratories after both the Site II and Site III tests. These series included triplicate samples of three different SO_2 concentrations; 14.6, 29.2, and 58.4 milligrams. The same series of standards, with different identification, was distributed after the two test periods.

The results from the standard solutions analyzed with the Site II and III test samples are presented in Table 24. Laboratory code designations are the same as those used for the field test data. The results of Laboratories

TABLE 22. SUMMARY OF ACCURACY OF SO₂
DETERMINATIONS BY LABORATORY

Laboratory	No. of Observations	Mean Percent Difference	Standard Deviation	Student's t	Conclusion (a)
A	6	8.09	22.28	0.89	N
B	8	-95.94	35.77	-7.35	S
C	8	- 0.69	9.30	-0.21	N
D	8	9.51	15.13	1.78	N
E	7	82.90	178.81	1.23	N
F	6	9.45	20.36	1.14	N
G	12	2.45	17.62	0.48	N
H	11	- 0.98	29.90	-0.11	N
I	12	22.20	30.19	2.55	N
J	12	0.74	23.90	0.11	N
Total	90	3.14	64.02	0.46	N

(a) N = t is not statistically significant at the 99 percent level and the test hypothesis that the true bias is zero is not rejected.

S = t is statistically significant at the 99 percent level, the test hypothesis is rejected, and it is concluded that the true bias is probably not zero.

TABLE 23. RESULTS OF ANALYSIS OF STANDARD SULFATE SOLUTIONS FOLLOWING PILOT PLANT TESTS

Laboratory	Standard 1		Standard 2		Standard 3	
	mg SO ₂ found	Difference, % ^(a)	mg SO ₂ found	Difference, % ^(a)	mg SO ₂ found	Difference, % ^(a)
A	1.8 ^(b)	-95.4 ^(b)	2.5 ^(b)	-96.8 ^(b)	4.0 ^(b)	-97.0 ^(b)
B	38.5	-2.3	82.5	4.6	142.5	8.4
C	34.5	-12.4	73.8	-6.5	122.0	-7.2
D	38.9	-1.3	77.8	-1.4	123.0	-6.5
E	35.3	-10.4	58.3 ^(b)	-26.1 ^(b)	45.0 ^(b)	-65.8 ^(b)
F	46.0 ^(b)	16.8 ^(b)	101.0 ^(b)	28.0 ^(b)	150.0	14.1
G	39.3	-0.3	76.7	-2.8	127.4	-3.1
H	37.5	-4.8	77.7	-1.5	112.0	-14.8
I	37.2	-5.6	71.0	-10.0	128.0	-2.7
J	39.5	0.3	77.6	-1.6	129.0	-1.9
Means ± Std. Dev.	38.5 ± 3.3	-2.2 ± 8.4	74.4 ± 7.3	-2.7 ± 4.6	129.2 ± 12.0	-1.71 ± 9.1
Actual Value, mg SO ₂	39.4		78.9		131.5	

(a) Based on actual value.

(b) Data rejected based on Dixon's criteria (95% confidence).

TABLE 24. RESULTS OF ANALYSIS OF STANDARD SULFATE SOLUTIONS FOLLOWING FIELD TESTS

Site	Laboratory	Milligrams of SO ₂ Found in Standards			
		S-1, 5, and 9	S-2, 4, and 6	S-3, 7, and 8	
II	A	8.2	21.3	21.3	
		18.2	19.8	23.0	
		13.5	11.1	36.0	
	B	13.7	28.7	57.4	
		14.3	29.4	58.8	
		15.0	29.0	58.1	
	C	0.1 (a)	0.8 (a)	1.4 (a)	
		3.5 (a)	2.0 (a)	3.0 (a)	
		4.2 (a)	3.2 (a)	2.8 (a)	
	D	14.8	28.4	56.8	
		13.9	29.4	56.3	
		13.2	27.1	56.4	
	III	A	<u>S-13, 17, and 19</u>	<u>S-12, 15, and 18</u>	<u>S-11, 14, and 16</u>
			12.7	27.0	55.3
			14.1	27.9	54.9
B		13.7	28.1	56.1	
		17.1	30.9	59.5	
		16.1	31.2	58.3	
C		15.5	30.7	58.6	
		15.9	31.1	62.0	
		16.7	29.2	56.7	
D		14.2	29.6	56.9	
		14.0	28.3	56.7	
		14.2	28.2	57.2	
F		14.2	28.5	57.2	
		13.7	24.7	55.8	
		14.1	27.2	57.2	
		14.4	27.5	59.4	
Actual Value, mg SO ₂		14.6	29.2	58.4	

(a) Rejected as outlying values.

A and C, Site II, indicate problems in the conduct of the sulfate analytical procedure.

Since analyses were performed in replicate by the various laboratories, the results may be treated statistically to obtain an estimate of both the within- and between-laboratory component of variance in the analytical portion of the method. The results of such a statistical analyses are summarized in Table 25. The method used to obtain the between- and within-laboratory standard deviations is the same as that employed in between- and within-laboratory component of variance analyses discussed previously.

The analysis of the accuracy of the Site III standards data gives mean differences of 0.33, -1.13, and -1.99 percent, for the 14.6, 29.2 and 58.4 mg. standards, respectively, between the experimentally determined and actual values. Based on Student's Test, these differences do not constitute a statistically significant bias at the 95 percent confidence level. It should be noted that in rigorous application Student's Test is applicable to independently sampled measurements, a condition which is not satisfied in this case since each laboratory performed triplicate determinations. However, a more sophisticated test did not seem warranted.

DISCUSSION AND CONCLUSIONS

The Project Threshold Study provides the following measures of precision and accuracy of ASTM D 3226-73T for determination of SO₂ and SO₃ in gaseous combustion products.

Between-Laboratory Component of Variance (Reproducibility)

The relationship of the between-laboratory component of variance, \hat{S}_B , and the mean SO₂ concentration, m , over the range 300 to 2500 ppm SO₂ may be estimated by the equation

$$\hat{S}_B = 12.48 \sqrt{m} - 96.70,$$

where \hat{S}_B and m are expressed in ppm SO₂.

The relationship of the between-laboratory component of variance, \hat{S}_B , and the mean SO₃ concentration, m , over the range 5 to 50 ppm SO₃ is estimated by the equation,

$$\hat{S}_B = 0.26 \sqrt{m} + 5.33,$$

TABLE 25. BETWEEN - AND WITHIN-LABORATORY VARIATION IN THE RESULTS OBTAINED FROM ANALYSIS OF STANDARD SULFATE SOLUTIONS

Site	Conc. of Standard, mg SO ₂	Number of Measurements		Mean of all Measurements, mg	Between-Lab Std. Dev, mg	Coefficient of Variation, %	Within-Lab Std. Dev, mg	Coefficient of Variation, %
		Per Lab	Total					
II	14.6	3	9	13.87	(a)	(a)	2.95	21.3
III	14.6	3	15	14.71	1.07	7.3	0.77	5.2
II	29.2	3	9	24.91	6.24	25.1	3.25	13.0
III	29.2	3	15	28.67	1.72	6.0	0.87	3.0
II	58.4	3	9	47.12	17.44	37.0	4.66	9.9
III	58.4	3	15	57.45	0.97	1.7	1.62	2.8

(a) Between-laboratory component of variance is not statistically distinguishable from zero.

where S_B and m are expressed in ppm SO_3 .

The between-laboratory component of variance for the sulfate analytical procedure expressed as the coefficient of variation ranged from 1.7 to 37 percent for standard solutions containing an equivalent of 14.6 to 58.4 mg SO_2 .

Within-Laboratory Component of Variance (Repeatability)

The relationship of the within-laboratory component of variance, \hat{S}_W , and the mean SO_2 concentration, m , over the range 300 to 2500 ppm SO_2 may be estimated by the equation

$$\hat{S}_W = 5.32 \sqrt{m} - 53.92,$$

where \hat{S}_W and m are expressed in ppm SO_2 .

The relationship of the within-laboratory component of variance, \hat{S}_W , and the mean SO_3 concentration, m , over the range 5 to 50 ppm SO_3 may be estimated by the equation,

$$\hat{S}_W = 2.43 \sqrt{m} - 4.76,$$

where \hat{S}_W and m are expressed in ppm SO_3 .

The within-laboratory component of variance for the sulfate analytical procedure expressed as the coefficient of variation ranged from 2.8 to 21.3 percent for standard solutions containing an equivalent of 14.6 to 58.4 mg SO_2 .

Between-Laboratory Standard Error

The field tests at three sites where the SO_2 concentrations ranged from about 200 to 2000 ppm yielded mean between-laboratory standard error estimates, expressed as the coefficient of variation, which varied from 20 to 94 percent. The corresponding mean between-laboratory standard error estimates for SO_3 measurements in the range of about 1 to 150 ppm varied from 85 to 174 percent.

Accuracy

The average of SO_2 determinations with known sulfur dioxide spikes added in the pilot plant tests differed from the true values by 11.4, -3.0, and 6.9 percent (based on true value) in the respective concentration ranges $X < 400$, $400 < X < 850$, and $X > 850$ ppm SO_2 . Student's t-test indicates that these biases are not statistically significant at the 99 percent confidence level. The average difference between the experimentally determined and true spike value for all measurements is 3.14 percent based on the true value. Statistically, this

difference can not be distinguished from zero.

The analysis of differences between experimentally determined and actual values of standard solutions indicates that there is not a statistically significant bias in determination of sulfate using the D 3226-73T analytical procedure.

As a whole, the Threshold study shows that ASTM D-3226-73T produces both SO_2 and SO_3 measurements which possess an inherent high degree of variability. Using the equations developed from the pilot plant study, the estimated between-laboratory standard error for determination of SO_2 at the levels of 225, 1000, and 2200 ppm would be 42, 32, and 24 percent, respectively, when expressed as the coefficient of variation. The field tests show even higher variability for SO_2 measurements at about 1000 and 2200 ppm with respective mean coefficients of variation of 45 and 94 percent. The mean coefficient of variation for the field measurements at 225 ppm (Site I) is about the same as predicted from the pilot plant study, 20 versus 24 percent.

The equations derived from the pilot plant study predict between-laboratory standard errors, expressed as the coefficient of variation, of 150, 100, and 30 percent, for determination of SO_3 at the levels of 4, 6, and 45 ppm, respectively. The mean coefficients of variation for field tests at comparable concentrations are 85, 93, and 174 percent, respectively.

The results of determination of SO_3 using the controlled condensation method in this study exhibit considerably more variation than observed by other investigators. Berger, Driscoll, and Morgenstern⁽¹⁷⁾ report a four to six percent coefficient of variation using the controlled condensation collection of SO_3 and a titration procedure for determination of sulfate. Studies by Forrest, et. al.⁽¹⁸⁾ and Hillenbrand, et. al.⁽¹⁹⁾ report a consistent set of SO_3 values when the controlled condensation method was applied to power plant emissions.

The work by Forrest, et. al.⁽¹⁸⁾ provides some possible explanations for the variation observed in the Threshold data. In Forrest's work it was found that sulfur trioxide was adsorbed on the quartz wool filter at the probe inlet and that heating the probe, even to 260C, did not prevent significant amounts of sulfuric acid from depositing on the probe walls. In the ASTM procedure, only the condenser wash is collected for the SO_3 determination.

It is particularly surprising that highly variable results were also obtained in the measurement of SO_2 in both the pilot plant and field studies. The collection of SO_2 in hydrogen peroxide is an accepted and widely used procedure. Berger, Driscoll, and Morgenstern⁽¹⁷⁾ report coefficients of variation ranging from 1.5 to 7.4 percent for collection of SO_2 in hydrogen peroxide followed by several different sulfate analytical methods. For the peroxide/barium chloranilate combination, the reported coefficient of variation is 2.6 percent. Collaborative testing of EPA Method 6 which involves collection of SO_2 in hydrogen peroxide followed by a barium perchlorate/thom titration for sulfate has been performed⁽²⁰⁾ and found to give acceptable precision.

The results of the study lead to the conclusion that ASTM D-3226-73T produces neither SO_2 nor SO_3 measurements with acceptable precision. The major source of the variability appears to be associated with the sampling portion of the method. However, analysis of the test data and discussions with the test participants failed to identify specific sources of sampling error.

Some difficulties with the sulfate analysis were noted as evidenced by results of several laboratories following the pilot plant and Site II tests. However, the Site III standards data shows that the sulfate analytical method can be performed with satisfactory accuracy and precision.

RECOMMENDATIONS

Based on the results of the Threshold of D 3226-73T study, it is recommended that the method be withdrawn as an ASTM Standard. It is further suggested in view of the environmental concern for sulfur compounds in the atmosphere and the need for a satisfactory reference method to determine sulfur oxides in source emissions, particularly SO₃, that additional study of the method be performed in order to correct its deficiencies and restore it to ASTM Standard status. Experience by other investigators using variations of the same procedure indicates that it can be developed to give sulfur oxide measurements with satisfactory accuracy and precision.

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APPENDIX

DETERMINATION OF SULFUR OXIDES IN FLUE GASES
(BARIUM CHLORANILATE METHOD)

SULFUR OXIDES IN FLUE GASES
(BARIUM CHLORANILATE METHOD)

ASTM Designation 71. This Standard of the American Society of Testing and Materials is issued under the fixed designation D ; the number immediately following the designation indicates the year of original adoption.

1. SCOPE

1.1 This method is intended for high precision determination of sulfur oxides emissions in flue gases.

1.2 This method is applicable to the determination of SO_2 (26-7950 mg/m^3 or 10-3000 ppm) and SO_3 (33-990 mg/m^3 or 10-300 ppm). A 25-liter flue gas sample containing about 30 mg/mm^3 or 10 ppm by volume of sulfur oxides will yield an absorbance at 530 nm of twice the blank value for a 1-cm cell.

1.3 Higher concentrations of either SO_2 or SO_3 may be determined by suitable aliquoting provided that the sulfate concentration in the final solution is within the region where Beer's law applies (up to 350 μg sulfate/ml).

2. SUMMARY OF METHOD

2.1 Sulfur trioxide is condensed as sulfuric acid by controlled cooling of the flue gas. The resulting sulfuric acid aerosol is collected on a filter which is maintained above the water dewpoint. This eliminates the problem of oxidation of dissolved sulfur dioxide, and provides improved precision and accuracy in SO_3 collection. Sulfur dioxide is collected in midget impingers (in series with the SO_3 collector) and oxidized to sulfuric acid by aqueous 3 percent hydrogen peroxide absorbing solution. The sulfate concentration of each solution is determined

separately by reaction with barium chloranilate in a pH-controlled, 50 percent alcohol solution to yield the highly colored acid chloranilate [1]. The concentration of the product colored species is determined spectrophotometrically at 530 nm. From the measured concentration of the sulfur oxides and the volumetric flow which is determined by a pitot tube traverse [2], the emission may be calculated.

3. SIGNIFICANCE

This method is useful for compliance testing, determining the validity of instruments, etc., in flue gases containing sulfur oxides.

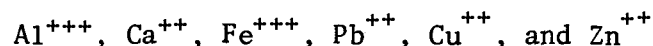
4. DEFINITIONS

4.1 For definitions of terms used in this method, refer to ASTM Definitions D1356, Terms Relating to Atmospheric Sampling and Analysis.¹

5. INTERFERENCES

5.1 Cationic Interferences

Cations such as



cause interference by precipitation of the acid chloranilate ion.

K^+ , Mg^{++} , Na^+ , and NH_4^+ reportedly cause 1 percent or less interference [1]. Cationic interferences are generally eliminated by use of a particulate (glass wool) filter in the probe.

5.2 Anionic Interference

The following substances have been found to give the percent interference listed [3] when added to a solution containing 250 $\mu\text{g}/\text{ml}$ of sulfate:

¹Annual Book of ASTM Standards, Part 23.

<u>Interfering Substance</u>	<u>Concentration in Final Solution</u>	<u>Percent Interference</u>
Oxalate	0.01 M	86 ^a
Phosphate	0.01 M	46 ^a
Fluoride	0.02 M	2
Bicarbonate	0.01 M	2
Chloride	0.02 M	2
Nitrate	0.02 M	nil
Formaldehyde	0.02 M	nil
Hydrogen peroxide	0.18%	nil

a) Reported not to interfere at 100 ppm concentration level [1]

If a glass wool filter is used to remove particulates containing sulfates, there appear to be no major anionic interferences since phosphate or oxalate anions are not expected to be important in fossil fuel effluents.

6. APPARATUS

6.1 Sampling Components

The following sections describe an integrated modular flue gas sampling apparatus for collection of SO₃ by the condenser method and collection of SO₂ in midget impingers.

6.1.1 Probe and Probe Heating - The probe is constructed of a 6-foot length of pyrex tubing with a 12/5 socket joint on the downstream end. The other end of the probe, which protrudes into the stack, is fitted with a 38-mm diameter by 4-cm length of pyrex tube, loosely packed with quartz or pyrex wool for particulate filtration. The glass probe is inserted into a stainless steel shell with stack adapter assembly which allows various probe insertion depths. The glass probe is wrapped with 20-gauge asbestos-covered wire to allow heating of the glass insert above the acid dewpoint. The probe temperature is controlled by a variable transformer which is preset (160 C) in the laboratory. A stainless steel extension tube could permit the sampling probe to be extended to approximately 4 meters.

6.1.2 SO₃ Condenser - The condenser is constructed of a glass coil with a medium porosity sintered glass frit at the downstream end. The upstream end of the condenser assembly terminates in a ball joint which mates with the probe. The downstream ball joint mates with the socket joint in the SO₂ impinger. The condenser is maintained above the water dewpoint (usually about 50 C) by immersion in an electrically heated, thermostatted water jacket.

6.1.3 Midget Impingers - Two conventional midget impingers are modified by addition of 12/5 ball and socket connectors. (Plastic or rubber tubing is not desirable because of absorption and desorption of gaseous species.)

6.1.4 Critical Orifice Meter - A critical orifice² with vacuum gauges provided upstream and downstream to monitor the critical flow condition, $\Delta P > \sim 380$ mm Hg. The meter is equipped with a filter upstream to prevent plugging and a thermometer for determining gas volume corrections.

6.1.5 Power Control - The power panel is a strip of 110 VAC power outlets with separate switches. The pump (capable of achieving a static vacuum of 660 mm Hg and maintaining pressure drop across a 3 liter/min critical orifice), the variable transformer, and the power line to the SO₃ condenser are plugged into the control panel and controlled by the separate switches.

6.1.6 Critical Orifices - Set of calibrated critical orifices, 0.5, 1.0, 3.0 liter/min.

6.1.7 Stop Watch - For measurement of sampling duration.

6.1.8 Thermometer - A dial thermometer or thermocouple (200-500 F) for measuring the stack gas temperature.

²Those manufactured by the Millipore Corp. have been found to be satisfactory.

6.1.9 Plastic Bottles - Polyethylene bottles for storage of impinger and condenser samples.

6.2 Laboratory Equipment

6.2.1 Shaker, wrist-action

6.2.2 Centrifuge, small clinical type (capable of 2800-3000 rpm)

6.2.3 Analytical balance

6.2.4 Spectrophotometer for use in the visible region (at 530 nm)

6.2.5 Oven or muffle furnace capable of maintaining 250 C

7. REAGENTS

7.1 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.³ Other reagents may be used provided it can be demonstrated that they are of sufficiently high purity to permit their use without decreasing the accuracy of the determination.

7.2 Purity of Water

Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to ASTM specification D1193, Reagent Water.⁴ Additionally, this method requires the use of sulfate-free water (see Section 7.12).

³"Reagent Chemicals, American Chemical Society Specifications," American Chemical Society, Washington, D.C. For suggestions on testing reagents not listed by ACS, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N.Y.

⁴Annual Book of ASTM Standards, Part 23.

7.3 Hydrogen Peroxide (3 percent) for SO₂ Collection

Prepare by tenfold dilution of 30 percent hydrogen peroxide. This reagent should be prepared fresh daily and stored in polyethylene containers.

7.4 Sulfuric Acid, 0.25 M

Add 10 ml of 18 M H₂SO₄ to 600-700 ml of water in a 1000-ml volumetric flask and mix by swirling the flask. Dilute to the mark with water and mix well. Dilute 145 ml of this 0.18 M solution to 1000 ml and again mix well. Standardize against anhydrous sodium carbonate.

7.5 Barium Chloranilate

7.6 Ethyl Alcohol

7.7 Methyl Alcohol

7.8 Buffer, pH 5.6

Add 50 ml of 0.2 M acetic acid (11.4 ml 99 percent acid in 1000 ml of distilled water) to 500 ml of 0.2 M sodium acetate (27.2 g NaC₂H₃O₃ · 3H₂O in 1000 ml of water).

7.9 Sodium Hydroxide, approx. 1 N

Slowly add 40 g of NaOH pellets to 800-900 ml of water in a 2-liter beaker with stirring until all pellets are dissolved. Dilute to 1000 ml with water and mix well. Store in a polyethylene or polypropylene container.

7.10 Hydrochloric Acid, approx. 1 N

Add 86.3 ml of 11.6 M HCl to 800-900 ml of water in a 2-liter beaker with stirring. Dilute to 1000 ml with water and mix well. This solution can be stored in glass.

7.11 Phenolphthalein, 0.05 percent

Dissolve 0.05 g phenolphthalein in 50 ml ethanol and dilute to 100 ml with water.

7.12 Sulfate-Free Water

Distilled water is poured through a column of mixed-bed ion exchange resin⁵ contained in a large funnel (150 mm diameter, 100 mm stem). The stem is indented near the bottom to hold a plug of glass wool in place. The resin (no pretreatment) is packed to a depth of 4-5 cm in the stem. Another plug of glass wool is placed above the resin bed. The remainder of the funnel is used as a water reservoir. The distilled water used is usually quite low in sulfate; however, the mixed bed exchanger has a capacity of about 0.5 meq/ml, thus changing the resin bed after 25-30 liters of water throughput is recommended. This volume may be adjusted after checking the effluent water for blank level.

7.13 Anhydrous Sodium Carbonate7.14 Potassium Acid Phthalate

Dissolve 2.000 + 0.002 g in 1 liter of water.

7.15 Methyl Orange Indicator, 0.1 percent

Dissolve 0.1 g in 100 ml of water.

7.16 Modified Methyl Orange Indicator

Dissolve 0.75 g xylene cyanol and 1.5 g methyl orange in 1 liter of distilled water.

7.17 Xylene Cyanol

Technical grade.

⁵Amberlite MB-3 has been found to be satisfactory.

8. SAMPLING

8.1 Preliminary Estimates

To estimate sampling rates, expected SO₂ concentrations may be calculated since sulfur oxide emissions depend primarily on the sulfur content of the fuel. For oil- and coal-fired units,⁶ SO₂ concentration may be estimated (within 20 percent) from the fuel analysis (C,H,S), the fuel feed rate and the amount of excess air. The SO₃ content is usually 1-3 percent of the SO₂ concentration.

8.2 Selection of Sampling Rates

SO₃ - The controlled condensation method for SO₃ collection has been shown to have a collection efficiency of 98 percent by a number of investigators [4-6]. The collection efficiency was examined as a function of flow rate (1-20 liter/min), concentration, and filter medium. In all cases, quantitative (> 97 percent) collection efficiency was obtained even at a flow rate of 20 liter/min. For SO₃ collection by the controlled condensation method, the flow rate is, therefore, not critical.

SO₂ - The collection efficiency of SO₂ absorbed in 3 percent peroxide solution in midget impingers was determined [3] as a function of concentration (200-2000 ppm), temperature (up to 40 C), and flow rate (0.05 liter/min) [3]. Over the temperature and concentration range examined, no change in the collection efficiency was observed. With 15 cc of 3 percent peroxide solution, 96 percent collection efficiency was obtained at sampling rates of 0.5 and 1 liter/min. Collection efficiency dropped to 90 and 87 percent at 3 and 5 liter/min, respectively. However, quantitative collection can still be obtained if two impingers in series are used. At the highest flow rate (5 liter/min), some blowover and loss of sample occurred. Thus, the recommended sampling rate for SO₂ is 3 liter/min or less.

⁶Sulfur compound emissions are insignificant for gas-fired units.

8.3 Sample Collection

The probe module is fitted to the stack flue. Power cords are connected between the SO_x probe heater and the variable transformer. The probe is then heated to the operating temperature of 160 C. The SO₃ condenser is electrically connected to the power control panel. After checking the water level in the SO₃ condenser jacket (adding water, if necessary), the condenser heater is switched on and allowed to come to operating temperature (60-70 C). The SO₂ impingers are charged with 15 ml of 3 percent peroxide solution. After the probe and SO₃ condenser have reached their respective operating temperatures, the collector module is assembled as shown in Figure 1. The pump is connected to the second impinger with a vacuum hose and started from the switch on the control module. The time is recorded. The operator checks ΔP across the critical orifice selected (0.5, 1.0, 3.0 liter/min) and records the pressure and temperature values (at 5-minute intervals) during sampling. The stack gas temperature and moisture content are also determined at this time. At the end of the 20-30 minute sampling period, the pump is switched off and the time is recorded. The sample volume is calculated from the time interval and the flow rate of the critical orifice. Disassemble the sample module. Rinse the SO₃ collector⁷ with several portions of sulfate-free water. Collect the sample in a polyethylene bottle for transport to the laboratory. Rinse the SO₃ collector with alcohol. Then draw clean air through the collector for a short period of time and the system is ready to be recycled. Transfer the contents of the two midget impingers (which contain the SO₂ sample) into a polyethylene bottle. Rinse the impingers several times with sulfate-free distilled water and add these washings to the contents of the polyethylene bottle. After the impingers are charged with 15 ml of 3 percent hydrogen peroxide, the system is ready for collection of additional samples.

8.4 Volumetric Flow Determination

See Reference 2.

⁷The water can be forced through the frit by applying a slight pressure from a squeeze bulb attached to a 12/5 ball joint.

9. PROCEDURE

9.1 Analysis for SO₃

Quantitatively transfer the contents of the polyethylene bottle into a 100-ml graduated beaker. Evaporate the solution to approximately 15 ml and transfer to a 50-ml volumetric flask. Pipet 5 ml of pH 5.6 sodium acetate buffer, then add 25 ml of ethanol and mix well. Dilute to the 50 ml mark with sulfate-free distilled water. Pour contents into a 100-ml volumetric flask containing 0.2-0.3 g barium chloranilate. Stopper the flask and shake for 20 minutes on a wrist-action shaker. Then centrifuge the solution at 2800-3000 rpm for five minutes, decant the supernatant liquid into a spectrophotometer cell and read the absorbance versus a water blank at 530 nm using 1-cm cells.

9.2 Analysis for SO₂

Quantitatively transfer the solution from the SO₂ impingers into a 50-ml volumetric flask and dilute the mark with sulfate-free distilled water. Pipet a suitable sized aliquot into a 50-ml volumetric flask. Add 1 drop of phenolphthalein solution to the flask, then add 1 N NaOH dropwise until the solution just turns pink. Add 1 drop of 1 N HCl to return the solution to colorless. Pipet in 5 ml of pH 5.6 buffer, then add 25 ml of ethanol and mix well. Dilute to the mark with sulfate-free water and again mix well. Pour contents into a 100-ml volumetric flask containing 0.2-0.3 g of barium chloranilate. Stopper the flask and shake for 20 minutes on a wrist-action shaker. Centrifuge 15 ml of the solution at 2800-3000 rpm for 5 minutes, decant the solution into 1-cm cells, and read the solution absorbance versus a water blank at 530 nm.

10. CALIBRATION AND STANDARDS

10.1 Sulfate

Standardization of the 0.025 M H₂SO₄ is accomplished with anhydrous sodium carbonate. Heat 2-3 g of anhydrous sodium carbonate in a crucible for 4 hours at 250 C to remove water and decompose any residual

bicarbonate. Cool in a dessicator. Accurately weigh 0.115 ± 0.005 g of the dried sodium carbonate into each of three 250-ml Ehrlemeyer flasks and dissolve the sample in 50 ml of water. A blank containing no added sodium carbonate should be determined with each set of samples. Add 2 drops of 0.1 percent methyl orange, or 2 drops of 0.1 percent modified methyl orange indicator solution and titrate with the 0.025 M H_2SO_4 in a 50-ml buret to a color change from yellow to red-orange (with methyl orange) or to a gray neutral shade (with modified methyl orange). A color reference of 50 ml of the potassium acid phthalate solution containing 2 drops of indicator should be used to identify the endpoint. The normality of the H_2SO_4 , N, is computed as follows (where V = ml H_2SO_4 used in titration):

$$N = \text{g Na}_2\text{CO}_3 / .053 V$$

10.2 Absorbance

A standard curve is prepared by pipetting 0.5, 1, 2, 5, and 7 ml of 0.025 M H_2SO_4 into 50-ml volumetric flasks. Add water to the first four to bring all volumes up to about 10 ml. Add 1 drop of phenolphthalein solution, then add 1 N NaOH dropwise to the appearance of a pink color. Add 1 N HCl dropwise to the disappearance of a pink color. (This will usually require just one drop.) Pipet 5 ml of pH 5.6 buffer into each flask. Pipet 25 ml of ethanol into each flask. Mix well, then bring to the mark with water, stopper, and again mix well. Pour the contents of each flask into a corresponding 100-ml volumetric flask containing 0.2-0.3 g of barium chloranilate. Shake for 20 minutes on a wrist-action shaker, then centrifuge 10-15 ml of this suspension for five minutes at 2800-3000 rpm. Decant the centrifugate into 1-cm cells and read the absorbance versus water at 530 nm. The blank (no sulfate) versus water should read no more than 0.01 to 0.03 absorbance units. Plot the absorbance versus sulfate concentration in ug/ml final solution.

10.3 Sensitivity

The minimum detection limit for SO_3 can be increased by collecting a larger volume of flue gas, by concentrating the condenser

washings (using 25-ml volumetric flasks and halving volumes of added reagent), by the use of longer path lengths cells (5 cm), or by use of a different pH (1.8 with phosphate buffer) [7] or wavelength (330 instead of 530 nm) [8]. The simplest of these is to increase the sampling time or use a long path cell (an immediate factor of 5 increase in absorbance can be gained by using a 5-cm rather than a 1-cm cell).

10.4 Temperature

The solution temperature has little effect on absorbance over the range of 25 ± 5 C; thus, samples do not have to be thermostatted and may be run with ± 5 C of the standard curve.

10.5 Mixing Time and Stability

A 20-minute mixing time has been determined to be the minimum time for maximum reaction to occur. Longer times, up to 35-40 minutes, will not affect results should solutions be inadvertently shaken too long.

10.6 Once centrifuged, stoppered solutions are stable for up to one hour's time.

11. CALCULATIONS

11.1 Calculate the concentration of SO_x in the sample as follows:

11.1.1 ppm SO_2 (dry basis) = corrected absorbance x slope
(from calibration curve) x 50 x (50/A) x (24.1/96) x (1/V)

where A = aliquot volume, ml

V = sample volume in liters [sampling rate of orifice (corrected to S.T.P.) x time]

11.1.2 ppm SO_3 (dry basis) = corrected absorbance x slope
(from calibration curve) x 50 x (24.1/96) x (1/V)

11.1.3 SO_x (mg/m^3) = 41.4 x MW x ppm SO_x

11.2 Calculation of SO_x Emissions

The emission procedure determines the mass (weight) rate of a pollutant leaving a stack into the atmosphere. The emission value represents the pollution intensity of a source; hence, it is one of the best pollution characterizations of an exhaust gas stream.

The general relationship for instantaneous emission is given by:

$$E_a = \int_A C_a \vec{V} \cdot \vec{n} \, dA$$

where E_a = emission of pollutant (a)

C_a = concentration of pollutant (a)

\vec{V} = velocity of the gas stream (determined by pitot tube traverse)

\vec{n} = unit vector normal to the cross-sectional area of the duct

A = cross-sectional area of the duct

Where the concentration of pollutant is constant over the cross-sectional area of the duct, the emission may be calculated from:

$$E = CQ \text{ (lb/hr or kg/hr)}$$

where C = pollutant concentration at duct conditions (lb/ft³ or kg/m³)

Q = the volumetric flow at duct conditions (ft³/hr or m³/hr)

12. PRECISION AND ACCURACY

12.1 Precision of Analytical Procedure

The average absorbance of ten samples of K₂SO₄, each containing 250 ug of sulfate per ml, was determined to be 0.474, with a standard deviation of +0.002, and a coefficient of variation of ± 0.4 percent (for the analytical method only).

12.2 Precision of Sampling and Analysis

The precision of SO₂ concentration determination in a flue gas has been found to be + 2.6 percent at 1500 ppm [9]. The precision of SO₃ determination is estimated as + 5 percent at 10 ppm.

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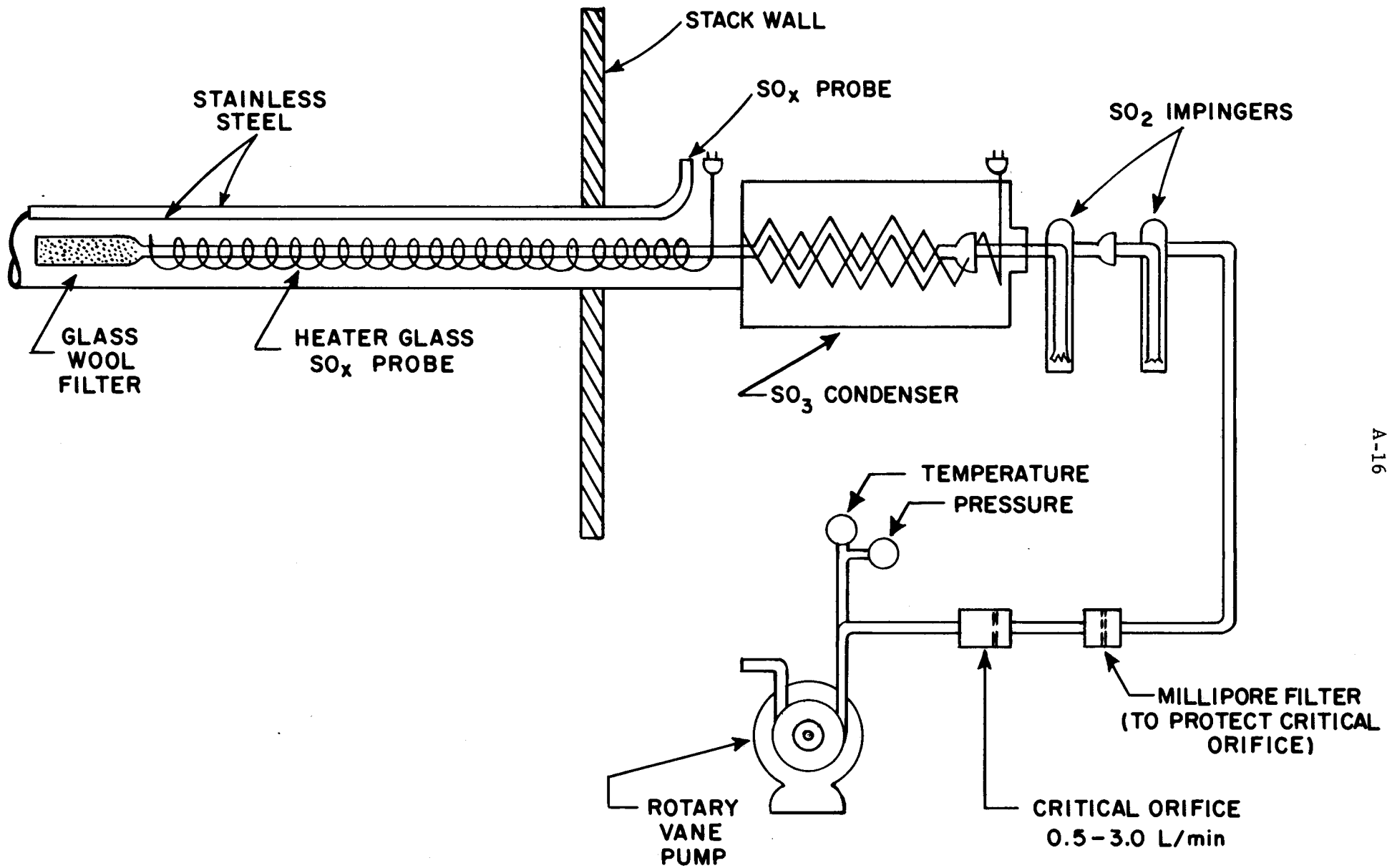


FIG. 1

