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INTERLABORATORY COOPERATIVE STUDY OF THE PRECISION AND ACCURACY OF THE MEASUREMENT OF LEAD IN THE ATMOSPHERE
USING THE COLORIMETRIC DITHIZONE PROCEDURE

J. F. Foster, G. H. Beatty, and J. E. Howes, Jr.
Battelle Memorial Institute

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INTERLABORATORY COOPERATIVE STUDY OF THE PRECISION AND ACCURACY OF THE MEASUREMENT OF LEAD IN THE ATMOSPHERE USING THE COLORIMETRIC DITHIZONE PROCEDURE

by

J. F. Foster, G. H. Beatty, and J. E. Howes, Jr.

INTRODUCTION

This report presents the results obtained from an experimental study of the accuracy and precision of measurements of particulate and vaporous lead using a colorimetric dithizone procedure as described in ASTM Method D-3112 (*). Measurements of lead concentration in spiked and unspiked atmospheric air samples were performed by eight participating laboratories at three test sites: Los Angeles, California; Bloomington, Indiana; and New York, New York. The first series of field tests were conducted at the University of Southern California on August 15-21, 1971; the second series of field tests were conducted at Indiana University on October 24-30, 1971; and the third series of field tests were conducted at Cooper Union (New York City), on January 9-15, 1972. All measurements were made according to a tentative ASTM method for lead in the

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(*) This study was funded by the American Society for Testing and Materials as part of a larger experimental program designated Project Threshold that involved the sampling of other atmospheric contaminants (nitrogen dioxide, sulfur dioxide, dustfall, total sulfation, and particulate matter). See References 1 through 5.

atmosphere from which ASTM Method D 3112(6)* evolved.

This report describes the experimental testing program, gives a complete tabulation of the experimental data used in the statistical analyses, and presents estimates of accuracy and precision of the lead method derived from the test results.

SUMMARY OF RESULTS

Particulate Lead

The statistical analysis of 126 particulate lead determinations performed at three different test sites produced the following precision and accuracy data.

Precision

Precision estimates derived from all determinations at each site are summarized below as the between-laboratory precision (reproducibility), S_B, the within-laboratory precision (repeatability), S_W, and the corresponding coefficients of variation, CV, in percent.

		Precision Estimates			
		Between-Laboratory		Within-Laboratory	
Site	Mean Lead Conc, μg/m^3	S_B, μg/m^3	CV,%	S_W, μg/m^3	CV,%
Los Angeles	1.22	(a)	(a)	0.12	10
Bloomington	0.46	0.06	13	0.03	8
New York City	1.45	0.16	11	0.07	5

(a) The within-laboratory variability accounted for essentially all the variation observed in the data. Consequently, a meaningful estimate of between-laboratory precision was not obtained.

Accuracy

Test results at one of the three sites in which known lead spikes were added to selected samples prior to analyses indicate that the test method may yield results which are slightly higher than the true value. Combined data for all sites (30 determinations) shows that, on the average, spike determinations were about 17 percentage points higher than the predicted value. This difference constitutes a bias which is statistically significant when subjected to Student's

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*References are listed on page 45.

t Test at the 95 percent confidence level.

Vaporous Lead

Statistical analysis of 19 vaporous lead samples performed at the three sites provide the following precision and accuracy data.

Precision

The between-laboratory standard error estimates, S_T (between-laboratory)*, of single vaporous lead determinations at Los Angeles and Bloomington expressed as the coefficient of variation are 64 and 14 percent, respectively. The respective mean vaporous lead concentrations at Los Angeles and Bloomington are 0.044 and 0.007 $\mu g/m^3$.

A limited number of duplicate determinations at New York City (mean vaporous lead concentration 0.079 $\mu g/m^3$) provide between-laboratory (S_B) and within laboratory (S_W) precision estimates of 0.032 and 0.016 $\mu g/m^3$, respectively. Expressed as the coefficient of variation, these estimates are 41 and 20 percent, respectively.

Accuracy

At Los Angeles and Bloomington, the analysis of a limited number of samples spiked with a known quantity of lead and subjected to the sampling procedure indicate that the test method may yield vaporous lead results which are less than the true value. However, based on only three determinations at Los Angeles and four at Bloomington, the difference (bias) between the experimentally determined and predicted values is not significant when Student's t Test is applied at the 95 percent confidence level.

In contrast, analysis of lead-spiked charcoal samples not subjected to the sampling procedure gave results which were slightly higher than the predicted value. However, the mean difference (15 percent) is not statistically significant at the 95 percent confidence level.

EXPERIMENTAL PROGRAM

Test Method Description

The method subjected to interlaboratory testing was a preliminary

---

*S_T (Between-Laboratory)=$\sqrt{S_B^2 + S_W^2}$

version of the current ASTM D 3112-72T procedure. The method describes equipment and procedures for measurement of atmospheric concentrations of particulate lead in the range of 0.01 to 10 $\mu g/m^3$ and vaporous lead at concentrations below 0.5 $\mu g/m^3$. Particulate lead is collected by filtration of a measured volume of air through glass fiber or membrane-type filters. Vaporous lead is collected by adsorption on a column of activated charcoal after removal of the particulate lead.

After digestion steps, lead on the filter and the charcoal is determined by colorimetric analysis of the reddish lead dithizonate complex.

A copy of the detailed test procedure used in the interlaboratory testing program is given in Appendix A. The method is essentially the same as ASTM D 3112-72T with the exception that D 3112-72T specifies the use of EDTA to decompose the lead dithizonate in the colorimetric analysis. Diethyldithiocarbamate is specified in the earlier version with an option to use EDTA. In this study, all lead analyses were performed using diethyldithiocarbamate to decompose the lead dithizonate.

Sampling Apparatus

Each cooperator used sampling apparatus as specified by the test procedure. All laboratories used glass fiber filters mounted in holders attached to the sample generating system by short pipe nipples. Figure 1 shows the filter holders as they were attached to the sampling manifold. TFE tubing was used to conduct the filtered air sample to the vaporous lead charcoal traps. Figure 2 shows the sampling manifold with projecting sampling lines and a pair of gas metering systems used for duplicate sampling by one of the cooperating laboratories. Figure 3 presents two views showing typical vaporous lead traps and the pump and metering equipment used by the various laboratories.

Figures 4, 5, and 6 present schematic diagrams of the equipment and sampling systems used by three of the laboratories at Site I. These diagrams typify the equipment and system arrangements used during the three site tests. Figure 6 also gives the dimensional aspects of a typical sampling system arrangement.

Sample Generating System

A special sample generating system shown schematically in Figure 7

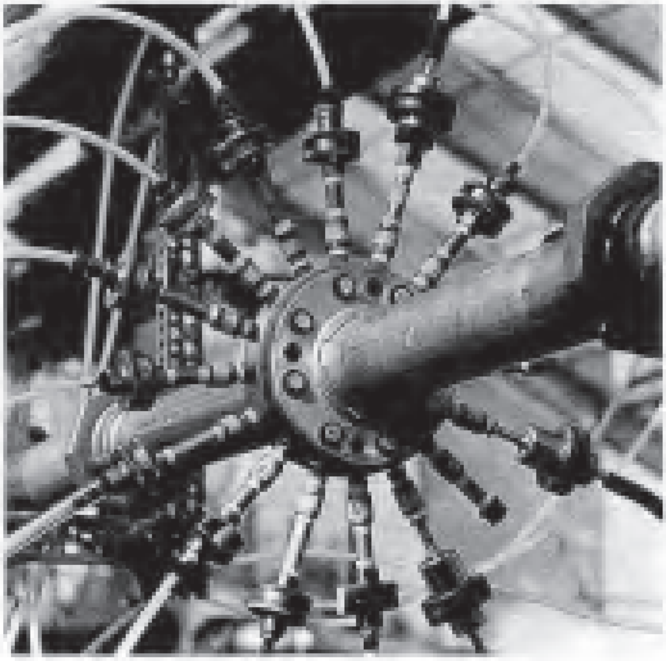


FIGURE 1. LEAD-SAMPLING MANIFOLD SHOWING PARTICULATE FILTER HOLDERS

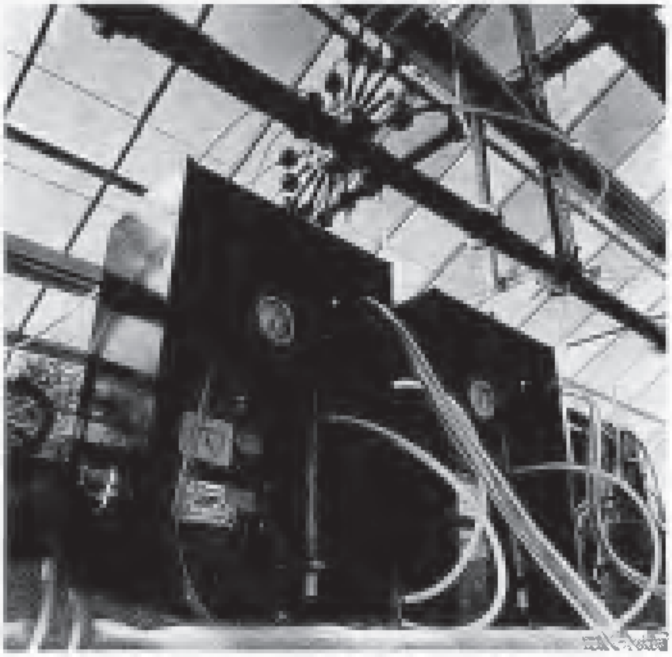
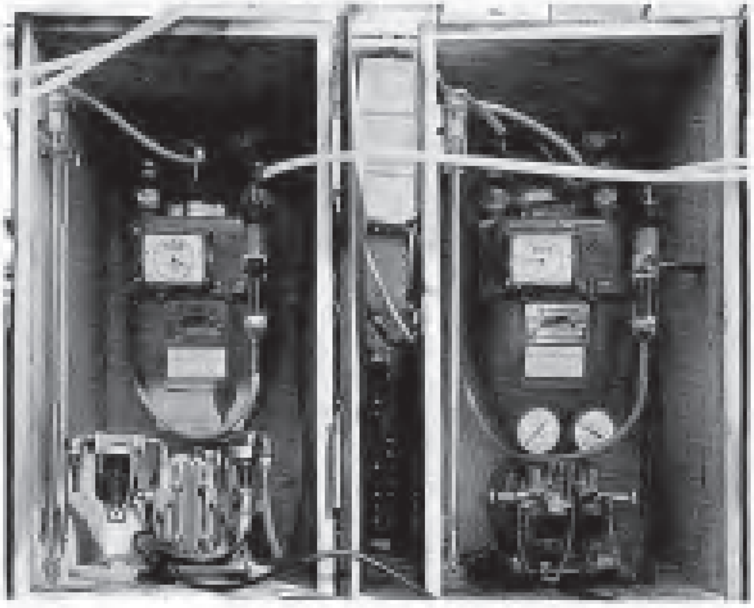


FIGURE 2. LEAD-SAMPLING MANIFOLD, SAMPLING LINES, AND TYPICAL GAS-METERING SYSTEMS



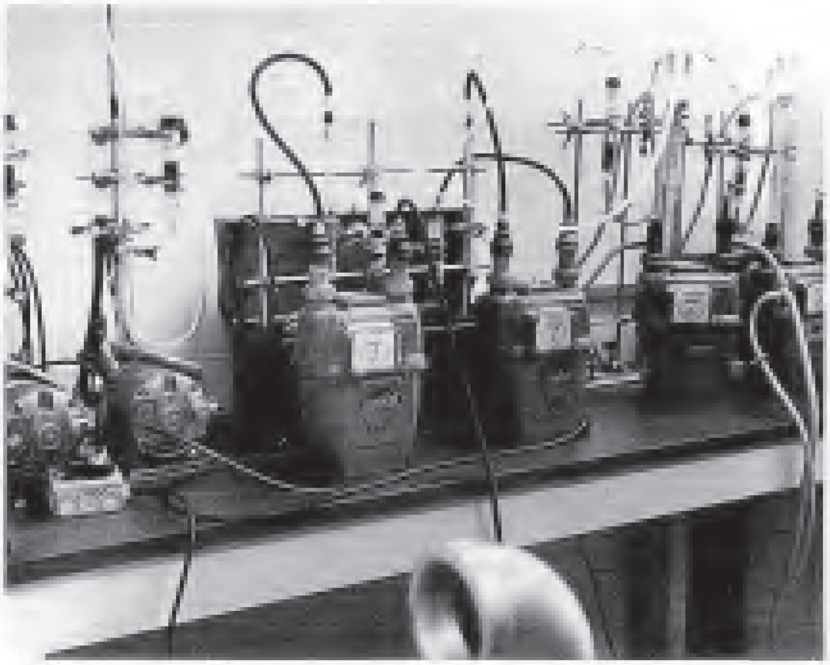


FIGURE 3. TWO PHOTOS SHOWING CHARCOAL TRAPS FOR COLLECTION OF VAPOROUS LEAD AND TYPICAL PUMP AND GAS-METERING SYSTEMS

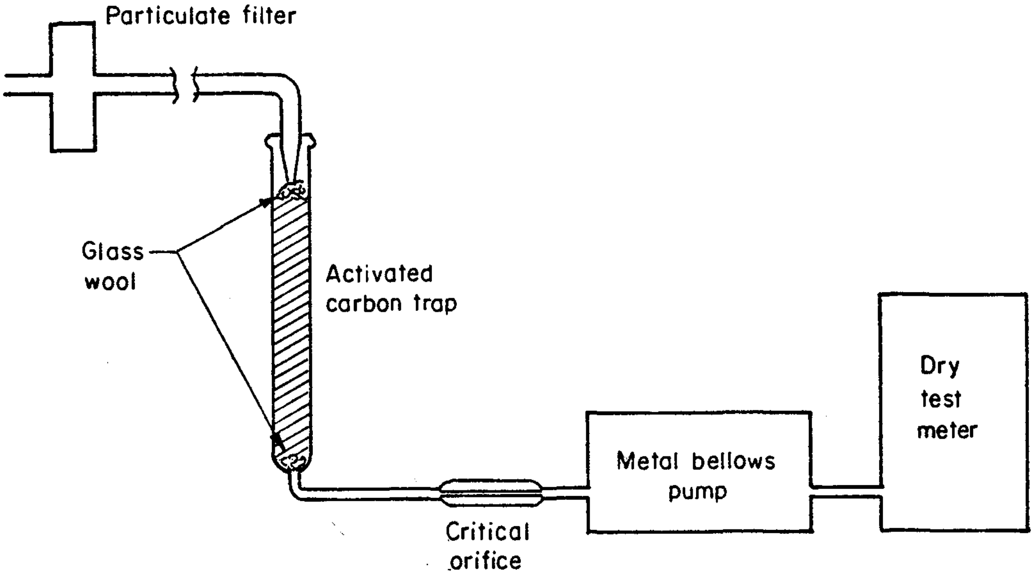


FIGURE 4. SCHEMATIC DIAGRAM OF SYSTEM USED FOR SAMPLING PARTICULATE AND VAPOROUS LEAD. LABORATORY N_1, SITE I

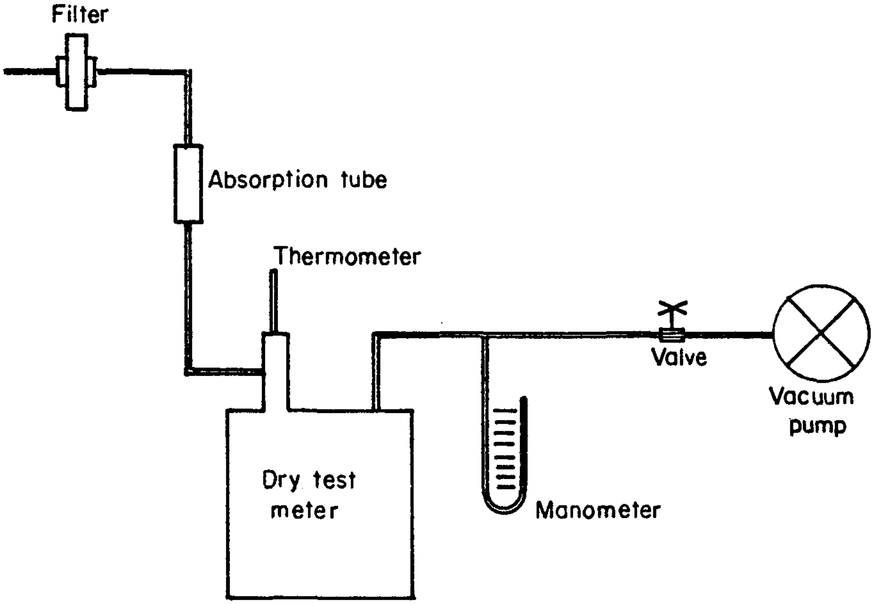


FIGURE 5. SCHEMATIC DIAGRAM OF SYSTEM USED FOR SAMPLING PARTICULATE AND VAPOROUS LEAD. LABORATORY K_1, SITE I.

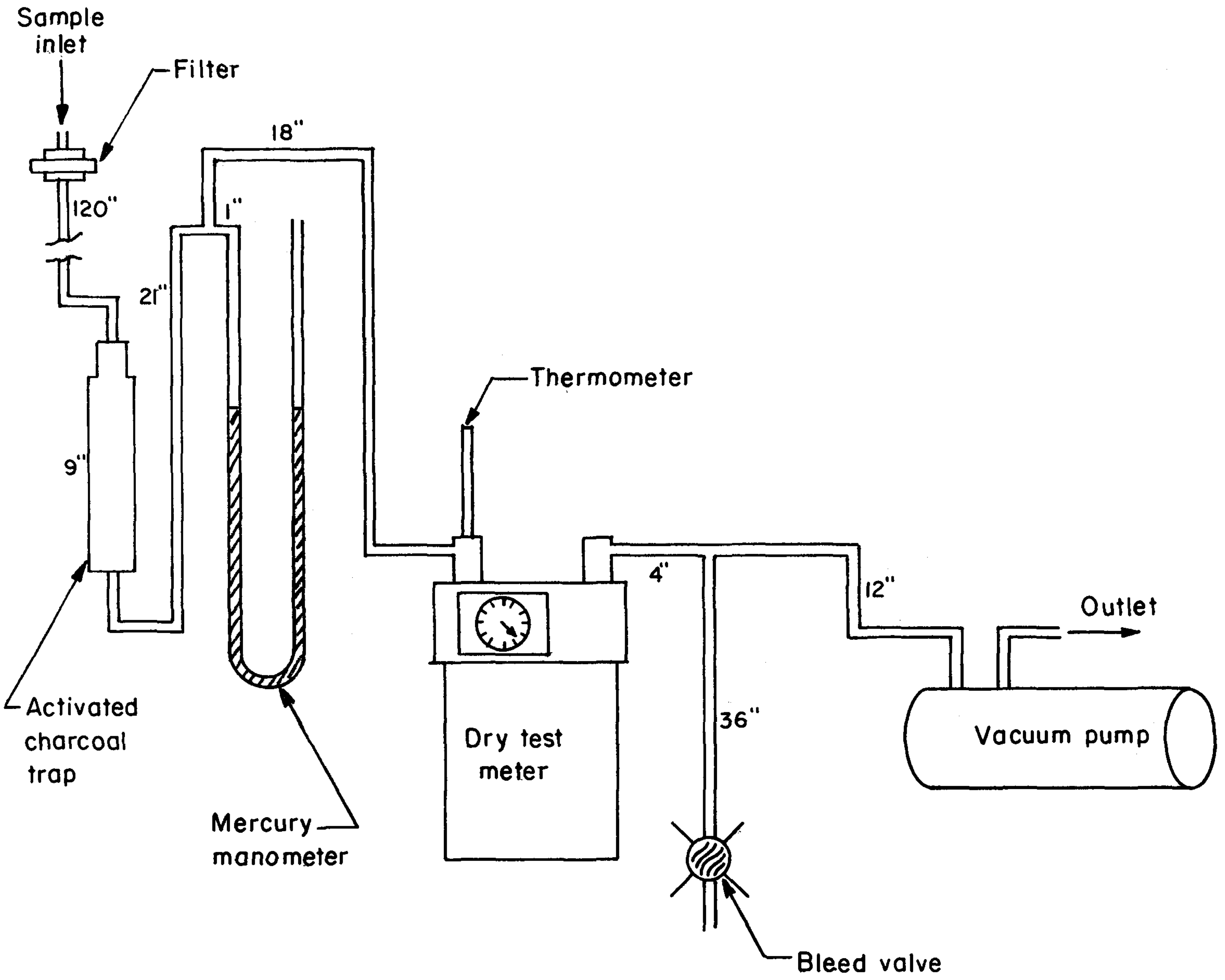


FIGURE 6. SCHEMATIC DIAGRAM OF SYSTEM USED FOR SAMPLING PARTICULATE AND VAPOROUS LEAD LABORATORY J_1, SITE I.

was designed and constructed to deliver a stream of outside air to a convenient indoor sampling location at the three test sites. The system which was constructed of 3-inch aluminum pipe, consisted of a vertical air intake section which extended well above roof levels, a horizontal section (Figure 7) containing the sampling manifold and an induction fan to draw in an ambient air stream. The system was fitted with a 2-inch orifice and manometer and a Hastings Model AHL5 mass flow meter for flow measurement and control valves to regulate flow. System flow was maintained at 143 cfm for all test series.

The sampling manifold contained individual nozzles to permit simultaneous withdrawal of 16 identical samples from the air stream. Figure 8 shows the sampling manifold with its radial arrangement of 16 nozzles spaced a equal angles around the periphery of a special pipe union. Each nozzle had a knife-edged opening with an area of .036 in^2 which permitted sampling under isokinetic conditions when the generating system flow was 143 cfm and the sample flow rate was 0.7 cfm as specified by the test method.

Separate studies showed that there was not a significant difference in lead concentrations at the 16 sampling nozzles in the manifold, consequently simultaneously drawn ambient atmospheric samples are considered to contain identical concentrations of lead.

Test Pattern

Interlaboratory testing was performed at three different test sites: Los Angeles, California (Site I); Bloomington, Indiana (Site II); and New York (Manhattan), New York (Site III). Five days of testing was conducted at each site. One particulate lead test, approximately 24 hours in duration, was conducted each day during the first four days and a 36-hour test was conducted on the final day. In each test, the laboratories sampled concurrently with two sampling systems. The same pair of vaporous lead charcoal traps were used throughout the test week and accumulated sampling times of approximately 130 hours. Eight laboratories participated in the Site I tests. A total of 80 particulate lead determinations were performed using the test pattern shown in Table 1. Seven laboratories participated in the tests at Sites II and III. Seventy particulate lead determinations were made at each of the sites in accordance with the test patterns given in Tables 2 and 3.

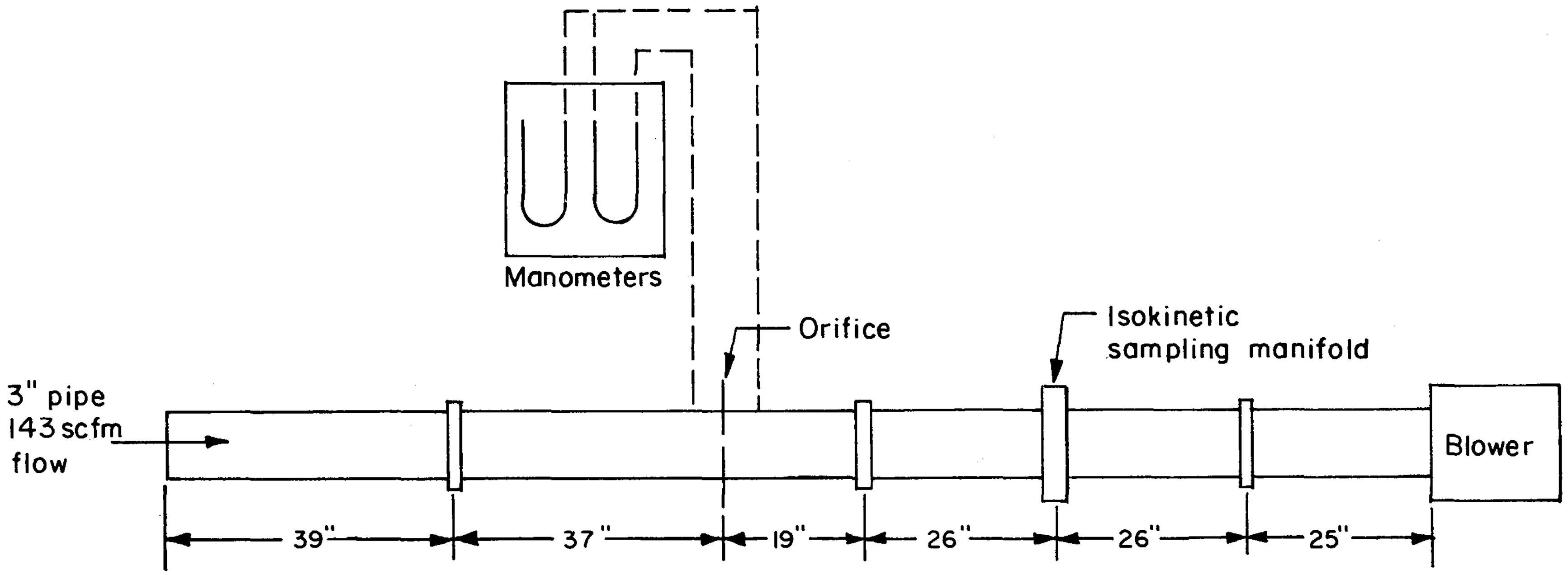


FIGURE 7. SYSTEM USED TO GENERATE SAMPLES FOR PARTICULATE AND VAPOROUS LEAD DETERMINATIONS

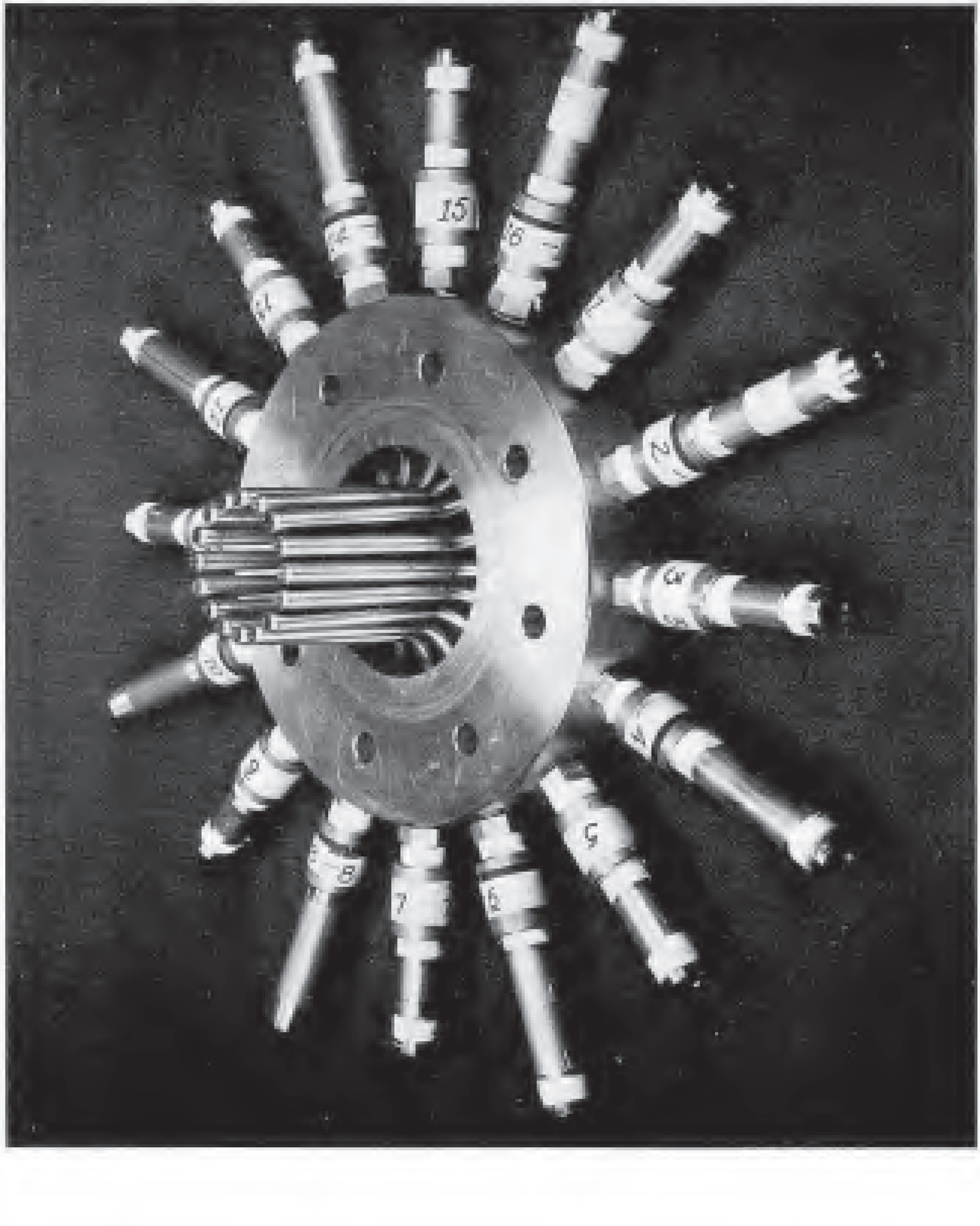


FIGURE 8. SIXTEEN-POSITION MANIFOLD USED FOR ISOKINETIC SAMPLING FOR PARTICULATE LEAD DETERMINATIONS

TABLE 1. TEST PATTERN FOR PARTICULATE LEAD DETERMINATIONS AT SITE I

Day	Type of Sample	Laboratory								Total
		J_1	K_1	L_1	M_1	N_1	O_1	P_1	Q_1(a)	
1	Unspiked	1	1	1	1	2	2	0	0	8
	Spiked	1	1	1	1	0	0	2	2	8
2	Unspiked	1	1	1	1	0	0	2	2	8
	Spiked	1	1	1	1	2	2	0	0	8
3	Unspiked	1	1	1	1	0	0	2	2	8
	Spiked	1	1	1	1	2	2	0	0	8
4	Unspiked	1	1	1	1	2	2	0	0	8
	Spiked	1	1	1	1	0	0	2	2	8
5	Unspiked	2	2	2	2	2	2	2	2	16
	Spiked	0	0	0	0	0	0	0	0	0
Total	unspiked	6	6	6	6	6	6	6	6	48
Total	spiked	4	4	4	4	4	4	4	4	32
Total		10	10	10	10	10	10	10	10	80

(a) Laboratory analyzed spike sample separately contrary to test pattern. Two unspiked measurements reported for each test day.

TABLE 2. TEST PATTERN FOR PARTICULATE LEAD DETERMINATIONS AT SITE II

Day	Type of Sample	Laboratory J_2	K_2	L_2	M_2	N_2	O_2	P_2	Total
1	Unspiked	1	1	1	2	2	0	0	7
	Spiked	1	1	1	0	0	2	2	7
2	Unspiked	1	1	1	0	0	2	2	7
	Spiked	1	1	1	2	2	0	0	7
3	Unspiked	1	1	1	0	0	2	2	7
	Spiked	1	1	1	0	0	2	2	7
4	Unspiked	1	1	1	2	2	0	0	7
	Spiked	1	1	1	0	0	2	2	7
5	Unspiked	2	2	2	2	2	2	2	14
	Spiked	0	0	0	0	0	0	0	0
Total	unspiked	6	6	6	6	6	6	6	42
Total	spiked	4	4	4	4	4	4	4	28
Total		10	10	10	10	10	10	10	70

TABLE 3. TEST PATTERN FOR PARTICULATE LEAD DETERMINATIONS AT SITE III

		Laboratory							
Day	Type of Sample	J_3	K_3(a)	L_3	M_3	N_3	O_3	P_3	Total
1	Unspiked	1	0	1	1	2	2	0	7
	Spiked	1	2	1	1	0	0	2	7
2	Unspiked	1	2	1	1	0	0	2	7
	Spiked	1	0	1	1	2	2	0	7
3	Unspiked	1	2	1	1	0	0	2	7
	Spiked	1	0	1	1	2	2	0	7
4	Unspiked	1	0	1	1	2	2	0	7
	Spiked	1	2	1	1	0	0	2	7
5	Unspiked	2	2	2	2	2	2	2	14
	Spiked	0	0	0	0	0	0	0	0
Total	unspiked	6	6	6	6	6	6	6	42
Total	spiked	4	4	4	4	4	4	4	28
Total		10	10	10	10	10	10	10	70

(a) Laboratory spiked one sample each day, instead of two on first and fourth days.

Each laboratory performed duplicate vaporous lead determinations at the three sites for a total of 16 at Site I and 14 each at Sites II and III. At Sites I and II vaporous lead spikes were added to one of the pair of charcoal traps prior to initiation of sampling. Spikes were not added to the vaporous lead adsorption traps at Site III. Instead the spiked charcoal samples were analyzed for lead as a separate sample.

Spiking Procedure

Particulate and vaporous lead spikes for the testing program were prepared by Dr. R. H. Johns, ASTM Research Associate, National Bureau of Standards. The preparation of the spikes and their method of introduction into the lead determination procedures is discussed below.

Particulate Lead

Spiked samples were generated by increasing the lead content of an unspiked (ambient) sample by the addition of NBS Certified Orchard Leaves (SRM 1571) before analysis. This standard material is reported by NBS to contain 45 μg lead per gram of the standard. Weighed quantities of the standard reference material were packaged in coded gelatin capsules and were to be combined with selected particulate lead filter samples after sampling and prior to the lead analysis according to the test patterns shown in Tables 1, 2, and 3. One laboratory (Q_1) departed from the assigned procedure for Site I and inadvertently analyzed the spikes and the atmospheric samples separately. These separate ambient sample analyses were treated as part of the unspiked sample group. Another laboratory (K_3) also deviated from the pattern at Site III by spiking one sample on each of four days rather than two samples on the first and fourth day.

Vaporous Lead

Vaporous lead spikes were prepared as lead-doped activated carbon. The doping material was prepared by the Ethyl Corporation and consisted of a solution of tetramethyl lead in methanol which was found by analysis to contain 10.1 μg lead per milliter. Volumes of 1.0 ml (10.1 μg) and 0.5 ml (5.05 μg) of the lead solution were added to 2-gram portions of activated carbon (previously analyzed for residual lead) to produce the Site I and the Site II and III spikes, respectively. These samples were supplied to the cooperating laboratories in coded vials and were to be combined with eight grams of unspiked charcoal to make up one of the two adsorbers for sampling at Sites I and II. At Site III the cooperating laboratories were instructed not to add the spike to the column of absorbent, but to analyze two unspiked samples and the lead-doped activated carbon separately.

Participitating Laboratories

A total of eight laboratories participated in the testing of the lead method. The laboratories were:

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

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

STATISTICAL ANALYSIS OF LEAD MEASUREMENTS

Statistical Measures

The experimental program was designed to permit statistical analysis of the test results with the objective of estimating the accuracy and precision of particulate and vaporous lead determinations using ASTM 3112-72T.

Measure of Precision

ASTM Method D 2906-70T(7) 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:

Single-operator standard error

$$S_T \text{ (single-operator)} = (S_S^2/_n)^{1/2}$$

Within-laboratory standard error

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

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 three site tests provide data for the estimate of between-laboratory and within-laboratory precision of both particulate and vaporous lead measurements. 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 some duplicate particulate and vaporous lead determinations. Differences among these concurrent measurements provide a means of estimating the variability among laboratories, while differences between duplicate measurements provide 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 and is denoted by the symbol S_W.

The between-laboratory component of variance, S_B^2, estimated by the analysis, 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, and is denoted by the symbol S_B. Details of the procedures used to calculate S_W^2 and S_B^2 are presented in the data analysis section and in Appendix B of this report.

The estimates of within-laboratory precision(repeatability) and between-laboratory precision (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). In addition, tests in which the laboratories made one determination per test, e.g. vaporous lead at Sites I and II, provide only estimates of between-laboratory standard error. These between-laboratory standard error estimates include the individual components of variance, S_B^2, S_W^2, and S_S^2, but the data do not permit their computation independently.

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(8). Others use less quantitatively oriented definitions, e.g. Davies(9). The usage in this report can be directly applied to statements of precision, as outlined in ASTM Method D 2906-70T and E 177(10), and is consistent with the usage in other Project Threshold reports.

Measure of Accuracy

Accuracy is defined in D 2906-70T "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.

In this study, the accuracy of particulate and vaporous lead procedures is estimated from duplicate determinations, one of which is spiked with a known quantity of lead. 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.

A measure of the accuracy of the vaporous lead analytical procedure was obtained from separate analyses of samples containing known quantitites of lead.

The accuracy data are reported as the percentage difference between the measured and true lead in the spikes, relative to the true spike value. Accuracy (bias) estimates are derived from the average of these differences.

Analysis of Particulate Lead Data

Experimental Results

The results of particulate lead determinations at Los Angeles, Bloomington, and New York City (Manhattan) are presented in Tables 4, 5, and 6. The tables give, for each day at each site, the experimentally determined lead concentrations (in $\mu g/m^3$) for unspiked samples and samples spiked with known quantities of lead just prior to the colorimetric lead analysis.

All sampling and analysis data were recorded by the cooperating laboratories and each laboratory calculated its final test results. The

TABLE 4. DATA FROM PARTICULATE LEAD ANALYSIS AT LOS ANGELES (SITE I)

(All values in micrograms/cubic meter)

	Day 1		Day 2		Day 3		Day 4		Day 5
Lab	Unspiked	Spiked	Unspiked	Spiked	Unspiked	Spiked	Unspiked	Spiked	Unspiked
J_1 (a)	1.25	2.18	2.05	2.76	2.02	2.69	2.28	2.63	1.17 1.23
K_1	0.88	3.49(b)	1.21	2.79	1.37	3.17	1.56	2.95	1.07 0.97
L_1	1.56(f)	1.91	1.34	2.57	1.41	3.31	1.55	2.44	0.94 0.98
M_1	0.90	1.67	1.67	3.03	1.32	2.64	1.71	2.77	4.61(c) 3.64(c)
N_1	0.90 0.89			2.08 1.67		1.98 0.94	1.59 1.52		0.94 1.39(f)
O_1	0.66 0.96			2.08 2.62		2.06 2.76	1.02(f) 1.66		(e) 1.14
P_1 (d)		3.25 13.16	0 1.56		0.91 1.33			9.27 0	0 0.69
Q_1 (g)	0.23(f) 0.61		1.29 1.56		(e) 1.55		1.54 1.47		0.84 1.09

(a) High lead blank, all data excluded from statistical analysis.

(b) Sample contaminated with charcoal from vaporous lead column, data excluded from statistical analysis.

(c) Incorrect sample volume, data excluded from statistical analysis.

(d) All data excluded from statistical analysis because of difficulties encountered in sample analysis.

(e) Pump failed during sampling period.

(f) Outlying value based on Dixon Criterion. Data excluded from statistical analysis.

(g) Laboratory deviated from spiking pattern. Data used in statistical analysis.

TABLE 5. DATA FROM PARTICULATE LEAD ANALYSIS AT BLOOMINGTON (SITE II)

(All values in micrograms/cubic meter)

	Day 1		Day 2		Day 3		Day 4		Day 5
Lab	Unspiked	Spiked	Unspiked	Spiked	Unspiked	Spiked	Unspiked	Spiked	Unspiked
J_2(a)	0.24	1.74	0.27	1.76	0.14	0.97	0.23	1.51	0.45 0.69
K_2	0.58	1.03	0.44	1.71	0.23	3.60	0.28	1.20	0.77 0.67
L_2	0.62	1.71	0.68	1.81	0.24	1.52	0.23	1.37	0.65 0.58
M_2	0.53 0.53			1.13 1.47		1.06 1.04	0.28 0.24		0.64 0.59
N_2	0.54 0.54			0.78 1.26		0.81 0.54	0.22 0.25		0.61 0.59
O_2		1.12 1.20	0.41 0.35		0.23 0.23			0.91 0.79	1.22(b) 1.51(b)
P_2		3.74(c) 4.39(c)	1.10(f) 0.90(f)		0.35(e) 0.24			1.30 (d)	0.70 (d)

(a) High lead blank, all data excluded from statistical analysis.
(b) Incorrect sample volume, data excluded from statistical analysis.
(c) Sampling period was not concurrent with other laboratories, data excluded from statistical analysis.
(d) Pump failure during test period.
(e) Outlying value based on Dixon Criterion. Data excluded from statistical analysis.
(f) Rejected as outlying data

TABLE 6. DATA FROM PARTICULATE LEAD ANALYSIS AT MANHATTAN (SITE III)

(All values in micrograms/cubic meter)

	Day 1		Day 2		Day 3		Day 4		Day 5
Lab	Unspiked	Spiked	Unspiked	Spiked	Unspiked	Spiked	Unspiked	Spiked	Unspiked
J_3	1.87	2.79	2.36	3.31	1.36	(a)	1.41	2.45	0.78
									0.75
K_3(b)(c)	2.48(d)	4.13	2.69	3.58	1.65	2.51	1.60	2.73	0.78
									0.94
L_3	2.07	3.83	2.69	4.49	1.67	3.41	1.66	3.57	0.90
									0.93
M_3	1.65	2.75	1.64(f)	3.38	1.42	2.09	0.86	1.79	0.91
									0.79
N_3	1.69			2.89		2.23	1.34		0.87
	1.69			4.18		2.42	1.03		0.84
O_3	1.86			3.72		2.53	1.54		0.89(e)
	1.91			3.45		2.29	1.50		0.87(e)
P_3		3.08	2.55		1.61			2.73	1.90(f)
		2.79	2.50		1.59			2.75	0.93

(a) Loose connection in sampling train, data excluded from statistical analysis.

(b) Spiking pattern deviated from design, however data were used in statistical analysis.

(c) Sample flow rates were significantly below isokinetic; all data excluded from statistical analysis.

(d) Pump off during sampling period, data excluded from statistical analysis.

(e) Original data reported by laboratory was not corrected for blank absorbance. Correction made by Coordinating Laboratory.

(f) Outlying value based on Dixon Criterion. Data Excluded from statistical analysis.

calculations were verified by the coordinating laboratory and the data were examined for erroneous experimental details which might compromise the determinations. Finally, all experimentally valid data were examined for statistical outliers using the Dixon Criterion ($\alpha = 0.95$)(11).

A summary of the data rejected from further analysis because of experimental or statistical reasons is given in Table 7. The major portion (85 percent) of the data was rejected because of experimental errors. All the data for one laboratory at Site I and one laboratory at Site II were rejected due to a high lead blank (about eight times normal level). All data from another laboratory at Site I were rejected due to problems encountered in the digestion of the particulate lead samples. All data from one laboratory at Site III were not used since sample flow rates (~0.4 to 0.5 cfm) were significantly less than required for isokinetic sampling. A lower flow rate may be tolerated in normal application; however, in this case, it represents a departure from the uniform sampling conditions required to determine variations inherent in the test method. Of the remaining rejected data, four determinations could not be used due to incorrect recording of sampling data. Calculational errors were detected in only two determinations and corrections were applied by the coordinating laboratory. In all, only nine determinations were rejected as statistical outliers.

The examination of the experimental data showed that, in nearly all lead analyses, the laboratories used aliquots in Step 11.2 and following, instead of using the entire 24-hour sample as directed by Note 3 of the test method. The aliquot sizes taken in Step 11.2.3 ranged from 10 ml to 50 ml, with the entire sample being used in a few instances. The possible implication of this departure from the specified procedure on the accuracy and precision estimates derived from the test data will be discussed in a later section of this report.

Between-Laboratory and Within-Laboratory Precision Estimates

Under ideal conditions, the precision of a test method would be determined by a large group of participating laboratories performing many determinations per laboratory with all sampling being conducted

TABLE 7. SUMMARY OF PARTICULATE LEAD DATA REJECTED FROM STATISTICAL ANALYSIS

Cause for Rejection of Data	Number of Determinations Rejected			
	Site I	Site I	Site II	Total
Incorrect recording of sampling data	2	2	0	4
Sample contaminated with charcoal	1	0	0	1
Pump failure during sampling	2	2	0	4
Leakage in system during sampling	0	0	1	1
Deviation from isokinetic sampling	0	0	10	10
Non-concurrent sampling period	0	2	0	2
High lead blank	10	10	0	20
Difficulty in sample analysis	10	0	0	10
Statistical outliers	4	3	2	9
Totals	29	19	13	61

simultaneously at a single site. Under such conditions, the computation of laboratory-to-laboratory variability (reproducibility) would be straightforward, albeit tedious. Obviously, such conditions are physically unattainable, and in a practical experimental program it is possible to accommodate only a small number of laboratories, each of which produces a limited number of determinations. Furthermore, it is usually desirable to conduct the experimental testing over a period of several days, and at more than one location to encompass a range of ambient conditions. All of these constraints place an additional burden on the statistical analysis of the resulting data. In order to obtain useful measures of precision, it is necessary to remove site and day effects, and to isolate the specific components of variance inherent in application of the test method. The following sections present a brief explanation of the analytical procedures used to derive the estimates of precision of the test method. A more detailed description of the statistical analysis procedures is presented in Appendix B.

If several laboratories each make replicate determinations, the expected value of the variance of laboratory means, after removing day and site effects, is

$$\sigma_B^2 + \sigma_W^2/K, \qquad (1)$$

where σ_B^2 = true variance of the population of laboratory means,
σ_W^2 = true run-to-run variance within laboratories
K = number of determinations

For the special case in which each laboratory makes just one determination ($K = 1$), expression (1) reduces to $\sigma_B^2 + \sigma_W^2$. For the case in which each laboratory makes exactly two determinations ($K = 2$), expression (1) becomes $\sigma_B^2 + \sigma_W^2/2$. As the number of determinations per laboratory becomes larger and larger ($K \to \infty$), expression (1) approaches σ_B^2 . If the number of determinations is not the same for all laboratories, as is the case in this study, then K is taken to be a weighted average of the number of determinations per laboratory. This weighted average is denoted as K_3 in this report. Thus the expected value of the variance of laboratory means is given by

$$\sigma_B + \sigma_W/K_3 \quad . \qquad (2)$$

In analysis of variance, data limitations usually yield an estimate of the quantity given by (2) above. This estimate, which is denoted by the expression

$$S_W^2 + K_3 S_B^2 \quad ,$$

is called the between-laboratory mean square and is the ratio of the between-laboratory sum of squares to the between-laboratory degrees of freedom. The between-laboratory sum of squares for each test site is the sum of several quantities (one for each day) of the form

$$\sum_{i=1}^{k} n_i(\bar{x}_i - \bar{x})^2 \quad ,$$

where $\bar{x}_i$ denotes the measurement value obtained by the ith laboratory, and $\bar{x}$ denotes the arithmetic mean of the measurements obtained by all k laboratories on a given day. For those laboratories making a single determination on a given day, $\bar{x}_i$ is equal to that determination and n_i is 1. For those laboratories making duplicate measurements, $\bar{x}_i$ is taken to be the average of the two measurements, and the mean is given a weight of 2 so that $n_i = 2$. The number of degrees of freedom associated with the between-laboratory sum of squares is obtained by summing k - 1 over all days. Since S_W^2 and K_3 are computed in the analysis of variance, the estimate S_B^2 is derived by subtracting the between-runs (within-laboratory) mean square, S_W^2, from the between-laboratory mean square, $S_W^2 + K_3 S_B^2$, and dividing the difference by K_3. The true variance, σ_B^2, of laboratory means cannot be negative. However, experimental results sometimes lead to overestimated values for σ_W^2, resulting in negative values for S_B^2. This anomoly is likely to occur when S_W^2 is a major component of the between-laboratory mean square and the number of determinations are limited. In such cases a meaningful estimate of variance S_B^2 cannot be derived.

The true run-to-run variance, which is designated by σ_W^2, is a statistical measure of within-laboratory variation. The square root of this variance is a measure of within-laboratory precision, or repeatability. In an ideal situation, the number of determinations would be unlimited. Generally, a limited number of determinations are available and the run-to-run variance computed from these determinations, which is designated by S_W^2, constitutes an estimate of the true variance of σ_W^2.

The quantity S_W^2 is called the within-laboratory mean square and it is the ratio of the within-laboratory sum of squares to the within-laboratory degrees of freedom. The within-laboratory sum of squares is the summation of $(x_2 - x_1)^2/2$ over all laboratories and all days at a given site, where x_1 and x_2 denote a pair of duplicate measurements made by a given laboratory. The number of degrees of freedom associated with this sum of squares is the total number of pairs of duplicate measurements.

The analysis of variance of the unspiked, particulate lead data by sites is summarized in Table 8. The "Between Labs Within Days" and "Between Runs within Labs" sources are variations related to precision of the test method. The square root of the mean square for the latter source yields the estimate of within-laboratory precision (repeatability). However, as noted in the previous discussion, the between-laboratory precision (reproducibility) estimate is not obtained by simply taking the square root of the "Between Labs within Days" mean square. The day-to-day variations (Between Days), which were not of primary interest in this study, are included to complete the analysis of variance summary and to indicate the magnitude of the normal daily variations relative to variations inherent in the test method performance.

A detailed analysis of the precision estimates of the unspiked particulate lead data by day and site is presented in Table 9. Each row, corresponding to a given day at a given site, summarizes an analysis of variance that separates out the between-laboratory precision (reproducibility), the within-laboratory precision (repeatability), and the between-laboratory standard error. Each daily summary includes the total number of determinations for that day, the mean lead concentration, and the components of variance and total variance expressed in the form of standard deviations and coefficients of variation, together with the associated number of degrees of freedom for each. The coefficient of between-laboratory variation is computed from the formula 100 S_B/m; the coefficient of within-laboratory variation is computed from the formula 100 S_W/m; and the standard error (between-laboratory) expressed as the coefficient of variation is computed from the formula 100 S_T/m.

TABLE 8. ANALYSIS OF VARIANCE, BY SITE, FOR ALL UNSPIKED SAMPLES OF PARTICULATE LEAD

Site	Source of Variation	SSD	df	MS	Expected Mean Square
I	Between Days	2.8176	4	0.7044	$\sigma_W^2+K_1\sigma_B^2+K_2\sigma_D^2$
	Between Labs within Days	0.2736	19	0.0144	$\sigma_W^2+K_3\sigma_B$
	Between Runs within Labs	0.1234	8	0.0154	σ_W^2
II	Between Days	0.8822	4	0.2206	$\sigma_W^2+K_1\sigma_B^2+K_2\sigma_D^2$
	Between Labs within Days	0.0917	15	0.0061	$\sigma_W^2+K_3\sigma_B$
	Between Runs within Labs	0.0120	10	0.0012	σ_W^2
III	Between Days	9.5356	4	2.3839	$\sigma_W^2+K_1\sigma_B^2+K_2\sigma_D^2$
	Between Labs within Days	0.7414	18	0.0412	$\sigma_W^2+K_3\sigma_B$
	Between Runs within Labs	0.0603	11	0.0055	σ_W^2

TABLE 9. ANALYSIS OF VARIANCE OF PARTICULATE LEAD DETERMINATIONS FOR UNSPIKED SAMPLES ACCORDING TO SITE AND DAY(a)

				Between-lab Precision			Within-lab Precision			Standard Error (Between-Lab)		
Site	Day	n	m ($\mu g/m^3$)	df	S_B ($\mu g/m^3$)	CV(%)	df	S_W ($\mu g/m^3$)	CV(%)	df	S_T ($\mu g/m^3$)	CV(%)
I (b)	1	7	0.83	4	0.00(b)	0(b)	2	0.15	18	6	0.15	18
	2	5	1.41	3	0.03	2	1	0.19	14	4	0.19	14
	3	4	1.41	3	0.10	7	0	--	--	3	0.10	7
	4	8	1.58	5	0.06	4	2	0.05	3	7	0.08	5
	5	8	1.00	4	0.00(b)	0(b)	3	0.11	11	7	0.11	11
Over All Days		32	1.22	19	0.00(b)	0(b)	8	0.12	10	27	0.12	10
II	1	6	0.56	3	0.04	7	2	0.00	0	5	0.04	7
	2	4	0.47	2	0.15	32	1	0.04	9	3	0.16	34
	3	5	0.23	3	0.01	2	1	0.00	0	4	0.01	2
	4	6	0.25	3	0.00(b)	0(b)	2	0.03	10	5	0.03	10
	5	9	0.64	4	0.04	7	4	0.05	7	8	0.06	10
Over All Days		30	0.46	15	0.06	13	10	0.03	8	26	0.07	15
III	1	7	1.82	4	0.16	9	2	0.03	1	6	0.16	9
	2	4	2.52	2	0.14	6	1	0.04	1	3	0.15	6
	3	5	1.53	3	0.14	9	1	0.01	1	4	0.14	9
	4	7	1.33	4	0.25	19	2	0.16	12	6	0.30	22
	5	11	0.86	5	0.05	6	5	0.04	5	10	0.06	7
Over All Days		34	1.45	18	0.16	11	11	0.07	5	29	0.17	11

(a) Column headings: n, number of determinations; m, mean lead concentration; df, degrees of freedom; S_B, between-laboratory standard deviation (reproducibility); S_W, within-laboratory standard deviation (repeatability); S_T, standard error (between laboratory); CV, coefficient of variation.

(b) The mean square for the variation between laboratories is equal to or smaller than the mean square for the variation within-laboratories so that zero or a negative value is obtained for S_B. In these cases, a zero is reported for S_B and CV.

The three rows labeled "Over All Days" contain precision estimates obtained from the data given in Table 8. These estimates are derived using all unspiked lead determinations at each site, consequently they probably represent the best estimates of precision of the test method under the particular site conditions. It may be noted that an estimate of between-laboratory precision (reproducibility) was not obtained from the Los Angeles data, since the within-laboratory component accounted for all the observed variation.

Accuracy

An estimate of the accuracy of particulate lead determinations using the ASTM method is provided by the results obtained from pairs of spiked and unspiked samples. The difference between the quantity of lead found in a sample pair is a measure of the known quantity of lead added prior to the analyses. Table 10 presents a summary of the analysis of the spiked-unspiked sample pairs. The data given in Table 10 include the known quantity of lead (NBS SRM 1571) which was added to selected samples and the corresponding quantity of lead which was determined experimentally from the difference between the lead content of spiked and unspiked sample pairs. The difference between the quantity of lead added and the quantity found experimentally is expressed as a percentage of the quantity added.

A summary of the data on the percentage difference between the quantity of lead spike added and found is presented in Table 11. The table gives for each site and for all sites combined the mean percentage difference, $\bar{x}$, the standard deviation of the difference, s, and data related to Student's t Test for significance of the observed differences.

The data for all sites indicates that, on the average, experimentally determined spike estimates are higher than the actual values. However, only the mean difference at Sites I constitutes a statistically significant bias based on Student's t Test. The combined data for all sites indicates that the average of the spike estimates is 17.4 percentage points greater than the "true" value. Based on Student's t Test applied at the 95 percent confidence level, it is concluded that this difference is statistically significant.

TABLE 10. SPIKE DATA FOR PARTICULATE LEAD SAMPLES

		Day 1			Day 2			Day 3			Day 4		
Site	Lab	μg Added	μg Found	% Difference	μg Added	μg Found	% Difference	μg Added	μg Found	% Difference	μg Added	μg Found	% Difference
I	J_1 (a)	21	25	+19	28	20	-29	25	18	-28	29	9	-69
	K_1	(b)	(b)	(b)	29	43	+48	32	52	+63	27	40	+48
	L_1	32	9(e)	-72(e)	30	35	+17	34	53	+56	24	25	+4
	M_1	28	20	-29	30	38	+27	26	35	+35	35	28	-20
II	J_2 (a)	24	32	+33	21	36	+71	19	21	+11	25	31	+24
	K_2	20	13	-35	25	39	+56	23	104	+352(e)	23	28	+22
	L_2	23	26	+13	24	30	+25	23	33	+43	22	30	+36
III	J_3	30	27	-10	30	27	-10		(c)	(c)	28	30	+7
	K_3	27	33(d)	+22(d)	30	20	-33	27	20	-26	32	27	-16
	L_3	32	48	+50	31	50	+61	28	50	+79	30	52	+73
	M_3	29	28	-3	27	45(e)	+67(e)	32	18	-44	31	26	-16

(a) High lead blank, all data excluded from statistical analysis.
(b) Sample contaminated with charcoal from vaporous lead trap. Data excluded from statistical analysis.
(c) Loose connection in sampling train, data unusable.
(d) Pump off during sampling period, data excluded from statistical analysis.
(e) Outlying value based on test of unspiked lead concentration data using Dixon Criterion.

TABLE 11. SUMMARY OF PARTICULATE LEAD SPIKE RESULTS

Site	n	$\bar{x}$	Standard Deviation, s	Student's t Statistic(a)	Test Conclusion(b)
I	10	24.9	31.6	2.49	S
II	7	22.9	29.2	2.07	NS
III	13	8.6	42.1	0.74	NS
All Sites	30	17.4	35.8	2.66	S
	20	13.61	37.9	1.60	

(a) Student's $t = \bar{x}\sqrt{n}/s$

(b) NS signifies that t is <u>not</u> statistically significant at the 95 percent confidence level, and that the test hypothesis that the true bias is zero is <u>not</u> rejected.

S signifies that t is statistically significant at the 95 percent confidence level, the test hypothesis is rejected, and it is concluded that the true bias is probably not zero.

Analysis of Vaporous Lead Data

Experimental Results

The results of vaporous lead determinations at the three test sites are given in Table 12. The table gives the results of vaporous lead determinations, in $\mu g/m^3$, for spiked and unspiked samples. At Sites I and II, lead spikes were introduced into one of a pair of samples prior to initiation of sampling. Consequently, each laboratory produced one unspiked and one spiked determination at these sites. At Site III, each laboratory produced duplicate unspiked determinations; spiked samples of charcoal were analyzed as separate samples.

Spike data are reported in Table 12 as the quantity of lead in the spike (µg Added), the experimentally determined spike value (µg Found) and the difference between the quantity of lead added and the quantity found experimentally expressed as a percentage of the quantity added (% Difference). In the analysis of the Sites I and II data, the difference between the unspiked and spiked sample results was used to determine the spike recovery.

The examination of the vaporous lead test data disclosed 18 determinations which were compromised by experimental problems or errors. These determinations which are identified in Table 12 were excluded from the statistical analysis. Three of the remaining determinations were excluded as statistical outliers based on the Dixon Criterion.

Precision Estimates

Single unspiked vaporous lead determinations were performed by the cooperating laboratories at Sites I and II. The statistical analysis of these determinations provides estimates of between laboratory standard error but do not yield separate estimates of between-laboratory and within-laboratory precision.

The between-laboratory standard error, S_T, was computed from the set of determinations at each site using the equation :

TABLE 12. VAPOROUS LEAD DATA

		Measured Lead Concentrations, μg/m³		Spike Recovery		
Site	Lab	Unspiked Samples	Spiked Samples	μg added	μg Found	% Difference
I	J_1	0.042(a)	0.079(a)	10.1	5.5(a)	-46 (a)
	K_1	0.034	(b)	10.1		
	L_1	0.041	0.052	10.1	1.7	-83
	M_1	0.043	0.090	10.1	6.9	-32
	N_1	0.012	0.032	10.1	3.1	-69
	O_1	0.088	(c)	10.1		
	P_1	(d)	(d)	10.1		
	Q_1	(e)	0.161(f)	10.1		
II	J_2	0.001(a)	0.009(a)	5.05	1.07(a)	-79 (a)
	K_2	0.006	0.027	5.05	3.59	-29
	L_2	0.006	0.025	5.05	2.68	-47
	M_2	0.016(n)	0.025	5.05		
	N_2	0.008	0.035	5.05	4.27	-15
	O_2	(g)	(g)	5.05	(g)	(g)
	P_2	(h)	(h)	5.05	(h)	(h)
III	J_3	0.051	(i)	5.05	6.65	+32
		(j)		5.05	7.26	+44
	K_3	0.15		5.05	(k)	
		0.036(l)		5.05	(k)	
	L_3	0.078		5.05	6.30	+25
		0.073		5.05	6.45	+28
	M_3	0.039		5.05	3.05	-40
		0.037		5.05	3.37	-33
	N_3	0.098(m)		5.05	7.75	+53
		0.052(m)		5.05	4.96	- 2
	O_3	0.081		5.05	7.11	+41
		0.081		5.05	5.24	+ 4
	P_3	0.075		5.05	69.33(n)	
		0.120		5.05	144.96(n)	

(a) High lead blank, data excluded from statistical analysis.
(b) Data not used, charcoal found on backside of particulate filter after Day 1 test.
(c) Pump failure during Day 5 test, charcoal transferred to back of particulate filter.
(d) Data excluded due to difficulties encountered in sample analysis.
(e) Sampling system off ~10 hours during third test day, data not used.
(f) High F value, data not used.
(g) Incorrect sample volume, data excluded from statistical analysis.
(h) Part of sampling period was not concurrent with other laboratories and pump failed during Days 4 and 5. Data excluded from statistical analysis.
(i) Spike samples were analyzed separately at Site III.
(j) Loose connection in sampling train during Day 3 test.
(k) Did not report results of spike analysis.
(l) White precipitate formed when reducing solution was added. Data not used.
(m) Sample aliquoted for analysis. Data excluded from statistical analysis.
(n) Outlying data based on Dixon's Criteria.

$$S_T = \frac{\sum_i^n (x_i - \bar{x})^2}{n - 1} ,$$

where $\bar{x}$ is the mean vaporous lead concentration, x_i is the vaporous lead concentration determined by the ith laboratory and n is the number of determinations. The coefficient of variation, expressed in percent, is calculated from the between laboratory standard error and the mean vaporous lead concentration, ($\bar{x}$), using the equation

$$CV,\% = \frac{100\ S_T\ \text{(Between-Laboratory)}}{\bar{x}}$$

The Site III test in which duplicate unspiked determinations were performed by each laboratory provides estimates of the between-laboratory and within-laboratory precision of the vaporous lead method. These estimates were calculated using the same procedures as described for the particulate lead analysis.

The summary of the statistical analysis of the vaporous lead data is given in Table 13. The between-laboratory standard error estimates expressed as the coefficient of variation are 64 percent based on the Site I (Los Angeles) data and 14 percent for the Site II (Bloomington) test. The mean vaporous lead concentrations at the two sites were 0.044 and 0.007 $\mu g/m^3$, respectively. The between-laboratory and within-laboratory precision estimates based on the Site III data (mean lead concentration 0.079 $\mu g/m^3$) are 41 and 20 percent, respectively, expressed as the coefficient of variation.

Accuracy

Accuracy estimates of the vaporous lead procedure are obtained from the spike data reported in the last three columns of Table 12. Statistical analysis of percentage difference data are summarized in Table 14. In the test series at the first two sites, lead spikes were introduced into the charcoal traps prior to sampling and were carried through the sampling portion of the procedure. The average differences between the quantity of spike added and the quantity found is about

TABLE 13. ANALYSIS OF VARIANCE OF VAPOROUS LEAD DETERMINATIONS BY SITE[(a)]

			Between-Laboratory Precision			Within-Laboratory Precision			Standard Error (Between-Laboratory)		
Site	n	m($\mu g/m^3$)	df	S_B($\mu g/m^3$)	CV(%)	df	S_W($\mu g/m^3$)	CV(%)	df	S_T($\mu g/m^3$)	CV(%)
I	5	0.044	0	--	--	0	--	--	4	0.028	64
II	3	0.007	0	--	--	0	--	--	2	0.001	14
III	10	0.079	5	0.032	41	4	0.016	20	9	0.036	46

(a) Column headings: n, number of determinations; m, mean lead concentration; df, degrees of freedom; S_B, between-laboratory standard deviation (reproducibility); S_W, within-laboratory standard deviation (repeatability); S_T, standard error (between-laboratory); CV, coefficient of variation.

TABLE 14. SUMMARY OF VAPOROUS LEAD SPIKE RESULTS

Site	n	$\bar{x}$	Standard Deviation,s	Student's[(a)] t Statistic	Test Conclusion[(b)]
I[(c)]	3	-61.3	26.4	-4.02	NS
II[(c)]	4	-42.5	27.6	-3.08	NS
III[(c)]	10	+15.2	32.1	1.50	NS

(a) Student's $t = \bar{x}\ \sqrt{n}/s$

(b) NS signifies that t is <u>not</u> statistically significant at the 95 percent confidence level and that the test hypothesis that the true bias is zero is <u>not</u> rejected.

(c) Spike added to charcoal column prior to start of sampling.

(d) Lead-spiked charcoal analyzed separately, not subjected to sampling.

-61 and -43 percent, respectively, for Sites I and II. Although these average differences appear quite large, Student's t Test based on the limited data does not show significance at the 95 percent confidence level.

Spike analyses at Site III were performed on samples which were not subjected to the sampling steps. Consequently, these data provide a measure of accuracy of the analytical procedure for vaporous lead. The average difference between the experimentally determined and true spike value is about +15 percent. Based on Student's t Test, it is concluded that the difference does not constitute a significant bias.

DISCUSSION AND CONCLUSIONS

The interlaboratory study provides the following conclusions regarding the accuracy and precision of the ASTM Method for determination of lead in the atmosphere.

Particulate Lead

1. Estimates of between-laboratory precision were obtained at two test sites. At Bloomington, where the ambient lead concentrations ranged from about 0.22 to 0.77 $\mu g/m^3$ with an overall mean of 0.46 $\mu g/m^3$, the coefficient of variation based on all determinations is 13 percent. At New York City, where ambient lead concentrations ranged from about 0.75 to 2.69 $\mu g/m^3$ with an overall mean of 1.45 $\mu g/m^3$, the coefficient of variation based on all determinations is 11 percent.
2. Within-laboratory precision estimates were obtained at three test sites. At Bloomington and New York City where ambient lead concentrations were as stated in the previous paragraph the coefficients of variation within-laboratories for all determinations are 8 and 5 percent, respectively. At Los Angeles, where the ambient lead concentrations ranged from 0.61 to 1.71 $\mu g/m^3$ with a mean of 1.22 $\mu g/m^3$, the coefficient of variation of all determinations was 10 percent.
3. Based on results of experiments at all test sites, experimentally determined spike concentrations were about 17 percentage points greater than the known quantity added prior to analysis. This difference, which may represent a bias in the test method, is statistically significant at the 95 percent confidence level.

Vaporous Lead

1. Standard error (between-laboratory) estimates were obtained at two sites. At Los Angeles and Bloomington where the mean ambient vaporous lead concentrations were 0.044 and 0.005 $\mu g/m^3$, respectively, the respective standard error (between-laboratory) coefficients of variation are 64 and 14 percent.
2. Between-laboratory precision expressed as the coefficient of variation estimated from the data obtained in New York City where the mean vaporous lead concentration was 0.079 $\mu g/m^3$ is 41 percent.
3. Within-laboratory precision expressed as the coefficient of variation estimated from the New York City data is 20 percent.
4. Experiments at two sites show a rather low recovery of known spikes carried through the entire procedure, i.e. sampling and analysis. However, mean differences at both sites (61 and 43 percent) are not statistically significant at the 95 percent confidence level.
5. The analysis of lead-spiked charcoal samples produced results which were an average of 15 percent higher than the true value. However, the mean difference is not statistically significant at the 95% confidence level.

The study results demonstrate that satisfactory precision can be achieved in the determination of particulate lead in the atmosphere. In characterizing the precision, the Bloomington and New York results are probably most typical. At these sites, within-laboratory variation is less than between-laboratory variation as would be expected. However, at Los Angeles, the first test site, the within-laboratory component accounts for all the observed variation. The higher within-laboratory variation may be attributed to unfamiliarity with the test method or difficulty in adapting to the test routine which included concurrent evaluation of other ASTM Methods.

The particulate lead spiking data taken by site do not provide conclusive evidence regarding the accuracy of the method. A significant difference between experimentally determined and true spike values was observed only at Los Angeles (Site I). However, as discussed in the previous paragraph, the precision data cast some doubt on the representativeness of the Site I measurements. The combined data for all three sites indicate a significant bias, while the combined Site II and III data show a bias which is not statistically significant. Based on the "best" data (Sites II and III) it appears that the method is not biased, however, additional study of accuracy is suggested.

It was noted earlier in the report that aliquoting inadvertently occurred during analysis of most particulate lead samples. The net result of using smaller sample volumes for analysis could be the introduction of an additional source of variation and error into the results. However, the magnitude of the precision estimates do not indicate a significant contribution to the variation as a consequence of the aliquotting.

The limited quantity of test data does not provide conclusive evidence concerning the performance of the vaporous lead procedure.
The estimates of standard error and between-and within-laboratory indicate that the precision may be unsatisfactory. The results of spiking experiments (Sites I and II), although not statistically significant, indicate that lead may be lost from the charcoal during sampling or may be fixed on the charcoal so that it is not quantitatively removed in the analysis. Analysis of the lead-spiked charcoal samples (Site III) indicate that the analytical procedure is probably satisfactory and is not responsible for the differences noted in the Site I and II spike results. In general, the test results dictate that additional study of the vaporous lead produced is required.

RECOMMENDATIONS

The results of the interlaboratory study demonstrate that the particulate lead procedure can yield results of satisfactory precision. Consequently, no modifications of the method are recommended. Additional investigation of the accuracy of the method is recommended to completely resolve the question of a possible bias in the method.

Additional study of the vaporous lead procedure is recommended. Although the interlaboratory tests do not offer conclusive proof, the limited data do suggest that the procedure may lack the desired accuracy and precision.

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APPENDIX A

TENTATIVE METHOD OF TEST FOR LEAD IN THE ATMOSPHERE

Colorimetric Dithizone Procedure

TENTATIVE METHOD OF TEST FOR LEAD IN THE ATMOSPHERE

Colorimetric Dithizone Procedure

1. SCOPE

1.1 This method covers the determination of atmospheric lead. It involves separate measurements of particulate lead and vaporous lead. For the purpose of this method particulate lead is that collected on an efficient filter. Vaporous lead is that which will pass through a 0.45 μm membrane filter or its equivalent and includes organic lead compounds.[1] It is satisfactory for measuring lead with an accuracy of ± 0.004 micrograms of lead/m^3 of air (1).[2]

2. SUMMARY OF METHOD

2.1 Sample - The sample of air is drawn through a sampling train consisting of 0.45 μm membrane filter or its equivalent and then through a special sampling tube containing activated carbon (1). A sample of 150 m^3 - 200 m^3 is collected.

2.2 Particulate Lead - The particulate lead sample is digested with nitric and perchloric acids and the dissolved lead is determined by a colorimetric dithizone procedure (1, 2).

2.3 Vaporous Lead - The activated carbon is extracted with hydrochloric and nitric acids overnight at a temperature of 90° C - 100° C. The carbon is removed by filtration and lead is determined in the filtrate by a colorimetric dithizone procedure (1, 2).

3. SIGNIFICANCE

3.1 This method is intended primarily for measuring weekly averages of:
(a) vaporous lead in air at concentrations below 0.2 microgram/m^3 and
(b) particulate lead in air at concentrations of 0.01 to 10.0 micrograms per cubic meter.[3]

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[1] Various tetraalkyllead compounds and/or their partially decomposition products.

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

[3] For measuring particulate lead in air only, smaller samples (24 hour) may be collected and analyzed (step 11.2) without aliquoting. In doing so, the perchloric acid should be volatilized down to approximately 0.5 ml in step 11.2.1 before adding 20 ml of nitric acid (1:4).

Special attention must be given to the selection of efficient filters containing low lead blanks and efficient filter holders to prevent particulate lead loss and erraneously high vaporous lead-in-air analyses.

4. DEFINITIONS

4.1 For definition of other terms used in this method, refer to ASTM Definitions D-1356, Terms Relating to Atmospheric Sampling and Analysis.

5. INTERFERENCES (Mixed-color method at high pH)

5.1 In the presence of a weakly ammoniacal-cyanide solution (pH 8.5-9.5) dithizone gives colored complexes with bismuth, stannous tin, monovalent thallium, and indium (1, 3, 4).

In strongly ammoniacal-citrate-cyanide solution (approximately, pH 11.0) the dithizonates of these ions are unstable and are only partially extracted with a chloroform-dithizone solution. The method as described here is highly selective for lead. It has been tested in the laboratory and found to be without interference from 20 micrograms of bismuth, 20 micrograms of monovalent thallium, 100 micrograms of stannous tin, and 200 micrograms of trivalent indium. Slight modifications are included to measure lead in the presence of larger amounts of interfering ions (11.3).

The interference from stannous tin and monovalent thallium is further reduced when these ions are oxidized in the ashing operation.

5.1.1 If interfering metal ions are suspected or if the analyst wishes to check for the presence of interfering ions, it is necessary to carry out a double extraction at high pH (step 11.3). Absence of interfering ions is indicated when the quantity of lead found after a double extraction at high pH is essentially the same as measured in the single extraction (step 11.2).

5.1.2 When only large amounts of bismuth (up to 200 μg) are present as an interference, lead is calculated after making absorbance measurements at 465 nm and 510 nm wavelengths. An equation is provided for this calculation (13.1.3).

5.1.3 Since volatile organic compounds of bismuth, thallium, tin, and indium are not normally found in ambient air (1) the determination of vaporous lead (step 11.1) is highly selective. Inorganic compounds of bismuth, thallium, tin, and indium if present are removed by the particulate lead filters and therefore do not interfere in the determination of vaporous lead.

5.1.4 Particulate lead is an ever-present interference when measuring vaporous lead in ambient air. It must be excluded from the activated carbon absorber by use of a highly efficient filter and filter holder, leak-proof glass and tubing connections, and proper seating of the filter in the filter holder to prevent leaks of non-filtered air. The particulate lead in air entering the carbon absorber must be reduced to less than 0.01 μg of lead/m^3 of air to avoid a positive interference in measuring vaporous lead.

6. PRECAUTIONS

6.1 The determination of micro quantities of lead requires meticulous attention to details. Good precision is not usually obtained without some experience with dithizone procedures. Precision may be improved by knowledge of, and close adherence to the suggestions that follow.

6.1.1 All glassware used in the method must be borosilicate glass and de-leaded by soaking in or rinsing with warm nitric acid (1 + 1) followed by rinsing with several portions of distilled water.

6.1.2 Use the same reagents and solutions in the same quantities for a group of determinations and the corresponding blank. When a new reagent is prepared or a new stock of filters is taken, a new blank must be prepared.

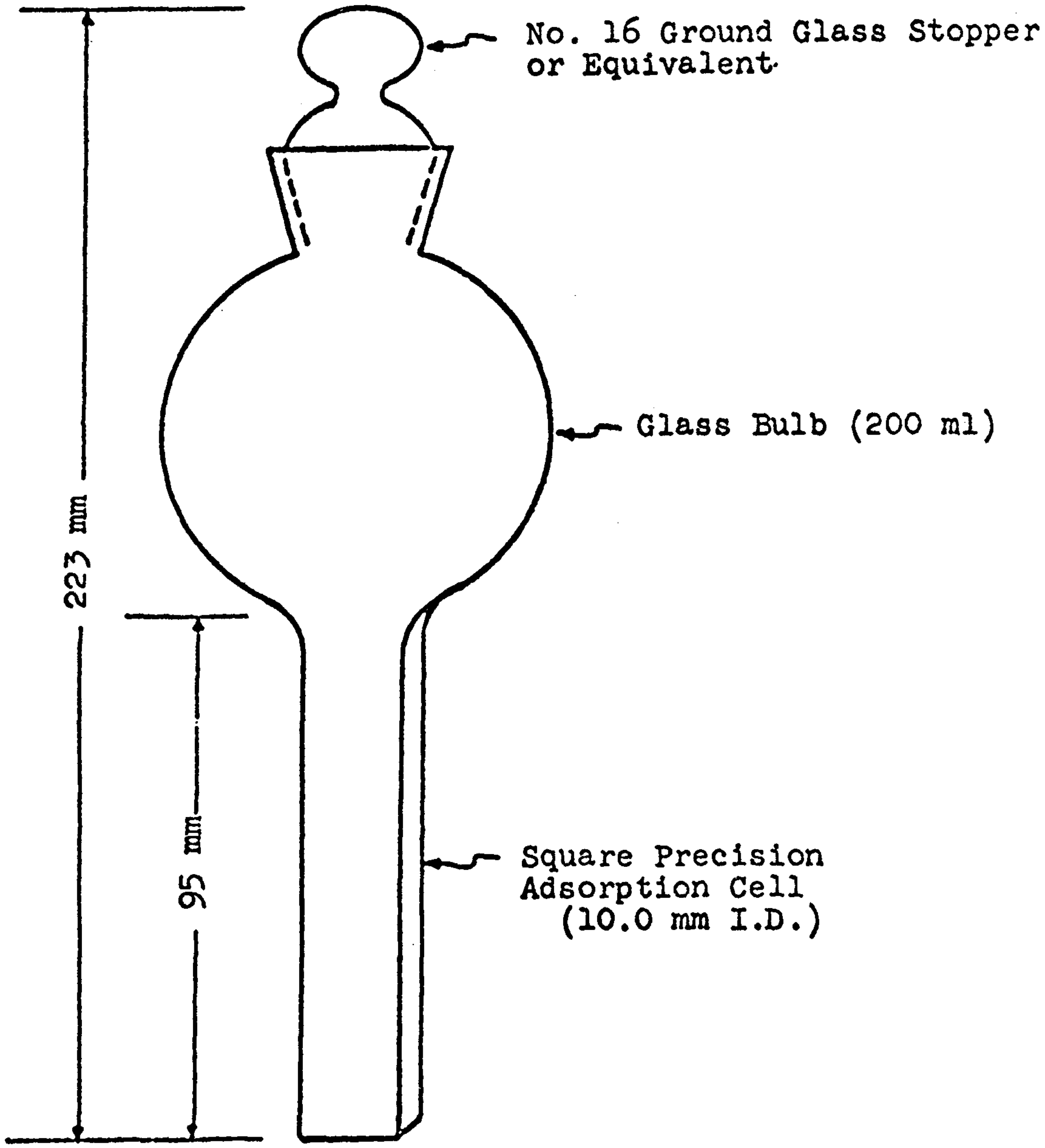
6.1.3 Keep the chloroform-dithizone solution out of direct sunlight or from trace quantities of halogen vapors, oxides of nitrogen, or other oxidizing agents. These will oxidize dithizone to diphenylcarbondiazone which is yellow-orange in color and does not react with lead. Small quantities of decomposition products in dithizone are satisfactory. The yellow-orange color will absorb light equally in the blank and sample to give no interference in the lead test.

7. APPARATUS

7.1 Absorption Cell. Use 200-ml modified absorption cell as shown in Figure 1 (5).

The 200-ml modified absorption cell is commercially available from E. Leitz Inc., Rock Leigh Industrial Park, Rock Leigh, N. J. 07647, Catalog No. 94626.

Figure 1. Modified Adsorption Cell



7.2 Cell Compartment Cover. A special cell compartment cover is required for use with the 200-ml modified absorption cell when using a spectrophotometer (see Figure 2). Appropriate cell compartment covers may be fabricated for any suitable spectrophotometer.

7.3 Filter and Filter Holder.[4]

7.4 Spectrophotometer.[5]

7.5 Activated Carbon Scrubber. See Figure 3 for details.

7.6 Gas meter. Capacity to measure up to 1 ft^3 of air/minute.[6]

7.7 Erlenmeyer Flasks, wide mouth, 500 ml capacity.

7.8 Vacuum pump, capable of drawing 1 ft^3 of air/minute.

7.9 Hot-plate, Lindberg type H-2 or equivalent.

7.10 Pyrex beakers, 150 ml.

7.11 Automatic dispensing burets for all reagents.

7.12 Elastic type electrical tape to seal glass joints of activated carbon scrubber.

8. REAGENTS[7]

8.1 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.

8.2 Activated carbon, 20-50 mesh or equivalent. Purchased from Pittsburgh Activated Carbon Division, Calgon Corporation, BPL 20x50, Box 1346, Pittsburgh, Pennsylvania 15230.

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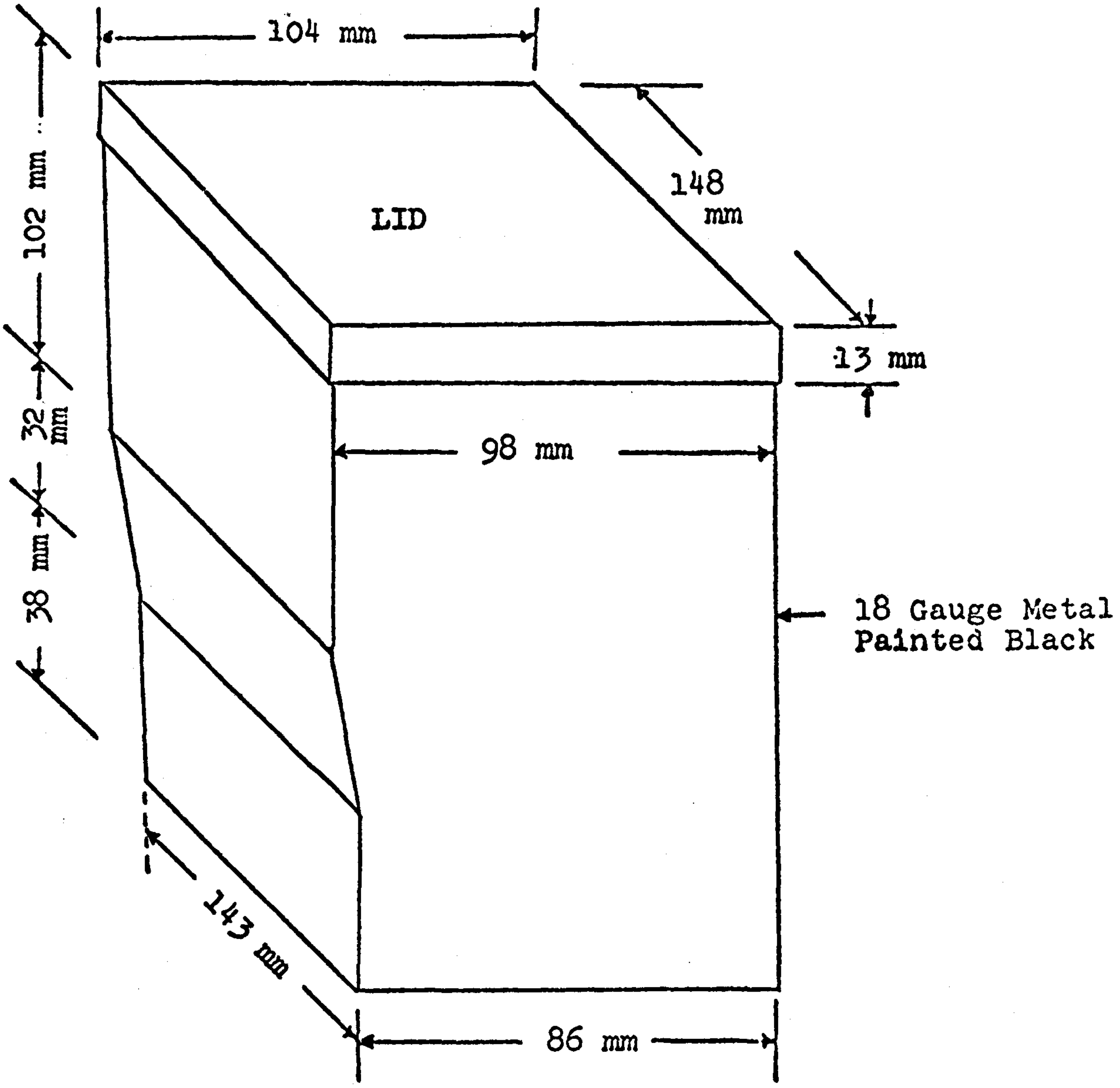
[4] A National Environmental Instruments (formerly Gelman) 47 mm stainless steel filter holder and glass fiber filter type E, 47 mm diameter, or Millipore membrane filter, type HA, and Millipore filter holder or equivalent are satisfactory.

[5] Beckman Model DU or equivalent has been found to be satisfactory. A simple Rouy filter photometer made by E. L. Leitz, Inc. is also satisfactory. The 200-ml modified absorption cell fits directly into the instrument without the need to fabricate a special cell compartment cover. However, the Rouy photometer does not give a straight line calibration curve.

[6] American Meter Co., AL110 or equivalent. Calibration marks are expressed in ft^3 units.

[7] The safety and pollution problems associated with the use and disposal of all hazardous chemicals must be considered by each laboratory. Cyanide is especially poisonous.

Figure 2. Cell Compartment Cover for Beckman Model DU Spectrophotometer



Note: Appropriate cell compartment covers may be fabricated for any suitable spectrophotometer. Use any material of construction (metal, wood, plastic, etc.).

Figure 3. Activated Carbon Scrubber

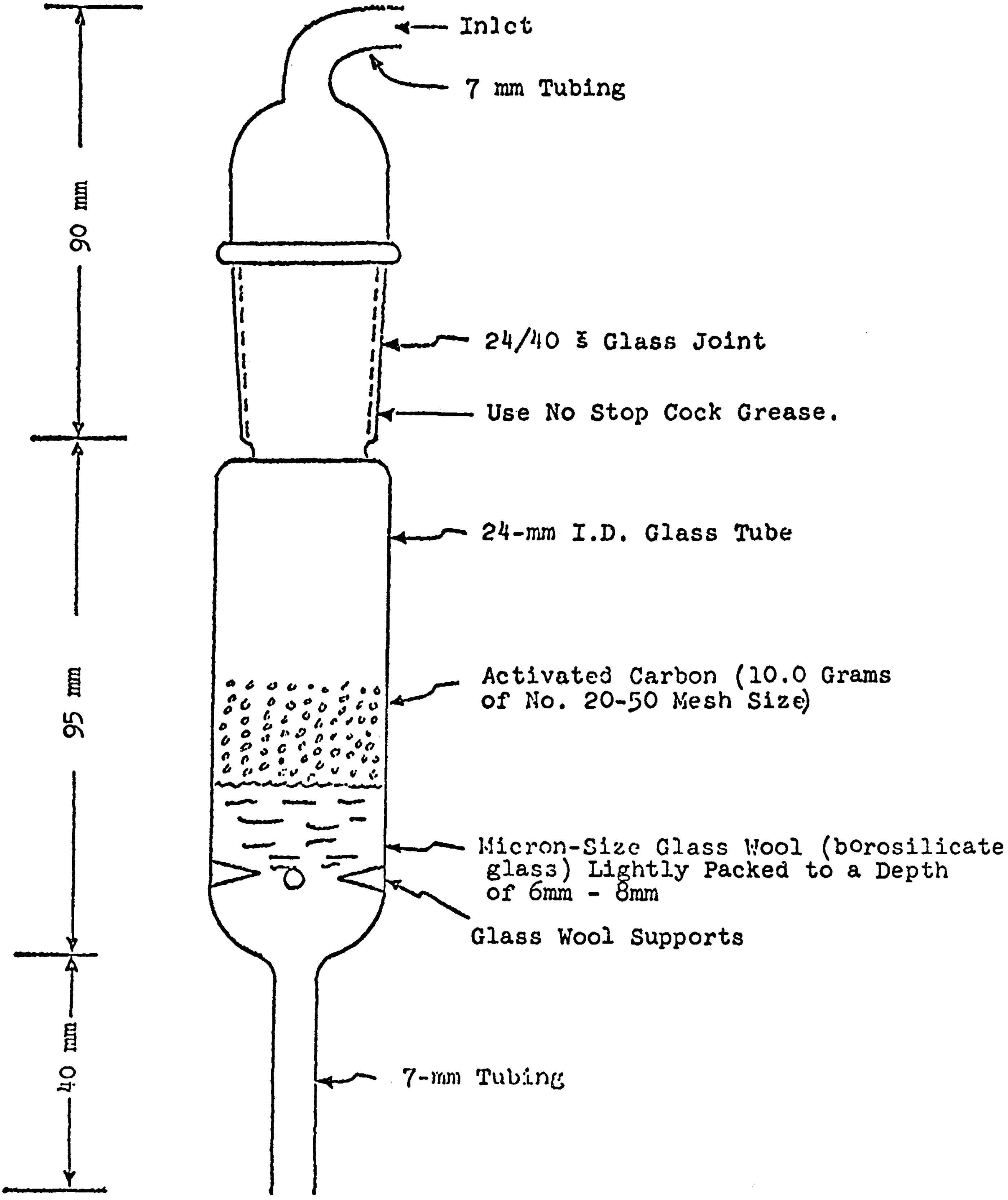
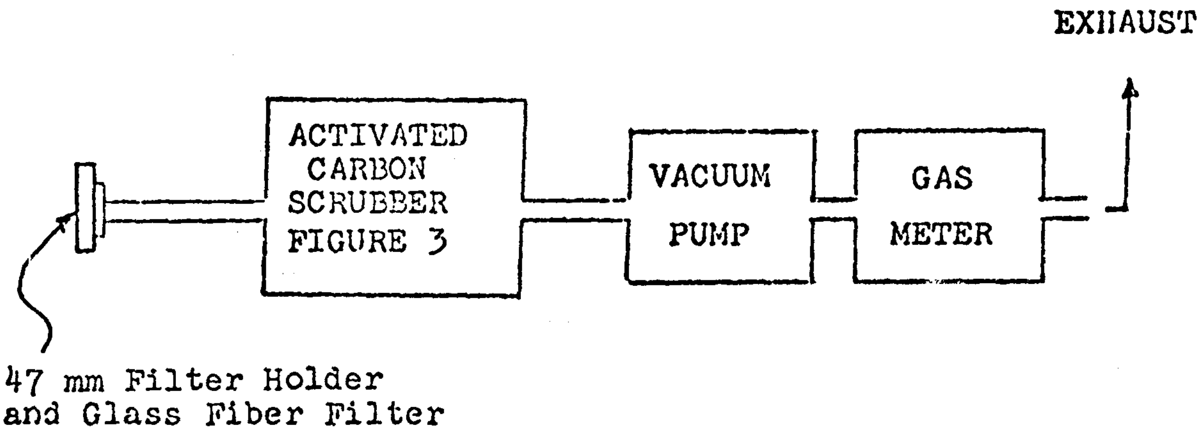


Figure 4. Sampling Train



Note: The output of the vacuum pump must be equal to the input. If there is a leak in the vacuum pump and the output is greater than the input, it is necessary to obtain a satisfactory pump or install the gas meter and a vacuum gauge between the activated carbon scrubber and the leaking vacuum pump. The absolute pressure is needed to calculate the volume of the air collected at atmospheric pressure.

8.3 Nitric-perchloric acid solution. Mix 300 ml of concentrated nitric acid with 200 ml of perchloric acid (72%).

8.4 Reducing Solution. Weigh 20 grams of potassium cyanide, 40 grams of dibasic ammonium citrate, and 200 grams of anhydrous sodium sulfite, and dilute to 1 liter with distilled water. Add 600 ml of concentrated ammonium hydroxide. Prepare this solution in a well ventilated hood.

8.5 Dilute nitric acid (1:4). Dilute 200 ml of concentrated nitric acid to 1 liter with distilled water.

8.6 Buffer Solution. Dissolve and dilute 400 grams of dibasic ammonium citrate, 10 grams of hydroxylamine hydrochloride and 40 grams of potassium cyanide to 1 liter with distilled water. Mix the 1 liter of citrate-cyanide-hydroxylamine solution with 2 liters of concentrated ammonium hydroxide (28%).

8.7 Dithizone Solution. Dissolve 40 mg of diphenylthiocarbazone in 1 liter of chloroform. Store at room temperature in the absence of direct light (in a brown bottle or in a pyrex bottle covered with aluminum foil).

8.8 Sodium diethydithiocarbamate solution.[8] Dissolve 1 gram of the reagent in 500 ml of distilled water.

8.9 Hydrochloric acid, conc.

8.10 Nitric acid, conc.

8.11 Standard Lead Solution I. Weigh approximately 0.16 grams of lead nitrate on an analytical balance to the nearest 0.1 mg. Dissolve in approximately 200 ml of lead-free water. Add 10 ml of concentrated nitric acid and dilute to 1 liter with distilled water.

8.12 Standard Lead Solution II. Pipet 20.0 ml of Standard Lead Solution I and dilute to 1 liter with distilled water Calculate the lead content of Standard Lead Solutions I and II from the exact weight of lead nitrate employed.

8.13 Diphenylthiocarbazone (Dithizone).

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[8] Disodium ethylenediaminetetraacetate (2 grams/500 ml water) may be substituted for sodium diethyldithiocarbamate solution (1). Both reagents quantitatively decompose lead dithizonate in chloroform solution. The disodium salt of EDTA decomposes lead dithizonate at a much slower rate than sodium diethyldithiocarbamate. Therefore, a longer shaking period (90 to 120 seconds) is required. The resulting solution is considerably more stable than when using sodium diethyldithiocarbamate; therefore, more time is permissible for absorbance measurements after decomposing lead dithizonate.

After using the EDTA or carbamate reagents, rinse the 200-ml absorption cell thoroughly with distilled water before running another lead test.

8.14 Chloroform.

9. CALIBRATION

9.1 Add 20 ml of dilute nitric acid (1:4), 25 ml of distilled water, and 40 ml of buffer solution to a 200 ml modified absorption cell, mix and cool to room temperature. Add 10.0 ml of dithizone solution and shake the mixture vigorously for 30 seconds. Insert the modified absorption cell into the spectrophotometer and measure the absorbance of the lower layer at 510 mm wavelength, using air as a reference (100% transmittance). Add 10 ml of Standard Lead Solution II (approximately 20 micrograms of lead), shake the mixture vigorously again for 30 seconds and read the increase in absorbance due to the addition of a known quantity of lead. Run a standard sample daily to ensure accuracy.

9.2 The calibration factor "F" (see Section 13.1 for lead dithizonate in 10 ml of chloroform when read in a Beckman Model DU spectrophotometer at 510 nm wavelength and in a 1 cm light path) is approximately 35. Therefore, the corrected absorbance of the sample times the factor is the quantity of lead present in the sample. If other photometers are used, additional calibration points should be run to establish an accurate factor.

10. SAMPLING[9]

10.1 Seal the dry glass joint of the activated carbon scrubber shown in Figure 3 with an elastic type tape and connect the top of this scrubber to a 47 mm filter holder containing a 47 mm glass fiber filter. Connect the bottom of the carbon scrubber to a vacuum pump and finally to a gas meter. Sample approximately 150-200 M^3 of air at the rate of about 0.7 ft^3/minute. See Figure 4.

Membrane filters (0.45 μm) have a significantly greater pressure drop than fiber glass filters when collecting air samples. It is necessary to use two membrane filters connected in parallel and to sample at a lower rate (approximately 0.5 ft^3/min.) to avoid excessive

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[9] Make certain the filter is properly seated in the filter holder. If after collecting the sample the filter cake is visible to the edge of the filter disk, or if the filter has been punctured as evidence by dark specks on the back side of the filter, discard the sample as the carbon tube has been contaminated with particulate lead.

pressure drop across the filters (less than 3" to 4" Hg). Larger filters (100 mm) and filter holders are satisfactory if particulate lead is not allowed to pass this filter assembly to contaminate the carbon scrubber.

11. PROCEDURE

11.1 Vaporous Lead in the presence of up to 20 μg of bismuth, 20 μg of monovalent thallium, 100 μg of stannous tin, and 200 μg of trivalent indium.

11.1.1 Disconnect the carbon scrubber from the sampling train and remove the tape from the 24/40 glass joint. Remove the male glass joint from the scrubber and pour the activated carbon from the scrubber into a 500-ml Erlenmeyer flask. Add 25 ml of concentrated nitric acid to the carbon in the Erlenmeyer flask, swirl and then add 75 ml concentrated hydrochloric acid and again swirl to mix.

11.1.2 Digest over night on a hot plate at (90°-100°C) and evaporate to a volume of 25-50 ml.

11.1.3 Add approximately 100 ml of distilled water and mix well. If upon heating overnight, the sample went to dryness, add 25 ml concentrated nitric acid, heat at 100°C for 2-3 hours, dilute with 100 ml of water, mix well, and allow to cool.

11.1.4 Decant off the supernatant liquid through a Whatman No. 41H filter paper or equivalent into another 500 ml Erlenmeyer flask. Rinse the residue carbon on the filter with three portions of distilled water. Discard the filter paper and carbon.

11.1.5 Add 10 ml of nitric-perchloric acid solution to the acid extract and heat on a hot plate (175°-200°C) to fumes of perchloric acid. If all carbon is not oxidized add an additional 5-ml portion of nitric-perchloric acid solution and heat to fumes of perchloric acid.[10]

11.1.6 To the slightly cooled perchloric acid sample, add approximately 25 ml of distilled water from a washbottle while washing down the sides of the Erlenmeyer flask and add 20 ml of dilute nitric acid (1:4). Allow

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[10] Caution! Oxidation with perchloric acid can be hazardous if perchloric acid hoods are not available. Oxidation with nitric acid and 2.0 ml of concentrated sulfuric acid is also satisfactory, but somewhat slower and more tedious.

approximately 30 minutes for complete solution of the sample and transfer the mixture to the 200 ml modified absorption cell.

11.1.7 To the sample in the modified absorption cell, add 50 ml of buffer solution and 10 ml of Reducing Solution, mix and allow approximately 15-20 minutes for complete reduction of the sample.

11.1.8 Add 10.0 ml of dithizone solution and shake the mixture vigorously for 30 seconds. Insert the modified absorption cell into the spectrophotometer and measure the absorbance of the lower layer at 510 nm wavelength, using air as a reference (100% transmittance). Add 5 ml of sodium diethyldithiocarbamate solution to the modified absorption cell, shake it vigorously for 10-15 seconds and measure the absorbance of the lower layer immediately after the two layers separate.[11] The difference between the two absorbance readings represents the quantity of lead present in the sample.

11.1.9 If a large quantity of lead is present in the sample (absorbance reading over 2.0) when attempting to make the first absorbance reading above (11.1.8) add an additional 10.0-ml portion of dithizone solution to the sample, shake it vigorously for 30 seconds and measure the lead as previously described for 10.0 ml of dithizone solution.[12]

11.2 Particulate lead in the presence of up to 20 μg of bismuth, 20 μg of monovalent thallium, 100 μg of stannous tin, and 200 μg of trivalent indium.

11.2.1 Remove the fiberglass filter from the filter holder. Place it, with the exposed side down, in a 150-ml beaker and add 10 ml of nitric-perchloric acid solution. Digest on the hot plate to fumes of perchloric acid and all of the dark carbonaceous material has oxidized. Add 20 ml of nitric acid (1:4), mix, crush the filter with a glass rod, and allow to cool.

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[11] If the analyst is interrupted and cannot make an absorbance measurement immediately after the 10-15 second shaking period, nothing is lost. The analyst may shake the mixture another 10-15 seconds and read the absorbance immediately after shaking.

[12] If the absorbance is still over 2.0 when using 20 ml of dithizone solution, add additional 10-ml portions of dithizone-chloroform solution until the absorbance is reduced to approximately 2.0.

11.2.2 Filter[13] the sample from the 150 ml beaker through Whatman No. 41H filter paper directly into a lead-free 100-ml glass-stoppered volumetric flask. Rinse the glass fibers in the filter with three 20-ml portions of distilled water, make up to the 100 ml mark, stopper the volumetric flask and mix well.

11.2.3 Pipet a suitable aliquot (usually 10 ml) of sample from the volumetric flask to a 200 ml modified absorption cell and add 20 ml of dilute nitric acid (1:4), 25 ml of distilled water, 50 ml of buffer solution, mix and cool to room temperature.

11.2.4 Add 10.0 ml of dithizone solution and shake the mixture vigorously for 30 seconds. Insert the modified absorption cell into the spectrophotometer and measure the absorbance of the lower layer at 510 nm wavelength, using air as a reference (100% transmittance). Add 5 ml of sodium dithyldithiocarbamate solution to the modified absorbance cell, shake it vigorously for 10-15 seconds and immediately measure the absorbance of the lower layer. The difference between the two absorbance readings represents the quantity of lead present in the aliquot.

If the initial absorbance readings is greater than 2.0 add additional 10-ml portions of dithizone solution to the sample to dilute the lead dithizonate color and repeat the absorbance measurements before and after adding sodium diethyldithiocarbamate solution as described above (11.1.9). This eliminates the need for repeating the test with a smaller aliquot.

11.3 Particulate lead in the presence of more than 20 μg of bismuth, 20 μg of monovalent thallium, 100 μg of stannous tin and 200 μg of trivalent indium.

11.3.1 When unexpectedly high lead values are obtained or when larger quantities of bismuth, thallium, tin, and indium are suspected, the lead dithizonate present in 10 ml of the dithizone-chloroform solution (11.2.4) is not discharged with sodium diethyldithiocarbamate. Instead the lead dithizonate is compared with a blank made up by starting with step 11.2.3, but without adding the sample aliquot.[14] The correct absorbance of the

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[13] If a membrane filter is sued to collect air samples the nitricperchloric acid solution will completely digest the filter and sample. Filtration is unnecessary.

[14] The isolation and determination of lead in dithizone solution is made in the presence of 20 ml of nitric acid (1:4), 25 ml of distilled water, and 50 ml of buffer solution. These conditions are necessary to maintain proper partitioning of dithizone and lead dithizonate between anaqueous and chloroform solution. Additions of up to 0.5 ml of concentrated perchloric acid do not significantly change this partitioning.

sample at 510 nm wavelength is obtained by subtracting the absorbance of the blank from the absorbance of the sample. Interferences are detected by converting the lead dithizonate to an aqueous solution of lead nitrate and again measuring by dithizone at high pH. The second extraction at high pH will again remove approximately 90 percent of the interfering ions. The procedure is as follows:

11.3.2 Transfer the entire contents of the 200-ml absorption cell to a lead-free, 250-ml separatory funnel. Drain the chloroform-lead dithizonate solution (10 ml) into a lead-free, 125-ml separatory funnel. Rinse the 200-ml absorption cell with 5 ml of pure chloroform[15] and transfer it to the 250-ml separatory funnel. Vigorously shake the 250-ml separatory funnel and drain the 5 ml of chloroform rinse solution into the 125-ml separatory funnel. To the combined chloroform-lead dithizonate solution in the 125-ml separatory funnel add 25 ml of distilled water and 20 ml of dilute nitric acid (1:4). Shake the stoppered 125-ml separatory funnel for 15 seconds and discard the chloroform solution. Transfer the 45 ml of dilute nitric acid solution containing all the lead to the original 200-ml absorption cell, add 50 ml of buffer solution and 10.0 ml of dithizone, shake as before, and again measure the absorbance of the lead dithizonate solution. Correct for a blank carried through all steps of the double-extraction procedure. If the corrected absorbance is near that found in measurement of the original lead dithizonate solution, no interference was present in the original sample. If the absorbance of the second extract is 10 percent or more below that of the original extract, interferences in amounts above the quantities given in 11.2 may be present.[16]

11.3.3 If in the application of the basic method (11.2), bismuth is known to be present in amounts up to 200 µg and thallium, tin, and indium are absent, the amount of lead present in the special 200-ml absorption cell may be calculated accurately as follows:

Record the optical absorbance of the blank and sample at 465 nm and

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[15] Do not use a dithizone-chloroform solution here. Increased quantities of excess dithizone will extract additional quantities of metal impurities. This separation depends upon pH and excess dithizone.

[16] To accurately measure interferences, select a lead dithizonate solution with an absorbance of greater than 1.0.

510 nm wavelength. Calculate micrograms of lead present in the sample aliquot from the equation shown in 13.1.3.

11.3.4 To check for bismuth interference only, occasionally, measure the optical absorbance of the lead dithizonate solution at 510 nm and 465 nm wavelength. The ratio of the corrected absorbance at 510 nm over the corrected absorbance at 465 nm is 2.08 for lead dithizonate and 1.07 for bismuth dithizonate. A marked change in ratio from 2.08 indicates interference in measurement of lead dithizonate.

12. BLANK CORRECTIONS

12.1 Since all of the reagents used in this method contain some lead it is imperative to run a blank on all reagents, including filters. A separate blank must be run for particulate lead and vaporous lead, and the corresponding blank must be subtracted from the individual analyses. The total lead blank, including carbon, is approximately 2.5 micrograms.[17] The blanks are run by the same method employed for the analyses, with the exception of the collection of the air sample.

It is advisable to run a blank and also a known sample containing lead nitrate daily to ensure accuracy.

12.2 In addition to running a blank on reagents and filters, it is necessary to test the air sampling apparatus (Figure 4) for particulate lead interference by inserting a pyrex tube (2 1/2" diameter and 22 inches long) containing activated carbon (10-30 mesh) ahead of the particulate filter to remove all vaporous lead from air [Anal. Chem. 39, 593 (1967)]. An analyses of the activated carbon scrubber (Figure 3) after collecting 200 m^3 of purified air should give a zero vaporous lead in air analysis if there are no leaks in the sampling train (Figure 4).

13. CALCULATION

13.1 Calibration Factor "F".

$$F = \frac{\text{micrograms of lead in calibration sample}}{\text{absorbance after addition of Pb - absorbance before addition of Pb}}$$

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[17] This is an absolute lead blank which is measured by use of sodium diethyldithiocarbamate. It can be reproduced to ± 0.2 mg of lead.

13.1.1 Vaporous Lead (C_V) expressed as micrograms/m^3 of air.

$$C_V = [(A-B) - (C-D)] \times F \times \frac{35.3}{ft^3 \text{ of air}} \times \frac{\text{ml of dithizone solution}}{10}$$

13.1.2 Particulate Lead (C_P) expressed as micrograms/m^3 of air.

$$C_P = [(A-B) \ (C-D)] \times F \times \frac{35.3}{ft^3 \text{ of air}} \times \frac{\text{ml dithizone soln.}}{10} \times \frac{100}{E}$$

A = Sample absorbance before carbamate treatment.

B = Sample absorbance after carbamate treatment.

C = Blank absorbance before carbamate treatment.

D = Blank absorbance after carbamate treatment.

E = Volume of aliquot in ml removed from the 100 ml glass stoppered volumetric flask.

13.1.3 Spectrophotometric calculation of lead in the presence of bismuth.

μg of Pb = 2.08 F[(corrected absorbance at 510 nm) - (1.07 corrected absorbance at 465 nm)]

14. <u>ACCURACY AND PRECISION (Vaporous Lead)</u>

14.1 The accuracy (standard deviation of the difference between the quantities found and present in known samples) is 0.004 μg of lead/m^3 of air (1).

14.2 The precision was not determined by repeated analyses of a single known sample. Past experience indicates a precision consistent with the above stated accuracy.

15. <u>PRECISION AND ACCURACY (Particulate Lead)</u>

15.1 The absolute accuracy and precision of the particulate lead-in-air measurement has not been established. The particulate lead-in-air filters are better than 99 percent efficient for collecting lead (1). Since the colorimetric dithizone method is standardized with known quantities of lead, there is no bias in the measurement of particulate lead.

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APPENDIX B

STATISTICAL ANALYSIS PROCEDURES

STATISTICAL ANALYSIS PROCEDURES

The following detailed illustrations show, in a stepwise manner, the procedures used in the statistical analysis of cooperative test data of the lead method. Example 1 describes the analysis of the data by days at each site. The determinations for unspiked, particulate lead samples on Day 1 at Los Angeles (Site I) which are given in Table 4 are used in this example. Example 2 shows the derivation of the precision estimates using all determinations at a particular site. Los Angeles data (Table 4) are used in this example. The analysis of all measurements at Los Angeles is a generalization of the analysis of Site I, Day 1, measurements in Example 1. Consequently, some of the formulas and computations in Example 1 also appear in Example 2.

Example 1. Analysis of Determinations by Days

Step 1. Compute the arithmetic mean of all measurements:

$$\bar{x} = (0.88+0.90+0.90+0.89+0.66+0.96+0.61)/7=0.8286.$$

Step 2. Compute the laboratory means:

Laboratory Code	Number of Determinations	Arithmetic Mean
K_1	$n_1=1$	$\bar{x}_1=0.88$
M_1	$n_2=1$	$\bar{x}_2=0.90$
N_1	$n_3=2$	$\bar{x}_3=0.895$
O_1	$n_4=2$	$\bar{x}_4=0.81$
Q_1	$n_5=1$	$\bar{x}_5=0.61$

Step 3. Compute the between-laboratory sum of squares:

$$\sum_{i=1}^{k} n_i(\bar{x}_i-\bar{x})^2=(0.88-0.8286)^2+(0.90-0.8286)^2+2(0.895-0.8286)^2$$
$$+2(0.81-0.8286)^2+(0.61-0.8286)^2=0.065036.$$

Step 4. Compute the within-laboratory sum of squares from the duplicate determinations (laboratories N_1 and O_1):

$$\Sigma\ (x_1-x_2)^2/2 \ = \ (0.90-0.89)^2/2+(0.66-0.96)^2/2=0.045050.$$

Step 5. Compute the total sum of squares:

$$\Sigma\ (x-\bar{x})^2 = (0.88-0.8286)^2+(0.90-0.8286)^2+(0.90-0.8286)^2+(0.89-0.8286)^2$$
$$+(0.66-0.8286)^2+(0.96-0.8286)^2+(0.61-0.8286)^2=0.110086.$$

Step 6. Add the between-laboratory sum of squares from Step 3 to the within-laboratory sum of squares from Step 4, as a check on Step 5:

$0.065036 + 0.045050 = 0.110086.$

Step 7. Determine the number of degrees of freedom associated with the between-laboratory sum of squares. This number is one less than the number k of laboratory means. From Step 2, k is seen to be 5):

Between-laboratory df $= k-1 = 5-1=4.$

Step 8. Determine the number of degrees of freedom associated with the within-laboratory sum of squares. This is equal to the total number of determinations less the number of laboratory means:

$\Sigma n_i - k = (1+1+2+2+1)-5=2.$

Step 9. Determine the number of degrees of freedom associated with the total sum of squares. This is equal to the total number of determinations less one:

$\Sigma n_i - 1 = (1+1+2+2+1)-1=6.$

Step 10. Compute the between-laboratory mean square. This is the ratio of the between-laboratory sum of squares to the associated number of degrees of freedom:

Between-lab mean square $= 0.065036/4=0.016259.$

Step 11. Compute the within-laboratory mean square. This is the ratio of the within-laboratory sum of squares to the associated number of degrees of freedom:

Within-lab mean square $= 0.045050/2=0.022525.$

Step 12. Compute a weighted average number of determinations per laboratory:

$$\frac{1}{k-1}\left[\Sigma n_i - \frac{\Sigma n_i^2}{\Sigma n_i}\right] = \frac{1}{5-1}\left[7-\frac{1^2+1^2+2^2+2^2+1^2}{7}\right]=1.3571$$

Step 13. Assemble analysis-of-variance table as follows:

Source	SSD	DF	MS	EMS
Laboratories	0.065036	4	0.016259	$\sigma_W^2+1.3571\sigma_B^2$
Determinations	0.045050	2	0.022525	σ_W^2
Total	0.110086	6		

Step 14. Compute the between-laboratory precision (reproducibility):

$s_W^2+1.3571s_B^2=0.016259$

$s_B^2=(0.016259-0.022525)/1.3571=-0.004617$

Since the value of S_B^2 is negative in this example, a meaningful estimate of σ_B cannot be obtained by the usual method of taking the square root of S_B^2. Instead, the value of S_B is arbitrarily set equal to zero.

Step 15. Compute the within-laboratory precision (repeatability):

$S_W = \sqrt{0.022525} = 0.150.$

Step 16. Compute the precision of a single determination:

$S_T(\text{between-laboratory}) = \sqrt{S_B^2 + S_W^2} = \sqrt{0+0.022525} = 0.150.$

Step 17. Compute the between-laboratory coefficient of variation:

$100\ S_B/m = 100(0)/0.8286 = 0.$

Step 18. Compute the within-laboratory coefficient of variation:

$100\ S_W/m = 100(0.150)/0.8286 = 18.1.$

Step 19. Compute the coefficient of variation of a single determination:

$100\ S_T(\text{between-laboratory})/m = 100(0.150)/0.8286 = 18.1.$

Step 20. Precision estimates are summarized in the first row of Table 9.

Example 2. Analysis of Determinations by Site

Step 1. Compute the arithmetic mean of all measurements:

$\bar{x} = (0.88+0.90+\ldots+1.09)/32 = 1.2216.$

Step 2. Compute the daily means:

Day	Number of Determinations	Arithmetic Mean
1	$m_1=7$	$\bar{d}_1=0.8286$
2	$m_2=5$	$\bar{d}_2=1.4140$
3	$m_3=4$	$\bar{d}_3=1.4125$
4	$m_4=8$	$\bar{d}_4=1.5750$
5	$m_5=8$	$\bar{d}_5=0.9962$

The value 0.8286 (Day 1 mean) in the first row was obtained in Step 1 of Example 1.

Step 3. Compute the between-day sum of squares:

$$\sum_{i=1}^{j} m_i(\bar{d}_i-\bar{x})^2 = 7\ (0.8286-1.2216)^2 + 5\ (1.4140-1.2216)^2 + 4\ (1.4125-1.2216)^2 + 8\ (1.5750-1.2216)^2 + 8\ (0.9962-1.2216)^2 = 2.8176.$$

Step 4. Compute the between-laboratory sum of squares for each day of testing, according to the method illustrated in Step 3 of Example 1, and obtain the total:

Day	Between-Laboratory Sum of Squares
1	0.065036
2	0.112870
3	0.029275
4	0.036900
5	0.029537

The value 0.065036 (Day 1 between-laboratory sum of squares) in the first row was obtained in Step 3 of Example 1. The total sum of squares, 0.2736, is called the "between-laboratory within days" sum of squares, and it is used in formulating a measure of laboratory-to-laboratory variability that has the day-to-day variability in lead concentration removed.

Step 5. Compute the within-laboratory sum of squares from the duplicate determinations:

$$\Sigma(x_1-x_2)^2/2=(0.90-0.89)^2/2+\ldots+(0.84-1.09)^2/2=0.1234.$$

This computation corresponds to Step 4 in Example 1.

Step 6. Compute the total sum of squares:

$$\Sigma(x-\bar{x})^2=(0.88-1.2216)^2+\ldots+(1.09-1.2216)^2=3.2146.$$

This computation corresponds to Step 5 in Example 1.

Step 7. Combine the between-day sum of squares (Step 3), the between-laboratory sum of squares (Step 4), and the within-laboratory sum of squares (Step 5), as a check on Step 6:

$$2.8176+0.2736+0.1234=3.2146.$$

Step 8. Determine the number of degrees of freedom associated with the between-day sum of squares. This number is one less than the number j of daily means. (From Step 2, j is seen to be 5).

Between-day $df=j-1=5-1=4$.

Step 9. Determine the number of degrees of freedom associated with the between-laboratory (within-days) sum of squares which is calculated by totaling the number of laboratory means for each day's measurements and subtracting the number of daily means:

$$\Sigma k_i-j=(5+4+4+6+5)-5=19.$$

Step 10. Determine the number of degrees of freedom associated with the within-laboratory sum of squares. This is equal to the total number t of determinations less the number of laboratory means for each day's measurements:

$t-\Sigma k_i=32-(5+4+4+6+5)=8.$

Step 11. Determine the number of degrees of freedom associated with the total sum of squares. This is equal to the total number of determinations less one:

$\Sigma n_i-1=(7+5+4+8+8)-1=31.$

Step 12. Compute the between-day mean square. This is the ratio of the between-day sum of squares to the associated number of degrees of freedom:

Between-day mean square=2.8176/4=0.7044.

Step 13. Compute the between-laboratory (within-days) mean square, the ratio of the between-laboratory (within days) sum of squares to the associated number of degrees of freedom.

Between-lab (within days) mean square=0.2736/19=0.0144.

Step 14. Compute the within-laboratory mean square, the ratio of the within-laboratory sum of squares to the associated number of degrees of freedom.

Within-lab mean square = 0.1234/8=0.0154.

Step 15. Compute a weighted average number of determinations per laboratory as shown in Step 12 of Example 1. The weighted average is 1.3041.

Step 16. Assemble analysis of variance table.

Source	SSD	DF	MS	EMS
Days	2.8176	4	0.7044	
Laboratories	0.2736	19	0.0144	$\sigma_W^2+1.3041\sigma_B^2$
Determinations	0.1234	8	0.0154	σ_W^2
Total	3.2146	31		

Step 17. Compute the between-laboratory precision (reproducibility):

$S_W^2+1.3041\ S_B^2=0.0144$

$S_B^2=(0.0144-0.0154)/1.3041=-0.00077$

Since the value of S_B^2 is negative in this example, a meaningful estimate of σ_B cannot be obtained by the usual method of taking the square root of S_B^2. Instead, the value of S_B is arbitrarily set equal to zero.

Step 18. Compute the within-laboratory precision (repeatability):

$S_W=\sqrt{0.0154}=0.1241$

Step 19. Compute the precision of a single determination:

$$S_T=\sqrt{S_B{}^2+S_W{}^2}=\sqrt{0+0.0154}=0.1241$$

This standard deviation is denoted in this report as S_T(between-laboratory) in accordance with the ASTM definition given in D 2906-70T.

Step 20. Compute the between-laboratory coefficient of variation:

$100S_B/m=100(0)/1.2216=0.$

Step 21. Compute the within-laboratory coefficient of variation:

$100S_W/m=100(0.1241)/1.2216=10.2.$

Step 22. Compute the coefficient of variation of a single determination:

$100S_T/m=100(0.1241)/1.2216=10.2.$

Step 23. Precision estimates are summarized in Table 9, Row 6.

APPENDIX C

PRACTICAL APPLICATIONS OF THE STATISTICAL MEASURES GENERATED FROM THE COOPERATIVE STUDY OF THE LEAD METHOD (D3112)

PRACTICAL APPLICATIONS OF THE STATISTICAL MEASURES GENERATED FROM THE COOPERATIVE STUDY OF THE LEAD METHOD (D3112)

The measures of reproducibility, repeatability and between-laboratory standard error generated in this study are useful as a means of quantifying the uncertainty associated with a single measurement of lead concentration using the test method. With these measures, it is possible to place confidence limits about several types of estimates, for example:

(1) A confidence limit for any single observation by a particular laboratory,

(2) A confidence limit for any single observation by any randomly chosen laboratory, and

(3) A confidence limit for an average of several observations by any randomly chosen.

In general, if it is assumed that the measurement of lead concentration by this method is unbiased, and that the distribution of these measurements follows a normal distribution, then a 95 percent confidence interval for any measurement can be determined as m ± 1.96s, where m is the observed measurement and s is the appropriate estimated standard deviation (e.g. S_W, S_B, or S_T).

If a particular laboratory were to make repeated simultaneous measurements at the same lead concentration, approximately 95 percent of these simultaneous measurements should be included in the confidence interval calculated as $m \pm 1.96\ S_W$, where m is the estimated concentration from a determination, and S_W is the within-laboratory component of variance (repeatability) estimated from the study. Alternatively, this confidence interval represents the best estimate of the range in which any randomly selected measurement by a particular laboratory will fall.

The confidence interval for any single estimate by any laboratory would be calculated as $m \pm 1.96\ S_T$, where S_T is a standard deviation which includes variability between laboratories as well as variability within a laboratory. Thus, for this situation, the appropriate standard deviation is calculated as $S_T = \sqrt{S_B^2 + S_W^2}$, where S_B and S_W are the reproducibility and repeatability estimates as determined by this study. If a large number of laboratories were to make repeated simultaneous determinations, 95 percent of such determinations would be expected to lie within the calculated interval. Alternatively, this interval represents the best estimate of the range in which any single measurement by any single laboratory will fall.

If each of several laboratories calculated an average lead concentration based upon several simultaneous determinations obtained concurrently by all laboratories, a 95 percent confidence interval for any one of these averages would be estimated as

$$\bar{m} \pm 1.96 \sqrt{S_B^2 + S_W^2/n} \ ,$$

where n is the number of determinations used in calculating the average.

The repeatability measure, S_W, allows for the direct calculation of confidence intervals concerning a particular laboratory's measurements. It also bears a relationship to the repeatability measure suggested by Mandel. Mandel defines repeatability as the quantity that will be exceed only about 5 percent of the time by the difference, taken in absolute value, of two randomly selected test results obtained in the same laboratory on a given material. This value is calculated as $2.77\ \sigma/\sqrt{n}$ where σ is the within-laboratory standard deviation, and n is the number of replicates which were averaged to yield a test result. The within-laboratory component of variance S_W, is an estimate of the σ used by Mandel; thus in terms of Mandel's definition the repeatability is estimated by

$$\frac{2.77\ S_W}{\sqrt{n}}$$

The statistical measures of precision developed in this study can also be related to Mandel's definition of reproducibility. Mandel states that if specimens of the materials are sent to a random selection of laboratories, and each laboratory provides a single test result, which is an average based upon n replicates, 95 percent of the time differences between any two such results, taken in absolute value, should not exceed $2.77\sqrt{\sigma_L^2 + \sigma^2/_n}$, where σ_L^2 is a measure of the between-laboratory variability and σ^2 is a measure of the within-laboratory variability. This value is defined by Mandel to be the reproducibility measure. Thus in terms of Mandel's definition, the reproducibility of this test method is estimated by $2.77\sqrt{S_B^2 + S_W^2/n}$, where S_B^2 and S_W^2 can be obtained from the expressions determined for this study.

This study's estimates of within-laboratory and between-laboratory precision (repeatability and reproducibility) can be directly used in statements on precision as outlined in ASTM Method D 2906. The within-laboratory component of variance, S_W^2, is equal to the square of the repeatability measure, S_W; likewise the between-laboratory component of variance, S_B^2, is equal to the square of the reproducibility measure, S_B. The single-operator component of variance, S_S^2, was not isolated from the within-laboratory variance in this study, and can be assumed to be a part of the within-laboratory variance.

INTERLABORATORY COOPERATIVE STUOY OF THE PRECISION OF SAMPLING STACKS FOR PARTICULATES AND COLLECTED RESIOUE

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INTERLABORATORY COOPERATIVE STUDY OF THE PRECISION OF SAMPLING STACKS FOR PARTICULATES AND COLLECTED RESIDUE

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 in source emissions have been evaluated in Phase 2 of Project Threshold. Evaluation of a pitot tube method (D 3154-72) (9) 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 is 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 have been performed by Battelle's Columbus Laboratories under contract to ASTM.

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*References are given on page 82.

This report presents the results obtained from an interlaboratory study of the precision of a proposed ASTM method for the determination of particulates and collected residue in stack emissions.

SUMMARY OF RESULTS

Nine different cooperating laboratories performed a total of 152 particulate and 153 collected residue determinations on four different types of source emissions. The statistical analysis of the test data provides the following estimates of precision of the proposed ASTM method.

Particulate Measurements

- Based on data obtained at an oil-fired and a coal-fired electrical generating station and a cement plant, the between-laboratory standard error, S_T (between-laboratory), of particulate concentration and emission rate determinations may be expressed by the equations:

Particulate Concentration

$$S_T \text{ (between-laboratory)} = -0.0003 + 0.060\ m$$

Particulate Emission Rate

$$S_T \text{ (between-laboratory)} = 0.290 + 0.067\ m$$

where the mean particulate concentration, m, and the corresponding standard error are given in grains/SCFD and the mean emission rate, m, and the corresponding standard error is given in lbs/hr. Particulate concentration and emission rate determinations at the three sites were in the range of 0.008 to 14 grains/SCFD and 10 to 6800 lbs/hr, respectively.

- Particulate determinations at a foundry (ferrous metallurgy) where the particulate concentration and emission rates ranged from 0.0007 to 0.0045 grains/SCFD and 1 to 3 lbs/hr, respectively, produced between-laboratory standard error estimates of particulate concentration and emission rate which are generally higher than the values predicted from the preceding equations.

- The following table summarizes the mean particulate concentrations and emission rates and the mean between-laboratory standard errors (expressed as the coefficient of variation) of measurements at the four sites where the test method was evaluated.

Site/Source	Mean Particulate Conc., grains/SCFD	Mean CV, %	Mean Emission Rate, lbs/hr	Mean CV, %
I Oil-fired power station	0.013	10.0	14.6	8.9
II Foundry	0.0015	45.1	2.3	37.7
III Coal-fired power station	0.14	7.6	3571	7.6
IV Cement plant (kiln)	5.70	6.0	1946	5.7

Collected Residue Measurements

- The following table summarizes the mean collected residue concentrations and the mean between-laboratory standard errors (expressed as the coefficient of variation) of measurements at the four sites where the test method was evaluated.

	Site/Source	Mean Collected Residue Conc., grains/SCFD	Mean CV, %
I	Oil-fired power station	0.0086	58.4
II	Foundry	0.0095	93.0
III	Coal-fired power station	0.037	33.5
IV	Cement plant (kiln)	0.059	25.4

- Analyses of residue samples from six tests performed at the coal-fired power plant show that sulfate (as SO_4) accounts for about 50 to 80 weight percent of the aqueous fraction collected residue. Similar analyses of samples from four tests at the cement plant show that sulfate (as SO_4) comprises from about 20 to 30 weight percent of the aqueous fraction collected residue.

EXPERIMENTAL PROGRAM

ASTM Test Method

The procedure subjected to evaluation in the interlaboratory testing program is a proposed ASTM method for simultaneous determination of particulates and collected residue. A copy of the method as tested in this study is reproduced in Appendix A.

The test method describes procedures and equipment for simultaneous determination of particulates and collectable residue in emissions from stationary sources. The method incorporates flexibility in both procedure and equipment which makes it applicable to compliance and performance testing of emissions from a variety of sources.

The method is similar to ASTM D 2928-71(10) in that a portion of the particulate-bearing emissions is removed from a stack or duct under isokinetic sampling conditions and the particulate material is collected by filtration with an Alundum® thimble, flat filter, or column of glass wool. The choice of primary filter media, which is located in-stack immediately behind the sampling nozzle, is dependent on the particulate concentration, stack gas temperature, and the moisture content of the emissions. In the proposed method, the in-stack filter is backed-up with a heated flat filter located at the exit of the sampling probe. The probe between the in-stack and backup filters is also heated to prevent condensation of moisture and sulfuric acid mist.

Sampling is performed at several points within the duct or stack to obtain a representative measure of emissions. The selection of the number of sampling points is determined by stack size and uniformity of the flow pattern at the sampling location. A type "S" pitot tube is used in conjunction with the sampling probe to continuously measure the velocity pressure and to permit rapid adjustment to isokinetic sampling conditions using commercially-available stack sampling equipment.

Particulate concentration in the duct or stack is determined from the measurement of gas volume sampled and the combined weight of particulate matter collected in the nozzle, in-stack filter, probe, and backup filter. The particulate concentration in the emissions is usually expressed in grains per standard cubic foot, dry basis (grains/SCFD)*. Particulate emission rate, which is commonly expressed in pounds per hour (lb/hr) may be calculated from the cross sectional area of the stack and stack gas velocity measurements which are performed concurrently as a part of the particulate sampling procedure.

Collected residue is trapped in a train of four impingers immersed in an ice bath. The impinger assembly is located after the backup filter. Following sampling, the condensed moisture is collected and the impingers are rinsed with water and acetone. The water rinse is combined with the condensed moisture. As soon as possible after sampling, the aqueous sample is extracted with chloroform and ether and then partially evaporated to expel dissolved gases, especially SO_2. Subsequently all samples (extracted aqueous phase, chloroform-ether extract and acetone wash) are evaporated to dryness at ambient temperature, desiccated, and weighed. The concentration of collected residue in the emissions (grains/SCFD) is computed from the gas volume sampled and the combined weight of the aqueous and two organic residue samples. The collected residue emissions rate (lbs/hr) may be calculated from the cross sectional area of the stack and the stack gas velocity which is determined from measurements made concurrently with the sampling.

Equipment

The tests were performed with commercially available source sampling systems consisting of components to:

a) Collect the particulates by filtration,
b) Collect condensable residue,
c) Iskoinetically control the sampling rate and measure the gas volume sampled,
d) Measure the flue gas velocity, and
e) Collect moisture to determine its content in the flue gas.

The components and the manner in which they are normally connected is shown in Figure 1. Additional description of the sampling system equipment and its maintenance, calibration, and operation is presented by Rom(11)

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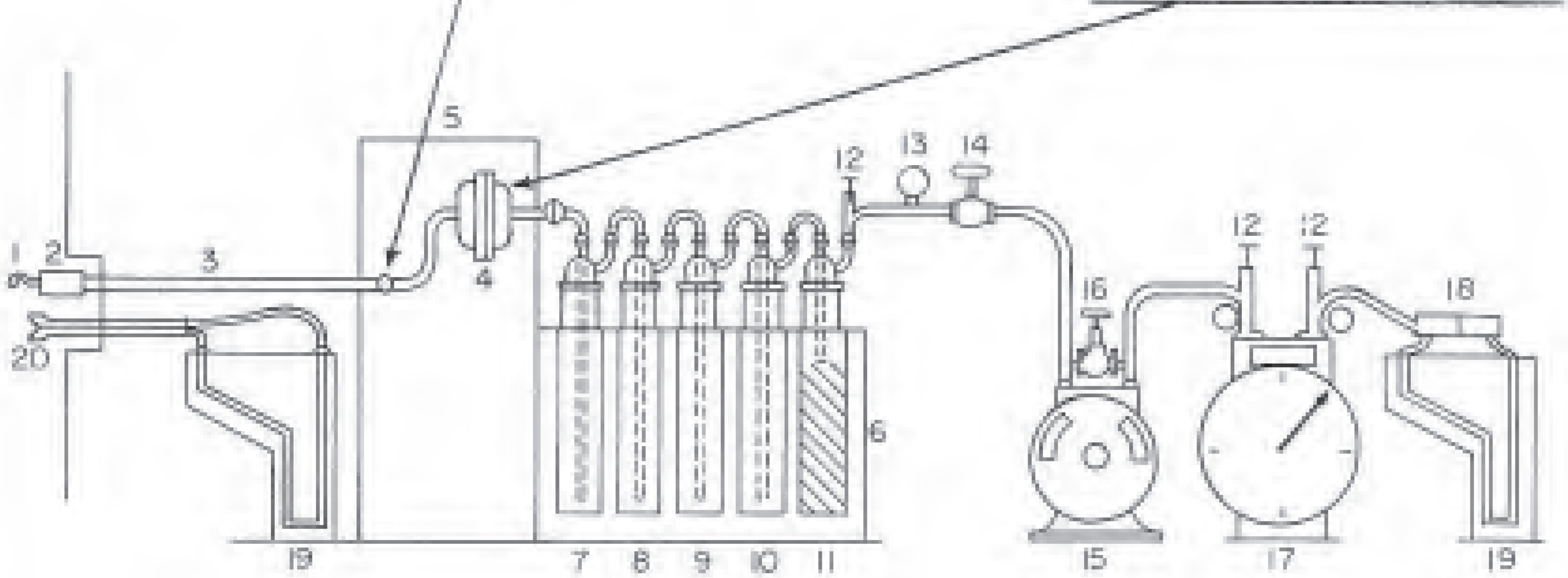
* Grains/SCFD may be converted to milligrams per standard cubic meter by multiplying by 2288.

Option: A flexible, heated Teflon® hose may be used between probe outlet and inlet to backup filter

Option: Heated filter may be directly coupled to probe. In this case a heated hose is not required between the filter outlet and the outlet and the inlet to the first impinger



1. Nozzle
2. Thimble or flat filter
3. Stainless steel probe
4. Backup filter holder
5. Heated box for filter
6. Ice bath for impingers
7. Modified impinger, dry
8. Modified impinger with 100 ml water
9. Modified impinger with 100 ml water
10. Modified impinger, dry
11. Silica gel trap
12. Thermometer
13. Vacuum gauge
14. Flow control valve
15. Pump
16. Flow control valve
17. Dry test meter
18. Calibrated orifice
19. Manometer
20. "S" type pitot tube

FIGURE 1. EQUIPMENT TRAIN USED FOR PARTICULATE AND COLLECTED RESIDUE MEASUREMENTS

Figure 2 is a photograph of a typical sampling train as assembled for a particulate and collected residue test. Photographs of the probe and the in-stack thimble and flat filter arrangements are shown in Figure 3. Additional details of the sampling system components used at the various site tests are given in Table 1.

At Sites I and II, some cooperating laboratories used sampling trains with optional configurations permitted by the test method. One modification consisted of mounting the backup filter in a heated box on the exit end of the probe and using an unheated Teflon® line to connect to the impinger train and remainder of the system. A second modification was the use of a heated Teflon® line, about seven feet long, between the probe and the backup filter. The alterations were intended to facilitate changes between ports during performance of the tests.

Static pressure was measured with a manometer connected to a 1/4-inch tap in the stack or duct.

The CO_2 and O_2 composition in the flue gas was determined by Orsat analysis. Nitrogen was assumed to comprise the balance of the gas composition.

Sampling System Operation

In all tests the sampling systems were operated, as nearly as possible, in isokinetic sampling mode in accordance with procedures given in the test method. Nozzle sizes were initially selected to give a meter sampling rate of about 1 cfm. However, at some sites the pressure drop in the trains limited the maximum attainable sampling rate and necessitated the use of a smaller nozzle.

Commercially available nomographs were used to make flow adjustments to maintain an isokinetic sampling rate throughout the tests. The function and use of the nomograph in field operation is described in Reference (11).

Test parameters were recorded once during the sampling period at each traverse point using the form shown in Table 6 of the test method. In addition to the parameters listed, the laboratories also recorded the backup filter box and probe temperatures. At all sites except III the filter box and probe temperatures were operated at 250 F or slightly higher. At Site III, the probes and filter boxes were operated at 320 F to prevent SO_3 condensation.

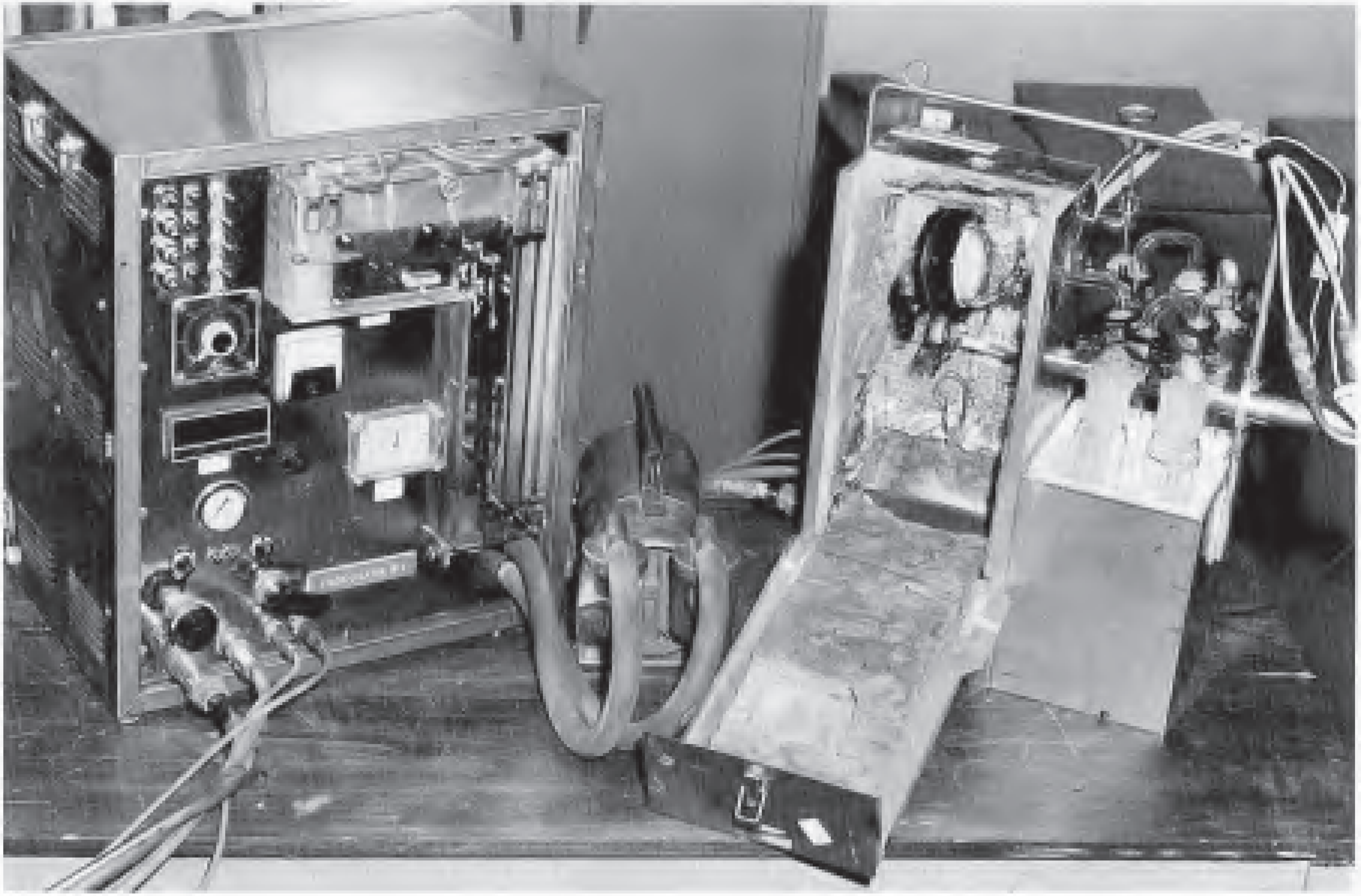
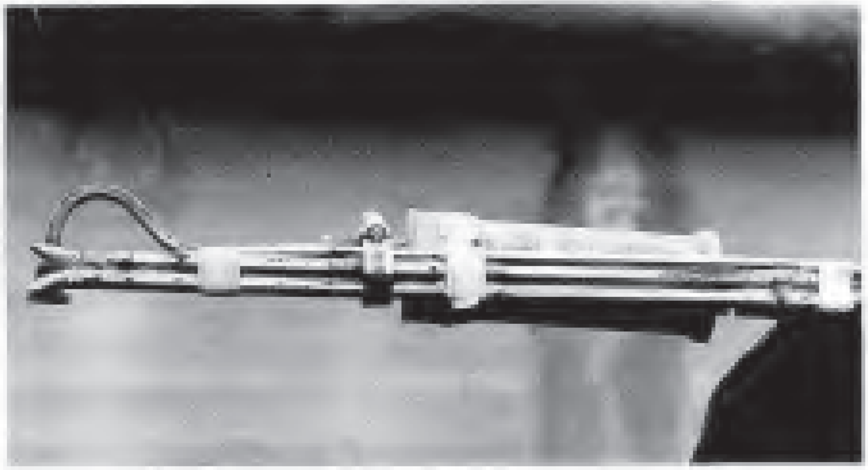


FIGURE 2. TYPICAL SAMPLING-TRAIN EQUIPMENT USED FOR PARTICULATE AND COLLECTED RESIDUE TESTS

a. Probe Equipped With Flat Filter



b. Probe Equipped With Thimble

FIGURE 3. TYPICAL PROBE-PITOT TUBE ARRANGEMENTS USED FOR PARTICULATE AND COLLECTED RESIDUE SAMPLING

TABLE 1. SAMPLING TRAIN COMPONENTS USED FOR PARTICULATE AND COLLECTED RESIDUE TESTS

Component	SITE I	SITE II	SITE III	SITE IV
Nozzle Lab A	3/16" and 1/4"[a]	1/4" and 3/8"[b]	3/16"	3/16" and 1/4"[c]
Lab B	3/16"	1/4" and 3/8"	13/64"	3/16" and 1/4"
Lab C	3/16"	1/4" and 3/8"	3/16"	3/16" and 1/4"
Lab D	1/4"	1/4" and 3/8"	3/16"	3/16" and 1/4"
Instack Filter[d]	Alundum® Thimble	47mm glass fiber flat filter	Alundum® Thimble	Alundum® Thimble with glass wool insert
Probe	6 to 7 ft stainless steel[e]	6 to 7 ft stainless steel[f]	14 to 15 ft stainless steel	6 to 7 ft stainless steel
Pitot Tube	Type "S"	Type "S"	Type "S"	Type "S"
Backup Filter	2-1/2" and 4" glass fiber filter	2-1/2" and 3" glass fiber filter	2-1/2" and 3" glass fiber filter	2-1/2" and 3" glass fiber filter
Impingers	1st and 4th-modified (g) Greenburg-Smith 2nd and 3rd-Greenburg-Smith	All modified (g) Greenburg-Smith	All modified (g) Greenburg-Smith	All modified (g) Greenburg-Smith
Desiccant	100-300g silica gel or Drierite	~200g Silica gel	200-300g Silica gel	~200g Silica gel

(a) 3/16" used for tests 2 and 3, 1/4" for remainder of tests.

(b) Labs A and B in Test 1, all labs in Test 2, and Labs A and C in Test 8 used 1/4" nozzles. 3/8" nozzles were used for other tests.

(c) All Labs used 1/4" nozzles for Test 1. 3/16" nozzles were used for remainder of tests.

(d) RA360 thimbles were used in all tests with exception of Laboratory D at Site I which used RA98 thimbles. Laboratory was unable to purchase specified thimbles due to a temporary shortage.

(e) Lab D used a glass-lined probe.

(f) Laboratories B and D, Test 3 and Laboratories A and C, Test 8 used glass-lined probes.

(g) Modified by removal of tip at the bottom of impinger inlet tube.

The sampling system assembly, disassembly, and sample recovery operations were generally performed at the sampling location. The particulate samples (filters and wash solutions) were sealed in containers and the cooperators returned the samples to their respective laboratories for gravimetric analysis. The extraction and evaporation of the aqueous collected residue samples was performed in laboratory facilities at the various test sites. Then, cooperators returned all liquid samples to their laboratories to complete the analyses.

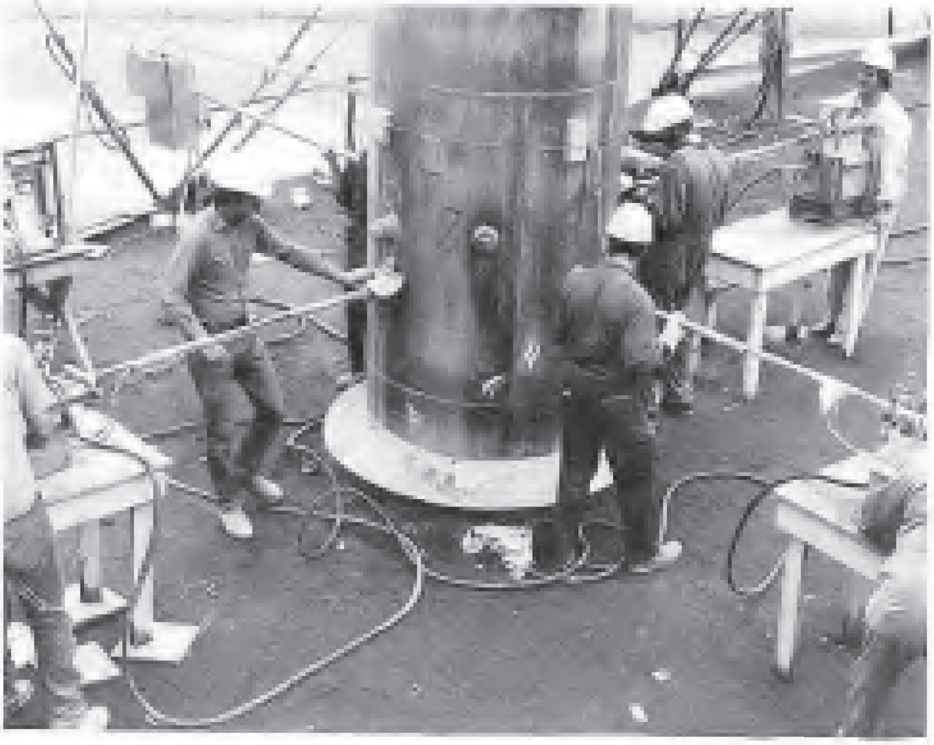
Interlaboratory Test Procedure

Test series were conducted at each site in which four cooperating laboratories concurrently performed particulate and collected residue sampling in accordance with the procedures described in the proposed ASTM method. Due to spatial limitations, all laboratories obviously could not perform particulate sampling at the same traverse point at the same time. Consequently, a test procedure was adopted in which the laboratories concurrently sampled at different traverse points and then moved from point-to-point and port-to-port in a pattern until samples were obtained at all traverse points. The photographs in Figure 4 show the manner in which the cooperating laboratories performed concurrent particulate and collected residue sampling at Sites I and IV.

The traverse points at which the laboratories sampled at each test site are shown in Figures 5 through 8. These figures also present typical values of velocity pressure (inches of water) and gas temperature (degrees F) at each traverse point used in the tests.

Tables 2 through 5 show the sequence in which laboratories moved from port-to-port in completing the sampling patterns. In all tests, sampling at each port was started at the point farthest from the duct or stack wall and proceeded to the traverse point nearest the wall. Sampling was continued as the probes were moved between traverse points. However, sampling was terminated and the sampling system was sealed when the laboratories changed ports. At several sites, spatial limitations necessitated the removal of the probe assembly from the impinger box to facilitate the movement of sampling equipment from port-to-port.

a. At Site I



b. At Site IV

FIGURE 4. COOPERATING LABORATORIES CONCURRENTLY PERFORMING PARTICULATE AND COLLECTED RESIDUE TESTS

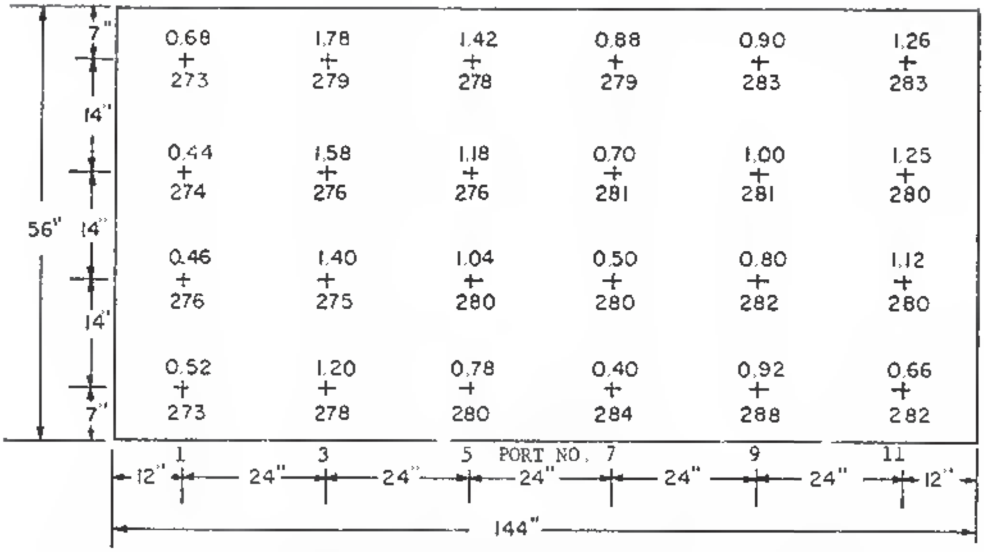


FIGURE 5. SITE I SAMPLING POINTS SHOWING TYPICAL VELOCITY PRESSURES AND TEMPERATURES

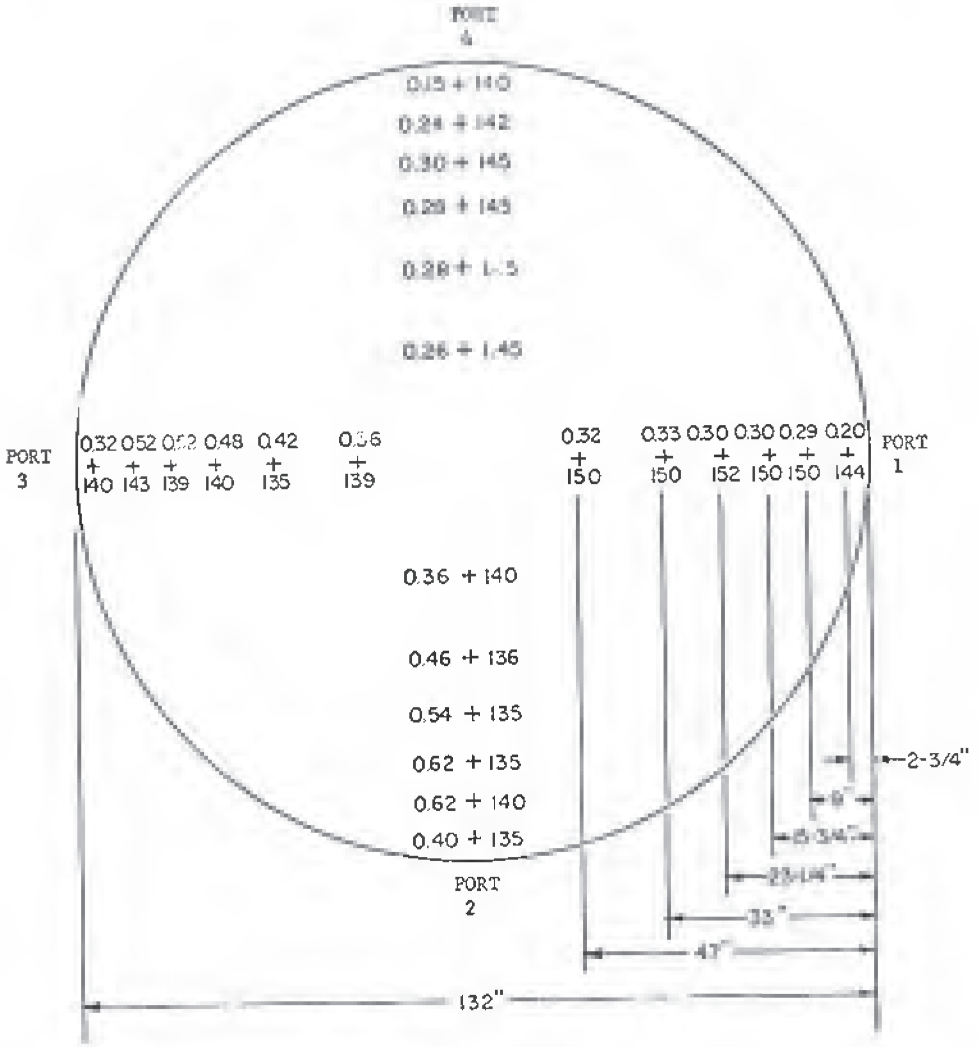


FIGURE 6. SITE II SAMPLING POINTS SHOWING TYPICAL VELOCITY PRESSURES AND TEMPERATURES

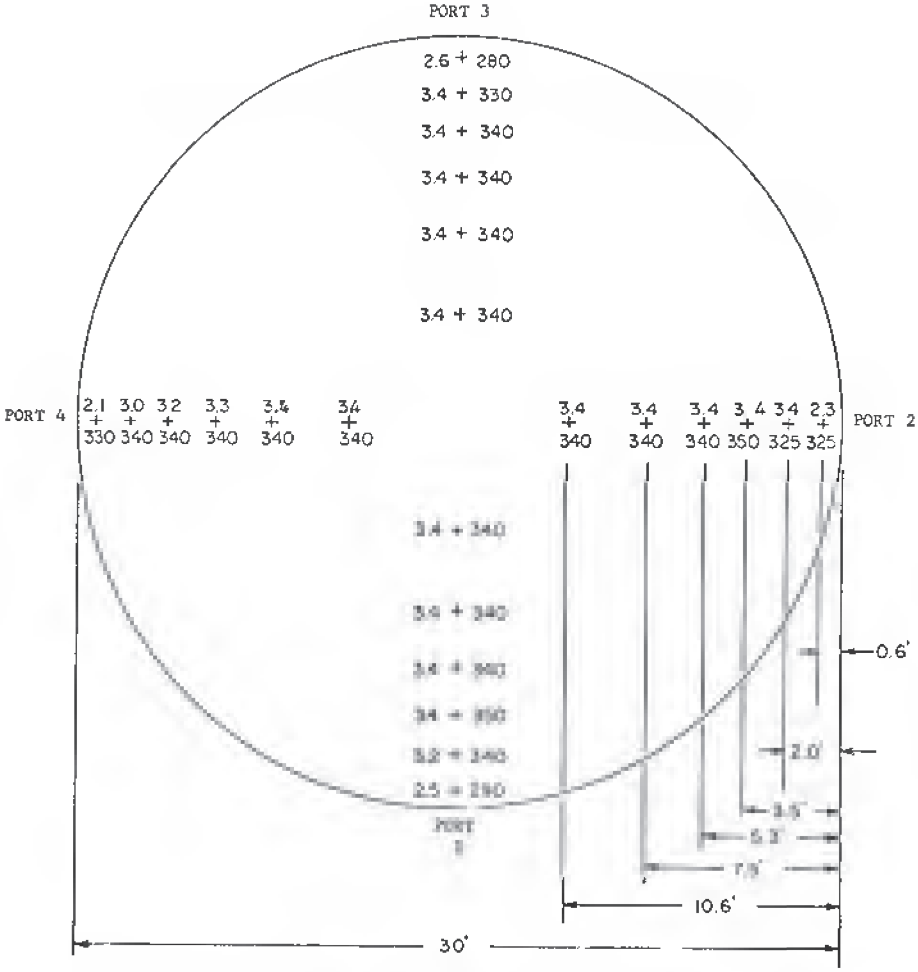


FIGURE 7. SITE III SAMPLING POINTS SHOWING TYPICAL VELOCITY PRESSURES AND TEMPERATURES

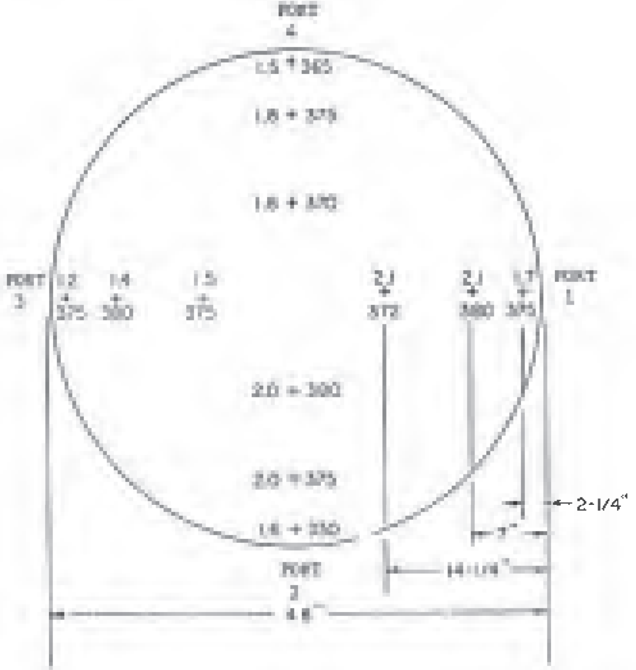


FIGURE 8. SITE IV SAMPLING POINTS SHOWING TYPICAL VELOCITY PRESSURES AND TEMPERATURES

TABLE 2. TEST PATTERN FOR PARTICULATE AND COLLECTED RESIDUE MEASUREMENTS AT SITE I

Time Period(b)	Port Number(a)					
	1	3	5	7	9	11
I	B	A	D		C	
II		B	A	D		C
III	C		B	A	D	
IV		C		B	A	D
V	D		C		B	A
VI	A	D		C		B

(a) Entries below are laboratory code designations.

(b) Test duration was 144 minutes.

TABLE 3. TEST PATTERN FOR PARTICULATE AND COLLECTED RESIDUE MEASUREMENTS AT SITE II

Time Period(b)	Port Number(a)			
	1	2	3	4
Odd-Numbered Tests				
I	D	B	C	A
II	A	D	B	C
III	C	A	D	B
IV	B	C	A	D
Even-Numbered Tests				
I	B	C	A	D
II	C	A	D	B
III	A	D	B	C
IV	D	B	C	A

(a) Entries below are laboratory code designations.

(b) Test duration was 120 minutes.

TABLE 4. TEST PATTERN FOR PARTICULATE AND COLLECTED RESIDUE MEASUREMENTS AT SITE III

Time Period(b)	Port Number(a) 1	2	3	4
Odd-Numbered Tests				
I	B	A	D	C
II	C	B	A	D
III	D	C	B	A
IV	A	D	C	B
Even-Numbered Tests				
I	A	D	C	B
II	D	C	B	A
III	C	B	A	D
IV	B	A	D	C

(a) Entries below are laboratory code designations.

(b) Test duration was 120 minutes.

TABLE 5. TEST PATTERN FOR PARTICULATE AND COLLECTED RESIDUE MEASUREMENTS AT SITE IV

Time Period(b)	Port Number(a) 1	2	3	4
Tests 1,3,5,7				
I	C	B	D	A
II	A	C	B	D
III	D	A	C	B
IV	B	D	A	C
Tests 2,4,6,8				
I	B	D	A	C
II	D	A	C	B
III	A	C	B	D
IV	C	B	D	A
Tests 9,11,13				
I	C	D	B	A
II	A	C	D	B
III	B	A	C	D
IV	D	B	A	C
Tests 10,12,14				
I	D	B	A	C
II	B	A	C	D
III	A	C	D	B
IV	C	D	B	A

(a) Entries below are laboratory code designations.

(b) Test duration was 48 minutes.

Table 6 summarizes the number of sampling points and sampling times for the various site tests. The velocity pressure and gas temperature readings were taken at each of the traverse points during the sampling periods. Each laboratory determined the moisture content of the flue gas from the quantity of moisture collected during the particulate and collected residue sampling period.

Measurements of the barometric pressure, static pressure of the stack and gas composition by Orsat analysis were performed by the Coordinating Laboratory at least once during each particulate test.

TABLE 6. SAMPLING TIMES FOR PARTICULATE AND COLLECTED RESIDUE TESTS

Site	Points Sampled	Sampling Time at each point, min	Total Sampling Time, min
I	24	6	144
II	24	5	120
III	24	5	120
IV	12	4	48

Test Site Descriptions

The characteristics of the four test sites at which the particulate sampling method and collected residue were evaluated are summarized in Table 7.

Site I

The 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.

The particulate measurements were made in six 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 particulate and collected residue concentrations for the six tests performed at this site were in the range of 0.008 to 0.016 grains/SCFD and 0.006 to 0.012 grains SCFD, respectively.

Site II

Site II tests were performed at a foundry on a stack carrying emissions from a total of five arc-melting, arc-holding, and induction furnaces. The operation of the arc melting furnaces is cyclic and results in nonuniform emission rates and relatively rapid (within minutes) gas temperature variations over a range of 90 to 200 F.

Particulate measurements were made at four ports of a 75-foot stack. The test ports, which are spaced at 90 degrees, are located about 40 feet (about four stack diameters) above the stack inlet. Eight tests were performed at this site which is characterized by particulate and collected residue concentrations in the range of 0.001 to 0.002 grains/SCFD and 0.005 to 0.026 grains/SCFD, respectively.

TABLE 7. SUMMARY OF TEST SITE CHARACTERISTICS

Site Characteristic	Site I	Site II	Site III	Site IV
Type of Operation	Electrical generation (120 Mw unit)	Foundry (ferrous metallurgy)	Electrical generation (two - 800 Mw units)	Portland Cement Mfg. (dry process)
Emission Source	Oil-fired boiler	Arc furnaces	Coal-fired boilers	Coal-fired kiln
Emission Control Equipment	Electrostatic precipitator	Baghouse	Electrostatic precipitator	Electrostatic precipitator
Fuel Data				
Feed Rate	63,000 lb/hr	NA(a)	500 ton/hr	5500 lb/hr
Excess Air	15% (30%)(b)	NA	30% (50%)(b)	150%(b)
Composition - C (wt. percent)	86.5	NA	(fixed, dry) 50.6	(fixed, dry) 52.9
- H	12.6	NA	--	--
- N	0.25	NA	--	--
- S	0.43	NA	3 - 4	2.8
			Volatiles 33.5	Volatiles 36.0
Flue Gas Data				
Average Velocity, fps	60	38	120	72-97
Average Gas Temperature, F	280	95-180	330	340-370
Composition - CO_2 Volume Percent	11.6	Negligible	12.0	10.0
- O_2 Volume Percent	5.4	21 (air)	6.8	13.4
- H_2O Volume Percent	8-10	1-2	5-7	4-6
- SO_2 ppm	225	Negligible	2200	800-1500
- NO_2 ppm	185	Negligible	400	120-250
Stack Data				
Size	4.67 ft x 12 ft	11 ft diameter	30 ft diameter	4 ft diameter
Height	(duct prior to stack)	100 ft	1200 ft	50 ft

(a) NA - not applicable.

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

Site III

A total of 15 tests were conducted at Site III, a large coal-fired electrical generating station. The station has two units which have 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.

Particulate 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-foot stack level. The port location is at least eight stack diameters above the inlets at the base of the stack. Particulate and collected residue concentrations during the test series ranged from about 0.1 to 0.3 grains/SCFD and 0.016 to 0.04 grains/SCFD, respectively.

Site IV

Test Site IV is a dry process portland cement manufacturing plant. At the site, 14 tests were conducted using two different stacks carrying emissions from 10-feet diameter by 154-feet-long coal-fired cement kilns.

Tests 1 through 8 and 9 through 14 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.

Particulate emissions which ranged from about 1 to 13 grains/SCFD caused some problems with restriction and plugging of pitot tubes at this site. Collected residue concentrations ranged from 0.03 to 0.1 grains/SCFD.

Participating Laboratories

A total of nine laboratories participated in the tests in which the sampling methods were evaluated. The participants teams from the following organizations:

George D. Clayton and Associates
The Detroit Edison Company
General Motors Corporation

Huron Cement Company
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 PARTICULATE AND COLLECTED RESIDUE MEASUREMENTS

Statistical Measures

The experimental program was designed to permit statistical analysis of the test results with the objective of estimating the precision of the ASTM method for determination of particulates and collected residue in source emissions.

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:

Single-operator standard error

S_T (single-operator) = $(S_S^2/n)^{1/2}$

Within-laboratory standard error

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

Between-laboratory standard error

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. (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 field tests of the particulate and collected residue method provide an estimate of between-laboratory standard error, S_T (between-laboratory), for the determination of particulate and collected residue concentrations and emission rates from source emissions. 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 particulate and collected residue determinations with each laboratory making one determination per test. For this situation the estimate of between-laboratory standard error, S_T (between-laboratory) from each test is the same as the standard deviation of the four concurrent particulate or collected residue determinations. An estimate of between-laboratory standard error based on test data from several sites is derived by regression analysis.

It should be noted from the above discussion that S_T (between-laboratory) includes the individual components of variance, but it should not be confused with either within-laboratory precision (repeatability) or between-laboratory precision (reproducibility) as defined and used in this or previous Project Threshold reports.

Accuracy

Accuracy is defined in D 2906-70T "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". Since neither determination of the true value of the particulate and collected residue concentration nor addition of known spikes was feasible, an estimate of the accuracy of the method was not obtained.

Analysis of Particulate Data

Experimental Results

A total of 43 tests by 9 different cooperating laboratories were performed at four different field sites to generate data for the statistical evaluation of the particulate sampling procedure. The sampling data, the flue gas measurements, particulate sample weights, and final results from all tests are presented in the following sections.

Flue Gas Measurements. The results of the measurements of flue gas parameters made in conjunction with the particulate sampling are reported in Tables 8 through 11. The tables list the following data.

CP	Type "S" pitot tube correction factor determined by comparison with NBS calibrated pitot tube (Type "S")
$(H)^{1/2}_{avg}$	Average of the square roots of the velocity pressures, (inches of water)$^{1/2}$
TS	Average of gas temperature measurements at each traverse point in the duct or stack, F
PS	Absolute pressure in duct or stack, inches of mercury
O2, %	Oxygen concentration in flue gas based on Orsat analysis, volume percent
CO2, %	Carbon dioxide concentration in flue gas based on Orsat analysis, volume percent
W, %	Moisture in flue gas, based on condensate volume and water collected on desiccant trap, volume percent
MD	Average molecular weight of flue gas, pound per pound mole, dry basis
U^*_{avg}	Average flue gas velocity, feet per second

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*U_{avg} is expressed in feet per minute in test method.

TABLE 8. SITE I FLUE GAS MEASUREMENTS

SITE	TEST	LAB	CP	$(H)^{1/2}$ AVG	TS AVG	PS	O2,%	CO2,%	W,%	MD	U* AVG ,FPS
I	1[(a)]	A	0.83								
		B	0.87								
		C	0.85								
		D	0.84								
I	2	A	0.83	1.02	278.	29.70	5.0	11.2	7.91	30.0	66.91
		B	0.87	0.91	278.	29.70	5.0	11.2	8.45	30.0	62.84
		C	0.85	0.91	274.	29.70	5.0	11.2	9.90	30.0	61.21
		D	0.84	0.93	280.	29.70	5.0	11.2	4.80	30.0	61.64
I	3	A	0.83	0.99	278.	29.75	5.0	11.2	9.42	30.0	65.16
		B	0.87	0.89	280.	29.75	5.0	11.2	9.06	30.0	61.13
		C	0.85	0.89	278.	29.75	5.0	11.2	9.71	30.0	59.94
		D	0.84	0.92	276.	27.75	5.0	11.2	7.56	30.0	62.87
I	4	A	0.83	0.96	275.	30.10	4.8	11.6	8.18	30.0	62.42
		B	0.87	0.94	278.	30.10	4.8	11.6	8.47	30.0	63.91
		C	0.85	0.92	267.	30.10	4.8	11.6	9.45	30.0	61.07
		D	0.84	0.89	258.	30.10	4.8	11.6	8.39	30.0	57.96
I	5	A	0.83	0.98	277.	30.00	4.8	11.6	10.58	30.0	64.00
		B	0.87	0.90	281.	30.00	4.8	11.6	8.87	30.0	61.98
		C	0.85	0.88	271.	30.00	4.8	11.6	9.29	30.0	58.46
		D	0.84	0.91	258.	30.00	4.8	11.6	9.43	30.0	59.43
I	6	A	0.83	0.97	279.	30.20	5.4	11.6	9.37	30.1	63.36
		B	0.87	0.95	281.	30.20	5.4	11.6	9.75	30.1	64.98
		C	0.85	0.91	256.	30.20	5.4	11.6	9.45	30.1	59.62
		D	0.84	0.91	260.	30.20	5.4	11.6	7.89	30.1	59.27
I	7	A	0.83	0.97	280.	30.20	5.4	11.6	8.59	30.1	63.36
		B	0.87	0.94	277.	30.20	5.4	11.6	9.24	30.1	64.33
		C	0.85	0.91	279.	30.20	5.4	11.6	10.06	30.1	61.04
		D	0.84	0.91	257.	30.20	5.4	11.6	5.99	30.1	59.01

(a) Equipment malfunctions by two laboratories, test aborted.

TABLE 9. SITE II FLUE GAS MEASUREMENTS

SITE	TEST	LAB	CP	1/2 (H) AVG	TS AVG	PS	O2,%	CO2,%	W,%	MD	U AVG ,FPS
	1	A	0.82	0.61	135.	28.83	21.0	0.0	0.80	28.8	36.40
		B	0.87	0.63	139.	28.83	21.0	0.0	0.56	28.8	40.01
		C	0.81	0.65	133.	28.83	21.0	0.0	0.54	28.8	37.92
		D	0.86(a)								
	2	A	0.82	0.63	155.	28.89	21.0	0.0	1.15	28.8	37.75
		B	0.87	0.59	161.	28.89	21.0	0.0	1.49	28.8	37.93
		C	0.81	0.63	152.	28.89	21.0	0.0	1.16	28.8	37.71
		D	0.86	0.62	165.	28.89	21.0	0.0	1.85	28.8	39.29
	3	A	0.82	0.60	142.	28.82	21.0	0.0	1.79	28.8	35.87
		B	0.87	0.62	137.	28.82	21.0	0.0	0.71	28.8	38.92
		C	0.81	0.64	139.	28.82	21.0	0.0	1.27	28.8	37.53
		D	0.86 (b)								
	4	A	0.82	0.62	106.	28.73	21.0	0.0	1.31	28.8	35.88
		B	0.87 (a)								
		C	0.81	0.64	107.	28.73	21.0	0.0	1.15	28.8	36.66
		D	0.86	0.61	111.	28.73	21.0	0.0	1.41	28.8	37.51
	5	A	0.82	0.63	112.	28.73	21.0	0.0	1.32	28.8	36.97
		B	0.87	0.63	115.	28.73	21.0	0.0	1.48	28.8	39.45
		C	0.81	0.65	110.	28.73	21.0	0.0	0.80	28.8	37.57
		D	0.86	0.61	110.	28.73	21.0	0.0	1.45	28.8	37.36
	6	A	0.82	0.57	166.	28.95	21.0	0.0	1.29	28.8	34.58
		B	0.87	0.59	159.	28.95	21.0	0.0	0.85	28.8	37.84
		C	0.81	0.61	162.	28.95	21.0	0.0	1.01	28.8	36.21
		D	0.86	0.59	171.	28.95	21.0	0.0	1.18	28.8	37.94
	7	A	0.82	0.55	137.	28.68	21.0	0.0	1.54	28.8	33.07
		B	0.87	0.57	127.	28.68	21.0	0.0	1.48	28.8	35.97
		C	0.81	0.56	133.	28.68	21.0	0.0	1.15	28.8	33.13
		D	0.86	0.57	142.	28.68	21.0	0.0	1.47	28.8	35.53
	8	A	0.82	0.57	129.	28.73	21.0	0.0	1.56	28.8	34.08
		B	0.87	0.58	136.	28.73	21.0	0.0	1.21	28.8	36.45
		C	0.81	0.59	129.	28.73	21.0	0.0	1.99	28.8	34.42
		D	0.86	0.57	136.	28.73	21.0	0.0	1.62	28.8	35.62

(a) Sampling equipment malfunction, laboratory unable to complete test.

(b) Glass liner of sampling probe broke during test.

TABLE 10. SITE III FLUE GAS MEASUREMENTS

SITE	TEST	LAB	CP	$(H)^{1/2}$ AVG	TS AVG	PS	O2,%	CO2,%	W,%	MD	U* ,FPS AVG
III	1	A	0.83	1.78	331.	28.53	7.2	12.0	6.56	30.2	122.76
		B	0.84	1.80	318.	28.53	7.2	12.0	5.59	30.2	124.31
		C	0.84	1.81	323.	28.53	7.2	12.0	6.34	30.2	125.61
		D	0.84	1.81	329.	28.53	7.2	12.0	6.23	30.2	126.26
III	2	A	0.83	1.76	329.	28.80	7.2	12.0	7.01	30.2	120.87
		B	0.84	1.80	331.	28.80	7.2	12.0	5.60	30.2	124.39
		C	0.84	1.74	323.	28.80	7.2	12.0	6.05	30.2	120.14
		D	0.84	1.75	328.	28.80	7.2	12.0	6.24	30.2	121.03
III	3	A	0.83	1.72	330.	28.82	7.6	11.6	6.65	30.2	117.93
		B	0.84	1.70	327.	28.82	7.6	11.6	6.53	30.2	117.76
		C	0.84	1.69	324.	28.82	7.6	11.6	6.33	30.2	116.71
		D	0.84	1.69	329.	28.82	7.6	11.6	6.22	30.2	117.00
III	4	A	0.83	1.77	330.	29.00	6.8	12.6	6.69	30.3	120.80
		B	0.84	1.77	334.	29.00	6.8	12.6	6.85	30.3	122.93
		C	0.84	1.78	326.	29.00	6.8	12.6	6.73	30.3	122.33
		D	0.84	1.76	333.	29.00	6.8	12.6	6.68	30.3	121.88
III	5	A	0.83	1.79	330.	28.92	6.8	12.4	6.91	30.3	122.10
		B	0.84	1.77	333.	28.92	6.8	12.4	6.77	30.3	122.48
		C	0.84	1.79	333.	28.92	6.8	12.4	5.80	30.3	123.62
		D	0.84	1.78	337.	28.92	6.8	12.4	8.85	30.3	124.56
III	6	A (a)	0.83	1.88	330.	28.11	6.2	12.8	7.87	30.3	130.57
		B	0.84								
		C	0.84	1.81	315.	28.11	6.2	12.8	7.42	30.3	125.75
		D	0.84	1.86	336.	28.11	6.2	12.8	7.73	30.3	131.15
III	7	A (a)	0.83	1.86	330.	28.07	6.8	12.4	8.18	30.3	129.46
		B	0.84								
		C	0.84	1.83	329.	28.07	6.8	12.4	7.31	30.3	128.64
		D	0.84	1.82	335.	28.07	6.8	12.4	7.38	30.3	128.74
III	8	A	0.83	1.87	300.	28.51	6.4	12.6	7.52	30.3	126.27
		B	0.84	1.84	341.	28.51	6.4	12.6	6.58	30.3	129.29
		C	0.84	1.82	302.	28.51	6.4	12.6	6.73	30.3	124.40
		D	0.84	1.86	335.	28.51	6.4	12.6	7.18	30.3	130.13

TABLE 10. (Continued)

SITE	TEST	LAB	CP	(H)$^{1/2}$ AVG	TS AVG	PS	O2,%	CO2,%	W,%	MD	U* ,FPS AVG
III	9	A	0.83	1.83	300.	28.55	6.4	12.6	7.48	30.3	123.58
		B	0.84	1.82	342.	28.55	6.4	12.6	6.67	30.3	127.39
		C	0.84	1.78	305.	28.55	6.4	12.6	6.54	30.3	121.79
		D	0.84	1.82	336.	28.55	6.4	12.6	6.86	30.3	126.82
III	10	A(b)	0.83								
		B	0.84	1.83	336.	28.71	6.2	12.6	7.37	30.3	127.45
		C	0.84	1.77	311.	28.71	6.2	12.6	6.68	30.3	121.18
		D	0.84	1.81	333.	28.71	6.2	12.6	7.28	30.3	125.85
III	11	A	0.83	1.84	330.	28.60	6.2	12.6	7.42	30.3	126.66
		B	0.84	1.83	345.	28.60	6.2	12.6	7.58	30.3	128.43
		C	0.84	1.78	311.	28.60	6.2	12.6	8.04	30.3	122.99
		D	0.84	1.82	338.	28.60	6.2	12.6	7.24	30.3	127.51
III	12	A	0.83	1.38	309.	28.72	9.6	9.4	5.92	29.9	93.83
		B	0.84	1.37	317.	28.72	9.6	9.4	5.10	29.9	94.64
		C	0.84	1.34	306.	28.72	9.6	9.4	5.76	29.9	91.99
		D	0.84	1.37	313.	28.72	9.6	9.4	5.92	29.9	94.68
III	13	A	0.83	1.51	330.	28.64	6.6	12.4	7.19	30.2	103.55
		B(c)	0.84								
		C	0.84	1.43	325.	28.64	6.6	12.4	7.14	30.2	99.22
		D	0.84	1.46	332.	28.64	6.6	12.4	6.99	30.2	101.87
III	14	A	0.83	1.84	330.	28.67	6.4	12.4	8.15	30.2	126.72
		B	0.84	1.83	341.	28.67	6.4	12.4	8.03	30.2	128.42
		C	0.84	1.80	316.	28.67	6.4	12.4	7.19	30.2	124.12
		D	0.84	1.86	334.	28.67	6.4	12.4	7.51	30.2	129.63
III	15	A	0.83	1.84	330.	28.66	6.4	12.6	8.12	30.3	126.95
		B	0.84	1.84	343.	28.66	6.4	12.6	5.99	30.3	128.72
		C	0.84	1.83	321.	28.66	6.4	12.6	5.80	30.3	126.35
		D	0.84	1.83	336.	28.66	6.4	12.6	7.86	30.3	127.78

(a) Laboratory unable to participate in test due to leak in particulate sampling probe.
(b) Particulate sampling thimble ruptured during test.
(c) Equipment malfunction, Laboratory did not complete test.

TABLE 11. SITE IV FLUE GAS MEASUREMENTS

SITE	TEST	LAB[(a)]	CP	$(H)^{1/2}$ AVG	TS AVG	PS	O2,%	CO2,%	W,%	MD	U* ,FPS AVG
IV	1	A	0.81	1.36	378.	29.36	13.4	10.0	5.17	30.1	92.31
		B	0.81	1.28	344.	29.36	13.4	10.0	4.72	30.1	85.40
		C	0.86	1.35	358.	29.36	13.4	10.0	5.51	30.1	96.64
		D(b)	0.86								
IV	2	A	0.81	1.31	361.	29.32	13.4	10.0	5.69	30.1	88.26
		B	0.81	1.37	353.	29.32	13.4	10.0	5.05	30.1	92.19
		C	0.86	1.33	367.	29.32	13.4	10.0	4.58	30.1	95.40
		D(b)	0.86								
IV	3	A	0.81	1.33	350.	29.28	13.4	10.0	5.23	30.1	89.50
		B	0.81	1.35	353.	29.28	13.4	10.0	4.50	30.1	90.26
		C	0.86	1.34	364.	29.28	13.4	10.0	4.82	30.1	96.03
		D	0.86	1.10	364.	29.28	13.4	10.0	5.02	30.1	78.64
IV	4	A	0.81	1.29	347.	29.29	13.4	10.0	6.17	30.1	86.85
		B	0.81	1.36	352.	29.29	13.4	10.0	3.69	30.1	90.71
		C	0.86	1.33	363.	29.29	13.4	10.0	4.45	30.1	95.48
		D	0.86	1.33	363.	29.29	13.4	10.0	6.82	30.1	95.74
IV	5	A	0.81	1.30	358.	29.32	13.4	10.0	5.57	30.1	87.50
		B	0.81	1.35	370.	29.32	13.4	10.0	4.49	30.1	91.32
		C	0.86	1.28	371.	29.32	13.4	10.0	4.25	30.1	92.23
		D	0.86	1.31	371.	29.32	13.4	10.0	5.43	30.1	94.36
IV	6	A	0.81	1.18	350.	29.35	13.4	10.0	5.69	30.1	79.21
		B	0.81	1.39	368.	29.35	13.0	10.0	4.13	30.1	93.68
		C	0.86	1.36	361.	29.35	13.4	10.0	4.79	30.1	97.36
		D	0.86	1.34	361.	29.35	13.4	10.0	4.99	30.1	95.57
IV	7	A	0.81	1.32	355.	29.45	13.4	10.0	5.41	30.1	88.52
		B	0.81	1.39	358.	29.45	13.4	10.0	4.52	30.1	93.04
		C	0.86	1.33	363.	29.45	13.4	10.0	5.74	30.1	95.00
		D	0.86	1.34	363.	29.45	13.4	10.0	5.30	30.1	95.88
IV	8	A	0.81	1.33	356.	29.46	13.4	10.0	6.51	30.1	89.17
		B	0.81	1.34	338.	29.46	13.4	10.0	4.44	30.1	89.04
		C	0.86	1.28	368.	29.46	13.4	10.0	5.77	30.1	92.24
		D	0.86	1.34	367.	29.46	13.4	10.0	6.00	30.1	96.35

TABLE 11. (Continued)

SITE	TEST	LAB(a)	CP	$(H)^{1/2}$ AVG	TS AVG	PS	O2,%	CO2,%	W,%	MD	U AVG ,FPS
IV	9	A	0.81	1.12	375.	29.26	12.0	12.0	7.15	30.4	76.45
		B	0.86	1.09	354.	29.26	12.0	12.0	4.44	30.4	77.40
		C	0.86	1.10	380.	29.26	12.0	12.0	6.33	30.4	79.46
		D	0.81	1.08	360.	29.26	12.0	12.0	6.49	30.4	72.74
IV	10	A	0.81	1.08	384.	29.25	12.0	12.0	7.76	30.4	74.34
		B	0.86	1.09	370.	29.25	12.0	12.0	4.79	30.4	78.03
		C	0.86	1.09	390.	29.25	12.0	12.0	5.24	30.4	78.99
		D	0.81	1.09	367.	29.25	12.0	12.0	5.74	30.4	73.37
IV	11	A	0.81	1.09	390.	29.21	12.0	12.0	8.23	30.4	75.45
		B	0.86	1.07	370.	29.21	12.0	12.0	4.46	30.4	76.85
		C	0.86	1.09	394.	29.21	12.0	12.0	6.37	30.4	79.45
		D	0.81	1.08	365.	29.21	12.0	12.0	7.30	30.4	73.42
IV	12	A	0.81	1.08	361.	29.19	12.0	12.0	6.29	30.4	72.96
		B	0.86	1.09	347.	29.19	12.0	12.0	1.59	30.4	76.87
		C	0.86	1.08	365.	29.19	12.0	12.0	4.48	30.4	77.55
		D	0.81	1.10	337.	29.19	12.0	12.0	5.27	30.4	72.95
IV	13	A	0.81	1.20	388.	29.16	12.0	12.0	7.63	30.4	82.43
		B	0.86	1.16	371.	29.16	12.0	12.0	3.95	30.4	83.13
		C	0.86	1.14	388.	29.16	12.0	12.0	5.25	30.4	83.05
		D	0.81	1.16	379.	29.16	12.0	12.0	5.91	30.4	79.40
IV	14	A	0.81	1.18	387.	29.18	12.0	12.0	6.69	30.4	80.68
		B	0.86	1.16	373.	29.18	12.0	12.0	3.99	30.4	83.60
		C	0.86	1.15	392.	29.18	12.0	12.0	5.19	30.4	83.67
		D	0.81	1.15	375.	29.18	12.0	12.0	5.91	30.4	78.42

(a) Participating laboratory group for Tests 1 through 8 is different than for Tests 9 through 14.

(b) Equipment failure, team unable to participate in test.

In calculating the moisture content of the flue gas in accordance with Equation (5) in Paragraph 5.5.1.3 of the test method, the term V_W, water vapor volume remaining in the meter volume, was omitted. In the equipment used for the tests, essentially all water vapor was removed by passing the gas sample stream through a desiccant trap prior to the dry test meter. Therefore, the gas was metered under dry conditions.

The average flue gas velocity, U^*_{avg}, was calculated using the Equation (9) given in Paragraph 5.6.1 of the test method. The average velocity is reported here in feet per second.

The volumetric flow rate at standard conditions on a dry basis was calculated from the equation: $Q_{STPD} = (U_{avg})\ (A_s)\ (530/T_s)\ (P_s/29.92)\ (1\text{-}W/100)$ where,

U_{avg} = average flue gas velocity, feet per minute

A_s = area of stack, square feet

T_s = average stack gas temperature, R

P_s = absolute stack pressure, inches of mercury

W = percent moisture in flue gas.

The preceding equation to calculate Q_{STPD} is not given in the test of test method.

The statistical evaluation of the average velocity measurements which were made concurrently with the particulate and collected residue determinations is presented in a separate report$^{(9)}$.

Sampling Data. The sampling data for all tests are listed in Tables 12 through 15. The tables show the following sampling parameters:

V_m	Gas volume sampled at meter conditions, cubic feet.
P_b	Barometric pressure, inches of mercury.
P^*_m	Average pressure (suction) at meter, inches of water. (average pressure drop across orifice, designated as ΔH when using a nomograph).
T^*_m	Average temperature at gas meter, F.
V_{STPD}	Gas volume sampled at standard conditions, dry basis, cubic feet.

TABLE 12. SITE I PARTICULATE AND COLLECTED RESIDUE SAMPLING DATA

Test Number[(a)]	Laboratory	Gas Meter Volume V_m	Barometric Pressure, P_b	Pressure @ Meter, P_m^* (avg)	Temperature @ Meter, T_m (avg)	Gas Volume Spld, V_{STPD}	Percent Isokinetic Sampling
1(b)							
2	A(c)						
	B	67.38	29.75	0.72	103	62.96	92
	C	72.40	29.75	0.86	113	66.68	101
	D	121.05	29.75	2.53	123	113.29	91
3	A	77.64	29.80	0.84	113	71.57	103
	B	66.10	29.80	0.71	105	61.67	93
	C	71.92	29.80	0.83	115	66.00	102
	D	120.39	29.80	2.30	126	108.98	95
4	A	124.86	30.15	2.47	112	117.17	95
	B	68.51	30.15	0.80	95	65.96	93
	C	72.66	30.15	0.90	106	68.43	101
	D	124.07	30.15	2.50	119	115.05	98
5	A	126.43	30.05	2.37	110	118.66	96
	B	68.22	30.05	0.72	106	64.25	95
	C	70.50	30.05	0.78	116	65.23	101
	D	127.24	30.05	2.60	125	116.42	98

TABLE 12. (Continued)

Test[a] Number	Laboratory	Gas Meter, Volume, V_m	Barometric Pressure, P_b	Pressure @ Meter, P^*_m (avg)	Temperature @ Meter, T_m (avg)	Gas Volume Spld, V_{STPD}	Percent Isokinetic Sampling
6	A	127.41	30.25	2.54	119	118.63	94
	B	67.55	30.25	0.75	102	64.52	91
	C	71.67	30.25	0.52	112	66.73	99
	D	127.10	30.25	2.67	118	118.50	98
7	A	128.67	30.25	2.54	127	117.90	95
	B	68.71	30.25	0.75	110	64.55	91
	C	72.52	30.25	0.87	125	66.51	100
	D	126.39	30.25	2.74	127	115.86	94

(a) Duration of each test was 144 minutes.
(b) Test aborted due to equipment malfunctions by two teams.
(c) Filter box overheated, laboratory did not complete test.

TABLE 13. SITE II PARTICULATE AND COLLECTED RESIDUE SAMPLING DATA

Test(a) Number	Laboratory	Gas Meter Volume, V_m	Barometric Pressure, P_b	Pressure @ Meter, P^*_m (avg)	Temperature @ Meter T_m (avg)	Gas Volume Spld, V_{STPD}	Percent Isokinetic Sampling
1	A	83.82	28.85	1.53	101	76.63	100
	B	83.45	28.85	1.58	96	76.98	92
	C	149.30	28.85	8.49	100	139.09	77 (b)
	D(c)						
2	A	83.81	28.91	1.59	94	77.71	101
	B	74.97	28.91	1.34	91	69.81	92
	C	83.70	28.91	1.64	82	79.39	103
	D	82.31	28.91	1.57	86	77.45	99
3	A	170.51	28.84	7.00	103	157.42	94
	B(d)						
	C	168.42	28.44	8.30	83	161.62	92
	D(d)						
4	A	174.36	28.75	8.16	87	165.53	92
	B(e)						
	C	176.10	28.75	8.73	95	165.16	91
	D	171.25	28.75	7.38	91	161.14	88

TABLE 13. (Continued)

Test(a) Number	Laboratory	Gas Meter Volume, V_m	Barometric Pressure, P_b	Pressure @ Meter P_m^* (avg)	Temperature @ Meter T_m (avg)	Gas Volume Spld, V_{STPD}	Percent Isokinetic Sampling
5	A	185.76	28.75	9.65	102	174.53	95
	B	172.77	28.75	7.56	94	161.67	85
	C	179.30	28.75	9.60	100	166.93	90
	D	175.35	28.75	7.62	97	163.32	89
6	A	157.03	28.97	6.21	95	147.29	94
	B	165.24	28.97	6.69	111	150.86	88
	C	162.68	28.97	7.14	99	152.01	93
	D	165.75	28.97	6.81	104	153.30	91
7	A	159.37	28.70	6.11	93	148.61	96
	B	161.07	28.70	6.31	98	149.54	88
	C	161.00	28.70	6.61	102	148.04	95
	D	163.35	28.70	6.83	98	151.31	92
8	A	78.32	28.75	1.38	88	72.96	101
	B	168.43	28.75	6.80	98	156.38	92
	C	78.45	28.75	1.43	81	74.13	103
	D	165.71	28.75	6.96	87	156.90	94

(a) Duration of each test was 120 minutes.
(b) Sampling rate limited by pressure drop in sampling train; unable to maintain isokinetic sampling rate.
(c) Filter box heater burned out during test.
(d) Glass probe liner broke during test.
(e) Equipment malfunction, laboratory did not complete test.

TABLE 14. SITE III PARTICULATE AND COLLECTED RESIDUE SAMPLING DATA

Test(a) Number	Laboratory	Gas Meter Volume, V_m	Barometric Pressure, P_b	Pressure @ Meter, P_m^*(avg)	Temperature @ Meter, T_m(avg)	Gas Volume Spld, V_{STPD}	Percent Isokinetic Sampling
1	A	73.99	28.97	1.40	55	73.96	72 (b)
	B	124.35	28.97	3.97	86	117.87	111
	C	104.80	28.97	3.00	77	100.83	95
	D	101.22	28.97	2.27	60	100.46	95
2	A	98.44	29.24	2.47	56	99.27	98
	B	123.23	29.24	3.95	88	117.44	111
	C	105.62	29.24	2.82	75	102.90	100
	D	95.06	29.24	2.09	58	95.47	93
3	A	92.25	29.26	2.30	55	93.23	94
	B	115.95	29.26	3.57	88	110.54	111
	C	100.87	29.26	2.62	81	97.20	98
	D	96.27	29.26	2.18	62	96.04	97
4	A	95.36	29.43	2.18	57	96.61	94
	B	125.22	29.43	3.97	95	118.68	115
	C	108.16	29.43	2.98	81	104.92	101
	D	100.57	29.43	2.23	61	101.11	98

TABLE 14. (Continued)

Test(a) Number	Laboratory	Gas Meter Volume, V_m	Barometric Pressure, P_b	Pressure @ Meter, P^*_m(avg)	Temperature @ Meter T_m(avg)	Gas Volume Spld, V_{STPD}	Percent isokinetic Sampling
5	A	95.37	29.35	2.30	64	95.11	92
	B	125.25	29.35	3.83	99	117.56	114
	C	109.00	29.35	2.99	91	103.54	99
	D	101.67	29.35	2.24	67	100.78	99
6	A	89.11	28.52	2.01	69	85.41	81
	B (c)						
	C	113.23	28.52	3.01	94	104.12	100
	D	108.70	28.52	2.52	73	103.61	98
7	A	94.69	28.50	2.20	73	90.10	86
	B (c)						
	C	112.34	28.50	3.12	97	102.56	98
	D	107.29	28.50	2.43	74	101.98	98
8	A	98.06	28.99	2.32	75	94.53	87
	B	129.48	28.99	4.19	91	121.94	115
	C	112.69	28.99	3.12	92	105.58	98
	D	104.64	28.99	2.37	70	101.91	95

TABLE 14. (Continued)

Test(a) Number	Laboratory	Gas Meter Volume, V_m	Barometric Pressure, P_b	Pressure @ Meter, P^*_m(avg)	Temperature @ Meter T_m (avg)	Gas Volume Spld, V_{STPD}	Percent Isokinetic Sampling
9	A	98.68	28.99	2.34	80	94.33	89
	B	127.68	28.99	4.11	98	118.70	113
	C	109.65	28.99	3.12	102	100.91	94
	D	105.67	28.99	2.28	77	101.55	97
10	A (d)						
	B	123.66	29.15	4.04	93	116.54	111
	C	109.36	29.15	2.93	94	102.70	99
	D	105.26	29.15	2.39	72	102.70	98
11 (e)	A	75.11	29.04	2.40	84	71.38	91
	B	96.57	29.04	4.17	97	89.51	114
	C	79.29	29.04	3.00	106	72.56	93
	D	79.69	29.04	2.42	80	76.31	97
12	A	80.77	29.07	1.55	77	77.64	95
	B	99.59	29.07	2.37	94	93.00	113
	C	86.11	29.07	1.84	95	80.20	100
	D	81.96	29.07	1.41	79	78.52	96

TABLE 14. (Continued)

Test[a] Number	Laboratory	Gas Meter Volume, V_m	Barometric Pressure, P_b	Pressure @ Meter T_m (avg)	Temperature @ Meter T_m (avg)	Gas Volume Spld, V_{STPD}	Percent Isokinetic Sampling
13	A	84.31	29.02	1.65	85	79.78	93
	B[f]						
	C	85.52	29.02	2.07	102	78.57	94
	D	89.88	29.02	1.72	83	85.39	101
14	A	93.52	29.10	2.18	81	89.57	86
	B	110.01	29.10	3.42	107	100.76	96
	C	112.88	29.10	3.15	99	104.84	100
	D	109.42	29.10	2.59	80	105.05	98
15	A	98.40	29.10	2.32	86	93.33	89
	B	131.39	29.10	4.24	116	118.75	111
	C	115.11	29.10	3.25	106	105.61	98
	D	107.86	29.10	2.48	81	103.33	99

(a) Duration of each test was 120 minutes except Test 11 which was 90 minutes.
(b) Sampling rate limited by pressure drop in sampling train; unable to maintain isokinetic sampling rate.
(c) Equipment malfunction, laboratory unable to participate in test.
(d) Thimble ruptured during test, laboratory unable to complete test due to high pressure drop in sampling system.
(e) Generating unit shut-down; test terminated after sampling at three ports.
(f) Leak developed in sampling train during test.

TABLE 15. SITE IV PARTICULATE AND COLLECTED RESIDUE SAMPLING DATA

Test(a) Number	Laboratory(b)	Gas Meter Volume, V_m	Barometric Pressure, P_b	Pressure @ Meter P_m^*(avg)	Temperature @ Meter T_m (avg)	Gas Volume Spld, V_{STPD}	Percent Isokinetic Sampling
1	A	47.07	29.46	3.23	81	45.73	89
	B	38.35	29.46	2.13	98	36.02	69(c)
	C	53.81	29.46	4.90	91	51.55	89
	D(d)						
2	A	32.80	29.42	1.43	80	31.74	109
	B	29.86	29.42	1.62	101	27.82	90
	C	31.86	29.42	1.50	88	30.39	95
	D(d)						
3	A	32.89	29.38	1.45	73	32.20	106
	B	32.68	29.38	1.56	92	30.91	101
	C	31.71	29.38	1.50	80	30.65	95
	D	25.99	29.38	1.10	79	25.15	96
4	A	31.63	29.39	1.33	72	31.03	105
	B	32.65	29.39	1.68	96	30.68	98
	C	31.23	29.39	1.50	78	30.31	94
	D	31.55	29.39	1.56	78	30.62	97
5	A	32.63	29.42	1.45	70	32.20	110
	B	33.16	29.42	1.65	99	31.01	102
	C	30.44	29.42	1.40	77	29.62	96
	D	31.33	29.42	1.50	78	30.44	98

TABLE 15. (Continued)

Test Number (a)	Laboratory (b)	Gas Meter Volume, V_m	Barometric Pressure, P_b	Pressure @ Meter, P_m^*(avg)	Temperature @ Meter, T_m(avg)	Gas Volume Spld, V_{STPD}	Percent Isokinetic Sampling
6	A	29.52	29.45	1.20	66	29.34	110
	B	33.73	29.45	1.73	90	32.11	102
	C	31.88	29.45	1.60	81	30.84	94
	D	30.04	29.45	1.47	74	29.43	92
7	A	32.76	29.55	1.49	65	32.75	110
	B	33.07	29.55	1.67	87	31.75	101
	C	30.62	29.55	1.40	74	30.10	95
	D	25.45	29.55	1.08	75	24.95	78
8	A	32.71	29.56	1.45	73	32.22	109
	B	33.32	29.56	1.83	99	31.33	101
	C	30.35	29.56	1.40	86	29.18	95
	D	31.77	29.56	1.60	87	30.50	96
9	A	27.27	29.33	1.03	78	26.38	107
	B	27.38	29.33	1.11	82	28.78	104
	C	26.06	29.33	2.00	83	25.04	98
	D	31.27	29.33	1.45	106	26.30	100
10	A	26.36	29.32	0.94	87	25.07	107
	B	27.60	29.32	1.09	89	28.56	103
	C	25.97	29.32	1.00	88	24.66	97
	D	31.04	29.32	1.40	106	26.16	101

TABLE 15. (Continued)

Test Number[a]	Laboratory[b]	Gas Meter Volume, V_m	Barometric Pressure, P_b	Pressure @ Meter, P^*_m(avg)	Temperature @ Meter, T_m (avg)	Gas Volume Spld, V_{STPD}	Percent Isokinetic Sampling
11	A	26.66	29.28	1.10	91	25.14	109
	B	26.81	29.28	1.04	93	28.63	104
	C	26.51	29.28	1.00	94	24.86	99
	D	31.21	29.28	1.39	107	25.19	99
12	A	26.29	29.26	0.92	84	25.08	106
	B	27.52	29.26	1.07	87	30.43	106
	C	26.52	29.26	1.00	89	25.08	97
	D	32.55	29.26	1.44	96	26.13	96
13	A	28.63	29.23	1.01	75	27.75	109
	B	28.41	29.23	1.21	78	31.05	105
	C	27.49	29.23	1.10	82	26.31	98
	D	32.99	29.23	1.62	92	27.40	99
14	A	28.35	29.25	1.09	76	27.48	109
	B	29.27	29.25	1.24	78	30.69	105
	C	27.92	29.25	1.10	85	26.60	99
	D	32.83	29.25	1.57	96	28.25	102

(a) Duration of each test was 48 minutes.
(b) Participating laboratory group for Tests 1 through 8 is different than for Test 9 through 14.
(c) Sampling rate limited by pressure drop in sampling train; unable to maintain isokinetic condition.
(d) Equipment malfunction, did not complete test.

The percent isokinetic sampling is calculated using the equation given in the Federal Register(13). In the statistical analysis, the results from tests in which the deviation from isokinetic sampling was greater than 15 percentage points (i.e. outside the range of 85 to 115 percent) were arbitrarily excluded. The test method does not include any criteria for rejection of data due to anisokinetic sampling.

It may be noted that in the initial tests at several sites, some laboratories were unable to sample at an isokinetic rate. This condition occurred because the pressure drop in the sampling train limited the sampling rate. The high pressure drop was due to the sampling train components (two filters and four impingers) and frequently to plugging of the desiccant trap when Drierite® was used. Selection of a smaller diameter nozzle and/or use of silica gel as the desiccant eliminated the problem.

Particulate Sample Weights and Final Results. Tables 16 through 19 present particulate sample weight data and the final results reported as particulate concentration and emission rate. The tables give the weight of particulates caught by the in-stack filter (Alundum® thimble or flat filter), the probe, and the backup flat filter. The probe catch was collected by rinsing the probe and nozzle, first with acetone, then with distilled water. The total weight is determined from the sum of particulate matter collected in each of the sampling train components. At Site II where the particulate loadings were relatively low, negative values were obtained for some sample weights. These values have been reported to indicate the magnitude of errors in the mass determination. The negative values were not included in the calculation of total weight.

The final results are presented in particulate concentration (grains/SCFD) and particulate emission rate (lbs/hr) calculated as described in Paragraphs 8.3 and 8.4, respectively, of the test method. It should be reiterated that in calculating the sample volume, V_{STPD}, the term V_m volume of water vapor remaining in the meter volume was omitted since the gas was metered at dry conditions.

TABLE 16. SITE I PARTICULATE WEIGHT DATA AND FINAL RESULTS

Test Number	Laboratory	Particulate Sample Weights, mgs.					Particulate Conc., grains/SCFD	Emission Rate, lbs/hr.
			Nozzle/Probe Wash					
		Thimble	Acetone	Water	Backup Filter	Total Particulates		
1(a)	A							
	B							
	C							
	D							
2	A(b)							
	B	48.1	2.9	10.0	1.2	62.2	0.0152	17.93
	C	34.2	4.9	24.4	0.0	63.5	0.0147	16.70
	D	53.4	12.5	21.7	1.5	89.1	0.0125	14.99
3	A	29.0	15.0	(c)	8.0	52.0	0.0111(d)	13.53(d)
	B	31.8	<0.1	9.0	1.5	42.3	0.0106	12.04
	C	37.6	2.3	19.3	1.0	60.2	0.0138	15.62
	D	53.0	10.0	21.7	2.8	87.5	0.0124	13.90
4	A	20.0	8.0	(c)	17.0	45.0	0.0059(d)	7.08(d)
	B	21.8	<0.1	14.3	1.3	37.3	0.0087	10.60
	C	24.8	4.3	12.0	0.0	41.4	0.0093	10.84
	D	42.2	5.3	13.9	1.5	62.9	0.0084	9.55
5	A	28.0	8.0	(c)	1.7	53.0	0.0069(d)	8.19(d)
	B	35.2	<0.1	12.6	1.3	49.1	0.0118	13.74
	C	34.1	1.8	21.1	0.0	56.9	0.0134	14.92
	D	65.1	8.1	18.2	1.9	93.3	0.0123	14.17
6	A	35.0	19.0	(c)	28.0	82.0	0.0106(d)	12.95(d)
	B	27.2	<0.1	11.1	1.6	39.9	0.0095	11.61
	C	35.0	4.0	17.2	0.4	56.6	0.0131	15.08
	D	60.3	8.6	23.1	2.9	94.9	0.0123	14.41
7	A	12.0	22.0	(c)	48.0	82.0	0.0107(d)	12.90(d)
	B	56.0	<0.1	13.4	1.5	70.9	0.0169	20.61
	C	52.0	1.6	16.1	0.1	69.8	0.0162	18.51
	D	69.8	8.1	32.8	2.1	112.8	0.0150	17.87

(a) Test aborted due to equipment failure by two laboratories.
(b) Filter box overheated. Residue deposited on filter.
(c) Laboratory did not wash probe and nozzle with water.
(d) Data excluded from statistical analysis because water wash of nozzle and probe was omitted.

TABLE 17. SITE II PARTICULATE WEIGHT DATA AND FINAL RESULTS

Test Number	Laboratory	Particulate Sample Weights, mgs.					Particulate Conc., grains/SCFD	Emission Rate, lbs/hr.
		Flat Filter	Nozzle/Probe Wash Acetone	Nozzle/Probe Wash Water	Backup Filter	Total Particulates		
1	A	2.3	45.8	13.5	0.8	62.4	0.0140(a)	21.13(a)
	B	-3.7	3.6	7.0	-1.0	10.6	0.0021	3.30
	C	4.3	4.7	2.9	-1.5	11.9	0.0013(b)	2.90(b)
	D(c)							
2	A	2.5	10.0	8.1	0.7	21.3	0.0045	6.77(a)
	B	1.4	4.5	3.0	0	8.9	0.0020	2.96
	C	2.7	5.0	2.2	-0.6	9.9	0.0019	2.92
	D	2.89	0.1	2.6	0.17	5.76	0.0011	1.77
3	A	5.5	10.3	6.4	0.8	23.0	0.0025	3.67
	B(d)							
	C	6.0	1.9	1.8	0.2	9.9	0.0009	1.46
	D(d)							
4	A	1.1	11.7	5.0	0.4	18.2	0.0019(a)	3.04(a)
	B(e)							
	C	2.6	3.4	1.4	-2.2	7.4	0.0007	1.10
	D	2.26	3.9	2.5	-0.19	8.66	0.0008	1.33
5	A	3.2	8.1	5.3	0.4	17.0	0.0017	2.74
	B	2.4	8.2	2.5	-1.6	13.1	0.0013	2.13
	C	3.2	3.5	1.0	0.0	7.7	0.0007	1.15
	D	2.85	3.2	2.8	-0.29	8.85	0.0008	1.34
6	A	6.0	10.2	6.2	0.4	22.8	0.0027	3.71
	B	5.6	2.3	6.3	1.5	15.7	0.0016	2.47
	C	6.9	3.1	0.9	-1.7	10.9	0.0011	1.59
	D	7.43	3.2	1.8	0.43	12.86	0.0013	1.92
7	A	5.1	8.0	6.0	-0.7	19.1	0.0022(a)	3.04(a)
	B	1.4	5.0	4.2	1.3	11.9	0.0012	1.86
	C	5.2	3.8	1.1	-1.0	10.1	0.0011	1.44
	D	4.93	3.4	1.9	0.02	10.25	0.0010	1.50
8	A	(f)	4.5	(f)	2.1	6.6	0.0026(f)	3.86(f)
	B	7.7	8.5	2.5	2.2	20.9	0.0021	3.13
	C	(f)	4.6	(f)	0.1	4.7	0.0010(f)	1.49(f)
	D	5.47	0.8	1.0	-0.01	7.27	0.0007	1.04

(a) Excluded as outlying data based on Dixon's Criterion

(b) Data excluded from statistical analysis because of departure from isokinetic sampling.

(c) Filter box heater burned out during test.

(d) Glass probe liner broke during test.

(e) Equipment malfunction. Team did not participate in this test.

(f) EPA Test Method 5 used. Data not included in statistical analysis.

TABLE 18. SITE III PARTICULATE WEIGHT DATA AND FINAL RESULTS

Test Number	Laboratory	Particulate Sample Weights, mgs.					Particulate Conc., grains/SCFD	Emission Rate, lbs/hr.
		Thimble	Nozzle/Probe Wash Acetone	Nozzle/Probe Wash Water	Backup Filter	Total Particulates		
1	A	406.5	55.9	49.0	49.8	561.2	0.1169(a)	3112(a)
	B	731.8	17.0	32.9	12.1	793.8	0.1037	2874
	C	582.0	10.1	62.8	51.5	707.3	0.1080	2981
	D	629.6	54.9	57.8	23.0	765.3	0.1173	3233
2	A	503.9	12.1	23.1	25.7	564.8	0.0876	2314
	B	689.4	17.2	42.1	7.9	756.6	0.0992	2731
	C	546.8	41.9	119.4	47.2	755.3	0.1130	3021
	D	360.1	64.8	60.6	81.5	567.0	0.0915	2441
3	A	396.0	21.9	35.4	70.2	523.5	0.0865	2235
	B	706.6	18.4	51.0	12.2	788.2	0.1098	2847
	C	520.0	26.4	170.0	48.0	764.4	0.1211	3183
	D	524.8	42.8	49.3	29.0	616.8	0.0989	2552
4	A	554.4	41.8	18.0	67.4	681.6	0.1087	2894
	B	822.6	16.5	38.7	9.7	887.5	0.1152	3099
	C	595.3	32.4	135.1	31.8	794.6	0.1166	3160
	D	596.6	49.7	145.3	29.0	820.6	0.1250	3346
5	A	581.0	26.7	11.9	34.6	654.2	0.1059	2837
	B	681.0	17.4	86.3	6.1	790.8	0.1036	2778
	C	558.9	36.1	106.1	25.3	726.4	0.1080	2953
	D	428.0	165.4	38.5	82.8	710.7	0.1086	2880
6	A	749.6	167.9	19.7	16.9	954.1	0.1720(a)	4740(a)
	B(b)							
	C	657.8	33.2	117.9	26.2	835.1	0.1235	3353
	D	651.9	197.3	30.5	62.2	941.9	0.1400	3851
7	A	698.1	10.8	15.2	18.1	742.2	0.1269	3349
	B(b)							
	C	638.5	31.3	200.3	19.4	889.5	0.1336	3643
	D	527.1	91.8	82.7	76.1	777.7	0.1174	3179
8	A	591.0	7.5	9.6	17.6	625.7	0.1019	2874
	B	796.1	19.0	43.7	21.5	880.3	0.1112	3074
	C	586.3	58.7	141.5	20.8	807.3	0.1178	3286
	D	641.8	43.5	74.0	29.8	789.1	0.1192	3324

TABLE 18. (Continued)

Test Number	Laboratory	Particulate Sample Weights, mgs.					Particulate Conc.. grains/SCFD	Emission Rate, lbs/hr.
			Nozzle/Probe Wash		Backup	Total		
		Thimble	Acetone	Water	Filter	Particulates		
9	A	651.5	11.2	10.7	18.0	691.4	0.1129	3121
	B	820.5	13.3	37.9	8.1	879.8	0.1141	3108
	C	583.5	19.6	49.8	20.8	673.7	0.1028	2860
	D	376.0	119.3	71.6	107.0	673.9	0.1022	2787
10	A(b)							
	B	828.0	12.0	102.9	42.0	984.9	0.1301	3569
	C	647.3	72.4	156.9	35.3	911.9	0.1367	3706
	D	676.5	26.5	49.4	23.8	776.2	0.1164	3165
11	A	380.1	29.7	33.6	57.4	500.8	0.1080	2953
	B	580.5	15.4	58.6	9.9	664.4	0.1143	3102
	C	453.7	46.6	130.0	25.9	656.2	0.1393	3761
	D	461.6	20.1	22.7	18.4	522.8	0.1055	2879
12	A	1,461.0	11.8	42.5	16.2	1,531.5	0.3038	6447
	B	1,872.3	15.8	25.4	8.9	1,922.4	0.3183	6802
	C	532.7	90.8	74.6	16.6	714.7	0.1372(d)	2871(d)
	D	1,416.3	125.5	14.3	15.6	1,571.6	0.3082	6549
13	A	736.9	42.1	17.8	70.0	866.8	0.1673	3753
	B(e)							
	C	745.4	87.7	85.5	25.4	944.0	0.1850	4003
	D	780.0	47.1	26.6	19.4	873.1	0.1575	3473
14	A	1,203.5	16.2	19.1	13.0	1,251.8	0.2152	5852
	B	1,379.2	14.6	45.1	15.3	1,454.2	0.2223	6051
	C	1,062.6	4.7	89.6	23.6	1,180.5	0.1734	4751
	D	1,292.3	25.5	17.9	15.3	1,351.0	0.1980	5519
15	A	716.1	50.1	42.0	99.3	907.5	0.1497	4079
	B	1,034.7	31.4	58.6	75.8	1,200.5	0.1557	4330
	C	843.9	54.0	75.4	29.9	1,003.2	0.1463	4108
	D	957.2	18.6	23.0	18.7	1,017.5	0.1516	4138

(a) Data excluded from statistical analysis because of anisokinetic sampling.
(b) Leak in probe. Team unable to participate.
(c) Thimble broke during test.
(d) Excluded as outlying data based on Dixon's Criterion.
(e) Leak developed in sampling train during test.

TABLE 19. SITE IV PARTICULATE WEIGHT DATA AND FINAL RESULTS

Test Number	Laboratory[(a)]	Particulate Sample Weights, mgs.					Particulate Conc., grains/SCFD	Emission Rate, lbs/hr
			Nozzle/Probe Wash		Backup	Total		
		Thimble	Acetone	Water	Filter	Particulates		
1	A	15,005.6	104.9	25.6	1.6	15,137.7	5.098	1790
	B	13,976.8	193.8	37.0	127.6	14,326.2	6.125(b)	2082(b)
	C	16,056.8	21.26	9.97	7.08	16,095.1	4.809	1803
	D(c)							
2	A	8,976.5	62.4	20.0	10.3	9,069.2	4.400	1495
	B	9,385.5	14.0	13.5	5.2	9,418.2	5.214	1883
	C	8,336.0	15.60	8.84	6.07	8,367.4	4.240	1566
	D(c)							
3	A	16,804.8	185.8	31.2	53.7	17,075.5	8.166	2861
	B	15,257.1	1535.1	93.2	746.9	17,650.3	8.795	3124
	C	16,141.2	15.06	12.64	5.04	16,173.9	8.126	3020
	D	13,996.1	1277.9	139.6	195.8	15,609.24	9.559	2903
4	A	13,193.6	1733.4	51.9	611.9	15,590.8	7.738	2616
	B	14,869.0	591.5	87.9	392.1	15,940.4	8.002	2882
	C	14,496.3	32.32	7.44	5.21	14,541.3	7.388	2745
	D	13,929.9	660.8	31.8	0.3	14,622.8	7.354	2672
5	A	15,947.9	114.5	27.4	23.0	16,112.3	7.707	2612
	B	17,021.6	35.8	11.6	3.8	17,072.8	8.478	2989
	C	15,009.6	40.76	48.9	4.66	15,059.9	7.830	2792
	D	11,239.9	821.8	172.4	379.9	12,632.0	6.390	2302
6	A	11,134.9	24.8	13.5	1.0	11,174.2	5.864	1814
	B	11,944.7	176.4	93.3	94.9	12,314.3	5.907	2152
	C	11,450.3	44.33	5.84	5.83	11,506.4	5.746	2179
	D	7,915.5	1333.6	145.3	1227.8	10,622.2	5.558	2064
7	A	18,942.8	21.9	5.9	1.6	18,972.2	8.920	3088
	B	20,437.6	67.4	17.9	4.7	20,527.3	9.956	3644
	C	17,489.6	98.53	9.90	5.01	17,601.0	9.006	3303
	D	10,783.0	2421.1	153.6	3334.4	16,692.1	10.305	3831
8	A	28,512.0	20.9	6.0	0.7	28,539.6	13.641	4693
	B	29,748.7	542.1	50.8	4.8	30,346.4	14.917	5362
	C	25,720.1	52.66	15.61	3.75	25,792.2	13.610	4817
	D	24,592.6	1483.5	91.0	8.9	26,176.0	13.215	4873
9	A	6,556.9	34.4	8.4	1.0	6,600.7	3.854	1095
	B	6,143.5	477.7	18.6	8.0	6,647.8	3.893	1184
	C	5,824.1	228.0	6.71	8.03	5,861.7	3.605	1069
	D	7,171.2	172.7	31.5	6.6	7,382.0	3.950	1097

TABLE 19. (Continued)

Test Number	Laboratory[a]	Particulate Sample Weights, mgs.					Particulate Conc., grains/SCFD	Emission Rate, lbs/hr
		Thimble	Nozzle/Probe Wash Acetone	Nozzle/Probe Wash Water	Backup Filter	Total Particulates		
10	A	5,797.0	80.9	13.9	2.7	5,894.5	3.621	983
	B	5,557.4	239.6	13.6	2.0	5,812.6	3.422	1025
	C	5,176.0	34.87	7.13	5.09	5,223.0	3.262	961
	D	6,563.5	53.0	40.7	5.9	6,663.1	3.593	1005
11	A	5,711.4	30.5	4.9	0.7	5,747.7	3.521	957
	B	5,548.1	83.2	20.4	6.9	5,648.6	3.459	1023
	C	5,170.1	14.66	3.88	7.06	5,195.7	3.218	937
	D	6,548.5	26.1	25.4	7.5	6,607.5	3.554	980
12	A	3,861.9	78.6	7.6	0.7	3,948.8	2.425	673
	B	3,762.3	209.5	24.2	0	3,996.0	2.355	737
	C	3,380.9	46.87	8.70	6.68	3,443.2	2.114	633
	D	4,615.6	35.4	20.8	7.3	4,679.1	2.368	686
13	A	4,920.3	44.6	12.9	1.4	4,979.2	2.763	826
	B	4,426.6	46.4	17.3	0.7	4,491.0	2.524	808
	C	4,027.2	52.20	6.70	5.98	4,092.1	2.395	741
	D	5,263.8	70.1	50.6	7.9	5,392.4	2.675	794
14	A	1,565.5	39.6	13.6	1.6	1,612.3	0.904	267
	B	1,481.4	36.5	13.7	3.2	1,534.8	0.837	269
	C	1,391.5	21.77	10.92	6.41	1,430.6	0.828	257
	D	1,714.6	42.9	30.0	7.5	1,795.0	0.900	265

(a) Participating laboratory group for Test 1 through 8 is different than for Tests 9 through 14.

(b) Data excluded from statistical analysis because of anisokinetic sampling.

(c) Equipment malfunction, unable to complete tests.

The final results given in Tables 16 through 19 were calculated by computer using the input data supplied by the cooperating laboratories. The discrepancies which were observed between the computer-calculated particulate concentration results and those reported by the cooperating laboratories appear to be the result of using the term V_w in calculating the sample volume. The inclusion of this term results in slightly higher values for particulate concentration. Significant differences were noted between computer-calculated and cooperator-reported values for emission rates. The errors were evidently due to misinterpretation of the equations used in the calculations or the fact that calculation of one of the terms, Q_{STPD}, used in calculation of the emission rate is not given in the method.

The test data were examined for outlying observations using Dixon's Criterion(14) and a total of nine determinations of particulate concentration and emission rate were excluded from statistical analysis on this basis. Twenty-four of a total of 176 determinations did not produce usable results due to equipment malfunctions or operational departures from the test method. Test data obtained at Site I by Laboratory D were included in statistical analysis. Although the laboratory used coarser porosity thimbles (RA98) which might have reduced filtration efficiency, any particulates passing through the thimble would be collected on the high efficiency backup filter. Actually, significantly higher backup filter catches are not observed with use of the RA98 thimble in this instance.

Analysis of Between-Laboratory Standard Error. The statistical analysis of the data by test is presented in Table 20. The table gives the following data for the tests at each site: the number of measurements per test, n; the mean particulate concentration or mean emission rate, m; the standard deviation of particulate concentration and emission rate determinations, σ, and the coefficient of variation, CV, in percent.

The standard deviation (σ) of the particulate concentration and emission rate determinations for each test was calculated by the equation:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (x_i - m)^2}{n-1}}$$

where m is the mean concentration or emission rate for the test, x_i is the particulate concentration or emission rate determined by the i^{th} laboratory and n is the number of measurements per test. As noted previously, the standard deviation in this case is an estimate of the between-laboratory standard error for each test.

TABLE 20. STATISTICAL ANALYSIS OF PARTICULATE CONCENTRATION AND EMISSION RATE DATA

Site	Test Number	Particulate Conc., grains/SCFD				Emission Rate, lbs/hr			
		n	mean, m	σ	CV, %	n	mean, m	σ	CV, %
I	2	3	0.0140	0.0017	12.1	3	16.54	1.48	8.9
	3	3	0.0123	0.0016	13.0	3	13.85	1.79	12.9
	4	3	0.0088	0.0005	5.7	3	10.33	0.69	6.7
	5	3	0.0125	0.0008	6.4	3	14.28	0.60	4.2
	6	3	0.0116	0.0019	16.4	3	13.70	1.84	13.4
	7	3	0.0160	0.0010	6.3	3	19.00	1.43	7.5
II	1	1	0.0021	(a)	(a)	1	3.30	(a)	(a)
	2	4	0.0024	0.0015	62.5	3	2.55	0.68	26.7
	3	2	0.0017	0.0011	64.7	2	2.57	1.56	60.7
	4	2	0.0008	0.0001	12.5	2	1.22	0.16	13.1
	5	4	0.0011	0.0005	45.5	4	1.84	0.73	39.7
	6	4	0.0016	0.0008	50.0	4	2.42	0.93	38.4
	7	3	0.0011	0.0001	9.1	3	1.60	0.23	14.4
	8	2	0.0014	0.0010	71.4	2	2.09	1.48	70.8
III	1	3	0.1097	0.0070	6.4	3	3029	184	6.1
	2	4	0.0978	0.0112	11.5	4	2626	315	12.0
	3	4	0.1041	0.0148	14.2	4	2692	386	14.3
	4	4	0.1164	0.0067	5.8	4	3125	186	6.0
	5	4	0.1065	0.0023	2.2	4	2862	74	2.6
	6	2	0.1318	0.0117	8.9	2	3602	352	9.8
	7	3	0.1260	0.0081	6.4	3	3424	233	6.8
	8	4	0.1125	0.0079	7.0	4	3140	208	6.6
	9	4	0.1080	0.0064	5.9	4	2969	171	5.8
	10	3	0.1277	0.0104	8.1	3	3480	281	8.1
	11	4	0.1168	0.0155	13.3	4	3174	402	12.7
	12	3	0.3101	0.0074	2.4	3	6599	183	2.8
	13	3	0.1699	0.0139	8.2	3	3743	265	7.1
	14	4	0.2022	0.0218	10.8	4	5543	572	10.3
	15	4	0.1508	0.0039	2.6	4	4164	113	2.7
IV	1	2	4.954	0.204	4.1	2	1797	9	0.5
	2	3	4.618	0.522	11.3	3	1648	207	12.6
	3	4	8.662	0.672	7.8	4	2977	119	4.0
	4	4	7.621	0.308	4.0	4	2729	115	4.2
	5	4	7.601	0.876	11.5	4	2674	292	10.9
	6	4	5.769	0.156	2.7	4	2052	166	8.1
	7	4	9.547	0.690	7.2	4	3467	334	9.6
	8	4	13.846	0.740	5.3	4	4936	294	6.0
	9	4	3.826	0.152	4.0	4	1111	50	4.5
	10	4	3.475	0.167	4.8	4	994	28	2.8
	11	4	3.438	0.152	4.4	4	975	37	3.8
	12	4	2.316	0.138	6.0	4	682	43	6.3
	13	4	2.614	0.157	6.0	4	792	37	4.7
	14	4	0.867	0.040	4.6	4	265	5	1.9

(a) Standard deviation and coefficient of variation was not computed; test included only one valid determination.

The coefficient of variation expressed in percent is calculated from the test means, m, and the standard deviation, σ, using the equation:

$$CV, \% = \frac{\sigma\ (100)}{m} \quad .$$

A summary of the test data by site is given in Table 21. The table presents the mean of the particulate concentration and emission rate determinations at each source and the mean coefficient of variation of the determinations. The standard deviations provide a measure of the variability about the mean coefficients of variation.

An expression for the relationship of between-laboratory standard error and particulate concentration is derived from the data shown in Figure 9. The figure is a scattergram which contains the estimates of the between-laboratory standard error for each test plotted versus the test mean of the particulate concentration for measurements made at Sites I, III, and IV.

A regression equation of the form $\hat{s} = a + bm$ was fitted to all the data points 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:

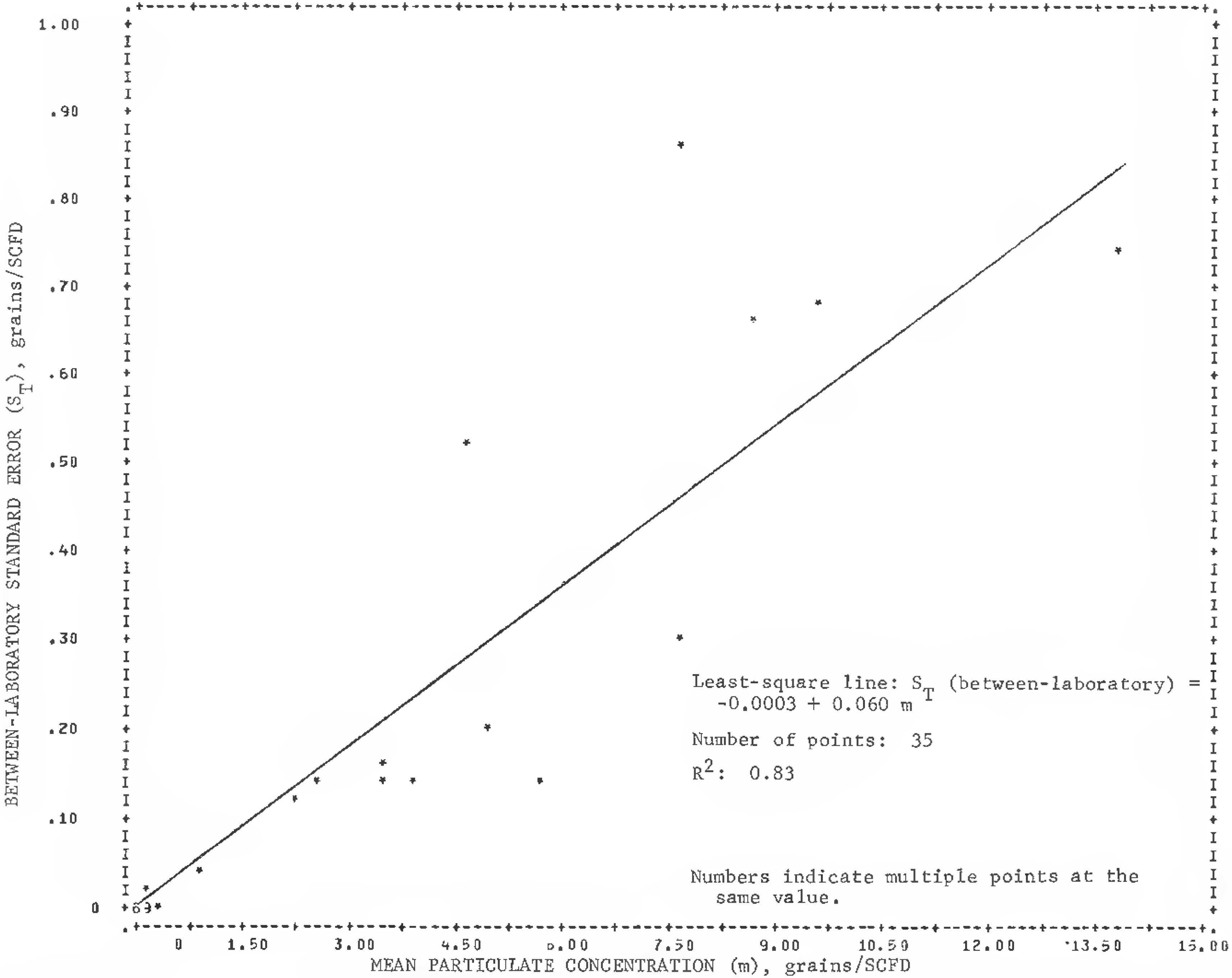
(1) The coordinates of the data points are averages, which are not always computed from the same number of observations;

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

The appropriate weighting formula is $W = f/\ (\beta\, m + \alpha)^2$, where W represents the weight, f denotes the number of degrees of freedom associated with the computed standard deviation S_T, 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.

TABLE 21. SUMMARY OF PARTICULATE CONCENTRATION AND EMISSION RATE DATA BY SITE

Site	Mean Particulate Concentration, grains/SCFD	Mean CV, %	Standard Deviation	Mean Emission Rate, lbs/hr.	Mean CV, %	Standard Deviation
I	0.013	10.0	4.5	14.6	8.9	3.6
II	0.0015	45.1	25.0	2.3	37.7	22.0
III	0.14	7.6	3.7	3571	7.6	3.6
IV	5.70	6.0	2.7	1946	5.7	3.5



Least-square line: S_T (between-laboratory) = -0.0003 + 0.060 m

Number of points: 35

R^2: 0.83

Numbers indicate multiple points at the same value.

FIGURE 9. SCATTERGRAM AND LEAST-SQUARES LINE RELATING BETWEEN-LABORATORY STANDARD ERROR TO MEAN PARTICULATE CONCENTRATION

The least-square fitting procedure yields the equation S_T (between-laboratory) = -0.0003 + 0.060m as the estimate of the true regression line. A line described by this equation is shown in Figure 9. The R^2 value of 0.83 indicates that the weighted regression from which the line was derived explains 83 percent of the total variation in the dependent variable about its mean. The dependent variable in the regression is the between-laboratory standard error of the particulate concentration measurements. The value of R^2 is indicative of a good fit for the regression analysis.

Based on the preceding analysis the equation S_T (between-laboratory) = -0.0003 + 0.060m provides an estimate of the between-laboratory standard error of the test method for determining particulate concentrations in the range of 0.008 to 14 grains/SCFD.

The relationship of between-laboratory standard error of emission rate measurements and mean emission rate was also determined using the Site I, III, and IV data. Using the previously described procedures, the equation S_T (between-laboratory) = 0.290 + 0.067m was derived from a regression of the form $\hat{s} = a + bm$ which was fitted to the data points shown in Figure 10 by the method of weighted least-squares. This equation was used to fit the line shown in the figure. The fitting procedure yields an R^2 value which indicates that the regression explains 77 percent of the total variation in the between-laboratory standard error about its mean. Again, the value of R^2 is indicative of a good fit for the regression analysis.

The equation, S_T (between-laboratory) = 0.290 + 0.067m, developed by the regression analysis provides an estimate of the between-laboratory standard error of the test method for determining emission rates in the range of 10 to 6800 lbs/hr.

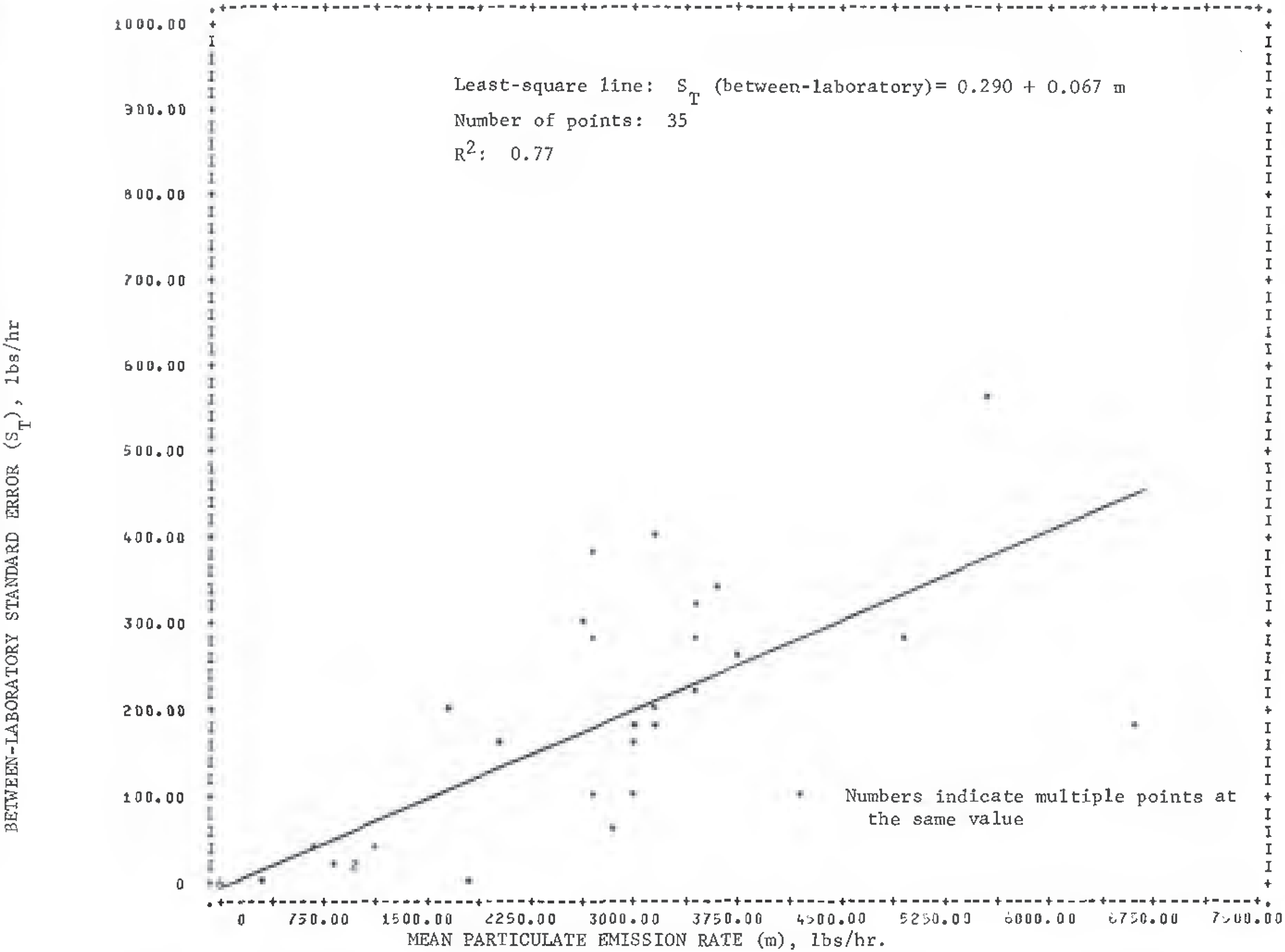


FIGURE 10. SCATTERGRAM AND LEAST-SQUARES LINE RELATING BETWEEN-LABORATORY STANDARD ERROR TO MEAN PARTICULATE EMISSION RATE

The observed between-laboratory standard error estimates in particulate concentration and emission rate determinations obtained from tests at Site II (foundry) are generally much higher than the values which would be predicted from expressions derived from the other site data. The Site II data reflect the errors inherent in recovery and weighing the small-sized samples obtained from sampling a well-controlled or low emission source.

Analysis of Collected Residue Data

Experimental Results

Flue Gas Measurements and Sampling Data. The test data presented in Tables 8 through 15 also apply to the collected residue sampling since the determinations were performed concurrently with the particulate measurements.

During the collected residue sampling the laboratories maintained a gas temperature of less than 70F at the outlet of the impinger train. An operating temperature range for collected residue sampling is not specified in the test method.

Collected Residue Sample Weights and Final Results. Tables 22 through 25 contain the collected residue sample weight data and the final results reported as the concentration of total collected residue in grains/SCFD. The collected residue concentration is computed from the sum of the weights of the extracted aqueous sample, the chloroform-ether extract, and the acetone wash residues.

In general, the data for all sites show considerable variation between laboratories in the acetone and organic residue weights and somewhat less variation in the weights of aqueous sample residues. In most cases, the variations result from ordered differences among the results obtained by the various laboratories.

In many instances, collected residue concentration determinations show wide deviation from the remainder of the test values. These variations appear to be partially connected with equipment options selected by some laboratories and/or with normal laboratory performance of the test procedure. For this reason, statistical tests for outliers was not applied to the collected residue data.

TABLE 22. SITE I COLLECTED RESIDUE SAMPLE WEIGHT DATA AND FINAL RESULTS

Test Number	Laboratory	Collected Residue Sample Weights, mgs.				Collected Residue, Grains/SCFD
		Impinger Solution	Acetone Wash	Organic Extract	Total Collected Residue	
1(a)	A					
	B					
	C					
	D					
2	A(b)					
	B	27.8	<0.1	5.4	33.2	0.0081
	C	10.6	17.4	45.9	73.9	0.0171
	D	20.1	33.4	35.7	89.1	0.0121
3	A	(b)	(b)	(b)	(b)	(b)
	B	28.6	0.1	3.5	30.4	0.0076
	C	15.9	12.3	75.3	103.5	0.0242
	D	19.2	10.7	6.3	36.2	0.0051
4	A	0	4.0	22.0	26.0	0.0034
	B	30.5	0.9	3.1	34.5	0.0081
	C	8.1	22.2	35.8	66.1	0.0149
	D	23.9	11.5	11.5	46.9	0.0063
5	A	0	3.0	26.0	29.0	0.0044
	B	25.5	<0.1	4.3	29.8	0.0071
	C	7.7	11.6	32.9	52.2	0.0123
	D	29.3	11.5	11.5	52.3	0.0069
6	A	0	0.0	19.0	19.0	0.0025
	B	22.7	<0.1	4.3	27.0	0.0064
	C	10.7	7.1	27.3	45.1	0.0104
	D	25.7	6.4	10.4	42.5	0.0055
7	A	0	7.0	11.0	18.0	0.0024
	B	18.8	<0.1	3.1	21.9	0.0052
	C	10.8	5.8	43.5	60.1	0.0139
	D	19.9	10.4	11.7	42.0	0.0056

(a) Test aborted due to equipment failure by two laboratories.

(b) Filter box overheated. Residue from filter holder deposited in impingers.

TABLE 23. SITE II COLLECTED RESIDUE SAMPLE WEIGHT DATA AND FINAL RESULTS

		Collected Residue Sample Weights, mgs.				Collected
Test Number	Laboratory	Impinger Solution	Acetone Wash	Organic Extract	Total Collected Residue	Residue Grains/SCFD
1	A	22.3	69.3	198.1	289.7	0.0649
	B	8.4	1.8	26.7	36.9	0.0074
	C	8.6	11.6	26.0	46.2	0.0051
	D(a)					
2	A	11.9	38.1	24.7	74.7	0.0157
	B	7.3	0.4	31.9	39.6	0.0088
	C	10.2	10.5	7.4	28.1	0.0055
	D	50.1	62.2	4.1	116.4	0.0231
3	A	29.7	61.7	26.5	117.9	0.0129
	B(b)					
	C	6.6	5.9	7.0	19.5	0.0019
	D(b)					
4	A	13.8	87.8	10.8	112.4	0.0120
	B(c)					
	C	4.0	8.8	2.7	15.5	0.0014
	D	10.0	26.4	2.2	38.6	0.0037
5	A	15.5	63.7	28.8	108.0	0.0092
	B	6.8	0.3	31.8	38.9	0.0033
	C	8.0	18.5	1.6	28.1	0.0026
	D	11.3	39.0	<0.1	50.3	0.0047
6	A	16.5	53.7	10.7	80.9	0.0096
	B	6.2	0.6	29.5	36.3	0.0038
	C	6.5	8.6	3.2	18.3	0.0019
	D	15.1	49.9	5.6	70.6	0.0071
7	A	18.8	137.1	23.2	179.1	0.0211
	B	10.8	0	2.1	12.9	0.0013
	C	6.0	11.5	1.4	18.9	0.0020
	D	31.4	27.6	0.8	59.8	0.0061
8	A (d)	27.8	42.9	6.5	77.2	0.0184
	B	6.2	7.3	26.5	40.0	0.0040
	C (d)	4.3	3.9	0.9	9.1	0.0019
	D	7.27	38.0	1.8	52.5	0.0052

(a) Filter box heater burned out during test.
(b) Glass probe liners broke during test.
(c) Equipment malfunction. Team did not participate in this test.
(d) Glass-lined sampling probes were used.

TABLE 24. SITE III COLLECTED RESIDUE SAMPLE WEIGHT DATA AND FINAL RESULTS

Test Number	Laboratory	Collected Residue Sample Weights, mgs.				Collected Residue Grains/SCFD
		Impinger Solution	Acetone Wash	Organic Extract	Total Collected Residue	
1	A	156.0	19.2	48.2	223.4	0.047
	B	152.6	46.4	9.2	208.2	0.027
	C	213.3	33.4	18.6	265.3	0.041
	D	65.4	7.9	13.2	86.5	0.013
2	A	242.3	46.1	88.6	377.0	0.058
	B	181.5	22.1	20.8	224.4	0.029
	C	169.0	21.4	17.5	207.9	0.031
	D	124.3	13.2	17.1	154.5	0.025
3	A	249.6	43.6	74.7	367.9	0.061
	B	128.2	77.5	6.7	212.4	0.030
	C	183.4	43.2	23.3	249.9	0.040
	D	114.5	19.5	14.1	148.1	0.024
4	A	250.8	45.8	70.8	367.4	0.059
	B	171.8	54.0	6.1	231.9	0.030
	C	289.6	26.6	31.1	347.3	0.051
	D	156.3	9.2	14.1	179.6	0.027
5	A	227.6	42.2	57.6	327.4	0.053
	B	158.8	71.6	10.2	240.6	0.032
	C	233.5	31.7	25.1	290.3	0.043
	D	174.8	21.8	17.3	213.9	0.033
6	A	161.7	40.9	22.2	224.8	0.041
	B (a)					
	C	214.5	28.2	10.9	250.6	0.038
	D	144.4	13.6	21.4	179.4	0.027
7	A	243.5	25.5	32.5	301.5	0.052
	B (a)					
	C	214.5	28.2	10.9	253.5	0.038
	D	139.5	7.2	14.3	161.0	0.024
8	A	240.1	33.1	34.0	307.2	0.050
	B	161.1	11.5	64.4	237.0	0.029
	C	262.9	51.9	22.7	337.5	0.049
	D	166.3	9.3	21.7	197.3	0.030

TABLE 24. (Continued)

Test Number	Laboratory	Collected Residue Sample Weights, mgs.				Collected Residue Grains/SCFD
		Impinger Solution	Acetone Wash	Organic Extract	Total Collected Residue	
9	A	255.2	31.1	28.5	313.8	0.051
	B	193.4	17.9	16.8	228.1	0.030
	C	262.9	51.9	22.7	331.5	0.052
	D	193.2	9.3	28.1	231.1	0.036
10	A(b)					
	B	170.4	26.6	11.0	203.0	0.028
	C	254.6	22.3	19.2	296.1	0.044
	D	227.4	10.1	22.7	260.2	0.039
11	A	165.9	30.9	14.1	210.9	0.046
	B	98.2	6.9	9.1	114.2	0.020
	C	180.2	28.9	22.1	231.1	0.049
	D	141.1	6.1	22.9	170.1	0.034
12	A	63.8	20.2	19.5	103.5	0.021
	B	63.4	8.8	7.8	80.0	0.013
	C	98.9	14.0	109.9	222.8	0.043
	D	59.2	3.7	16.2	79.1	0.016
13	A	96.2	49.3	30.6	176.1	0.034
	B(c)					
	C	109.6	25.7	89.5	224.8	0.044
	D	125.3	10.0	24.4	159.7	0.029
14	A	198.5	21.1	21.9	241.5	0.042
	B	118.0	11.0	12.6	141.6	0.022
	C	266.8	32.2	144.1	443.1	0.065
	D	179.7	10.5	14.3	204.4	0.030
15	A	216.0	31.0	42.0	287.0	0.048
	B	106.0	11.7	14.2	131.9	0.017
	C	226.7	36.1	94.6	357.3	0.052
	D	159.6	8.9	7.0	175.5	0.026

(a) Leak in probe, laboratory unable to participate in test.
(b) Thimble broke during test.
(c) Leak developed in sampling train during test.

TABLE 25. SITE IV COLLECTED RESIDUE SAMPLE WEIGHT DATA AND FINAL RESULTS

Test Number	Labor-(a) atory	Collected Residue Sample Weights, mgs. Impinger Solution	Acetone Wash	Organic Extract	Total Collected Residue	Collected Residue Grains/SCFD
1	A	49.3	9.5	21.2	80.0	0.027
	B	38.3	12.1	20.0	70.4	0.030
	C	82.01	22.82	29.69	134.52	0.040
	D(b)					
2	A	42.8	8.3	23.8	74.9	0.036
	B	65.2	23.9	8.0	97.1	0.054
	C	64.64	34.78	19.22	118.64	0.060
	D(b)					
3	A	141.2	3.9	8.0	153.1	0.073
	B	112.4	10.0	10.2	132.6	0.066
	C	121.03	24.56	13.23	158.82	0.080
	D	95.2	1.4	9.9	106.5	0.065
4	A	145.3	15.3	13.0	173.6	0.086
	B	116.8	12.5	11.0	140.3	0.070
	C	116.08	36.61	16.14	168.83	0.086
	D	122.3	2.1	14.8	139.2	0.070
5	A	133.7	8.1	6.8	148.6	0.071
	B	117.0	33.4(c)	19.6	170.0(c)	0.084(c)
	C	117.6	33.15	9.82	160.58	0.084
	D	280.4	8.4	68.7	357.5	0.181
6	A	98.4	7.1	9.1	114.6	0.060
	B	91.5	39.5(c)	16.9	147.9(c)	0.071(c)
	C	92.83	33.03	9.36	135.22	0.068
	D	104.7	0.7	2.2	107.6	0.056
7	A	143.3	7.3	10.7	161.3	0.076
	B	114.2	50.5(b)	17.9	182.6(c)	0.089(c)
	C	118.59	36.05	4.63	159.27	0.082
	D	102.6	3.0	7.5	113.1	0.070
8	A	172.9	10.0	10.2	193.1	0.092
	B	122.3	36.9(b)	21.1	180.3(c)	0.089(c)
	C	132.35	36.28	10.17	178.80	0.094
	D	143.4	10.3	86.0	239.7	0.121

TABLE 25. (Continued)

Test Number	Labor-atory[(a)]	Collected Residue Sample Weights, mgs. Impinger Solution	Acetone Wash	Organic Extract	Total Collected Residue	Collected Residue Grains/SCFD
9	A	38.4	8.5	11.3	58.2	0.034
	B	20.8	73.6	60.3	154.7	0.091
	C	30.38	47.99	16.43	94.8	0.058
	D	42.4	7.6	22.7	72.5	0.039
10	A	46.2	8.8	15.7	70.7	0.043
	B	23.8	8.2	51.8	83.8	0.049
	C	30.51	23.91	17.65	72.07	0.045
	D	47.2	10.0	9.0	66.2	0.036
11	A	34.6	7.8	6.6	49.0	0.030
	B	10.2	5.9	36.1	52.2	0.032
	C	17.60	30.03	17.64	65.27	0.040
	D	36.0	12.3	13.1	61.4	0.033
12	A	47.7	6.2	13.6	67.5	0.041
	B	9.7	76.9	24.1	110.7	0.065
	C	14.11	54.48	28.72	97.31	0.060
	D	11.6	8.9	10.3	30.8	0.016
13	A	46.3	8.6	17.1	72.0	0.040
	B	19.5	3.9	71.8	95.2	0.054
	C	33.95	34.89	16.45	85.29	0.050
	D	36.8	6.8	11.5	55.1	0.027
14	A	21.6	7.7	15.1	44.4	0.025
	B	2.0	43.0	70.0	115.0	0.063
	C	12.28	34.94	12.62	59.84	0.035
	D	28.6	5.1	10.8	44.5	0.022

(a) Participating laboratory group for Tests 1 through 8 is not same as for Test 9 through 14.

(b) Equipment malfunction, unable to complete tests.

(c) Did not use Teflon® inserts in sample bottle caps. Data excluded from statistical analysis.

Sulfate Analyses of Aqueous Sample Residues. A limited number of extracted aqueous sample residues from tests performed at Sites III (coal-fired power station) and IV (cement plant) were analyzed for sulfate content. The results, presented in Table 26, indicate that sulfate comprises a major weight fraction of the Site III residue samples (48 to 82 weight percent). However, in most samples the determinations of the sulfate content by the two laboratories vary considerably. The sulfate content of Site IV residue samples was determined to be in the range of 19 to 32 weight percent.

Analysis of Between-Laboratory Standard Error. Statistical analysis of the collected residue concentration data given in Tables 22 through 25 was performed to obtain estimates of between-laboratory standard error. Table 27 summarizes for each test the number of determinations, n, the mean of the collected residue determinations, m, the standard deviation (between-laboratory standard error) of the collected residue concentration determinations and the coefficient of variation, CV, in percent.

The collected residue concentration data summarized by site are presented in Table 28. The number of determinations, the mean of the collected residue determinations and the mean coefficients of variation are given. The standard deviations provide a measure of the variation about the mean concentration and the mean coefficient of variation. The standard deviations about the collected residue concentration means include process-related variations in source emissions.

The coefficient of variation means for the individual sites (sources) probably represent the best estimates of the between-laboratory standard error inherent in measurements made by the collected residue procedure. Considering the somewhat unique nature of measurement, derivation of an expression relating concentration and standard error based on data from four different types of sources does not seem appropriate.

TABLE 26. RESULTS OF SULFATE ANALYSIS OF IMPINGER RESIDUE SAMPLES FROM SELECTED TESTS AT SITES III AND IV

Site	Test Number	Laboratory	Impinger Water/ Condensate Residue Wt., mgs	Weight of Sulfate in Residue Sample, mg	Sulfate Content of Residue, Weight Percent
III	2	B	181.5	112.8	62.1
		D	124.3	90.9	73.1
	3	B	128.2	61.1(a)	47.6(a)
		D	114.5	92.7	81.0
	4	B	171.8	91.8	53.4
		D	156.3	123.1	78.8
	12	B	63.4	38.6	60.9
		D	59.2	42.0	70.9
	14	B	118.0	59.0(a)	50.0(a)
		D	179.7	132.8	73.4
	15	B	106.0	75.4	71.1
		D	159.6	115.9	72.6
IV	9	A	38.4	8.8	22.9
	10	A	46.2	11.3	24.5
	11	A	34.6	10.9	31.5
	13	A	46.3	9.0	19.4

(a) Analyzed for sulfate colorimetrically using barium chloroanilate method (ASTM D 3226-73T). All other samples analyzed gravimetrically by ASTM Method D 516.

TABLE 27. STATISTICAL ANALYSIS OF COLLECTED RESIDUE DATA

Site	Test Number	Collected Residue, gr/scfd			
		n	mean, m	σ	CV, %
I	2	3	0.0124	0.0045	36.3
	3	3	0.0123	0.0104	84.6
	4	4	0.0082	0.0049	59.8
	5	4	0.0077	0.0033	42.9
	6	4	0.0062	0.0033	53.2
	7	4	0.0068	0.0050	73.5
II	1	3	0.0258	0.0339	131.4
	2	4	0.0133	0.0078	58.6
	3	2	0.0074	0.0078	105.4
	4	3	0.0057	0.0056	98.2
	5	4	0.0055	0.0037	67.3
	6	4	0.0056	0.0034	60.7
	7	4	0.0076	0.0092	121.1
	8	4	0.0074	0.0075	101.4
III	1	4	0.0319	0.0148	46.4
	2	4	0.0358	0.0148	41.3
	3	4	0.0385	0.0163	42.3
	4	4	0.0418	0.0154	36.8
	5	4	0.0401	0.0101	25.2
	6	3	0.0349	0.0073	20.9
	7	3	0.0380	0.0136	35.8
	8	4	0.0395	0.0117	29.6
	9	4	0.0419	0.0112	26.7
	10	3	0.0370	0.0086	23.2
	11	4	0.0371	0.0133	35.8
	12	3	0.0164	0.0037	22.6
	13	3	0.0356	0.0078	21.9
	14	4	0.0396	0.0189	47.7
	15	4	0.0358	0.0168	46.9
IV	1	3	0.0323	0.0068	21.1
	2	3	0.0500	0.0125	25.0
	3	4	0.0710	0.0070	9.9
	4	4	0.0780	0.0092	11.8
	5	3	0.1120	0.0601	53.7
	6	3	0.0613	0.0061	10.0
	7	3	0.0760	0.0060	7.9
	8	3	0.1023	0.0162	15.8
	9	4	0.0553	0.0258	46.7
	10	4	0.0433	0.0054	12.5
	11	4	0.0338	0.0043	12.7
	12	4	0.0455	0.0222	48.8
	13	4	0.0428	0.0120	28.0
	14	4	0.0363	0.0187	51.5

TABLE 28. SUMMARY OF COLLECTED RESIDUE DATA BY SITE

Site/Source	Number of Determinations	Mean Concentration, grains/SCFD	Standard Deviation	Mean Coefficient of Variation, %	Standard Deviation
I Oil-fired power station	22	0.0086	0.0053	58.4	18.3
II Foundry	28	0.0095	0.0124	93.0	27.8
III Coal-fired power station	55	0.037	0.013	33.5	9.8
IV Cement plant	50	0.059	0.029	25.4	17.3

DISCUSSION AND CONCLUSIONS

Particulate Measurements

The results of this interlaboratory study provide estimates of the between-laboratory standard error inherent in stationary source particulate emission measurements performed with the proposed ASTM method. Potential applications of these precision estimates are discussed in Appendix B.

Based on regression analyses of data from sampling three different source emissions, between-laboratory standard error estimates for particulate concentration and emission rate determinations, expressed as the coefficient of variation, are 6.0 and 6.7 percent, respectively. The estimates were derived from determinations at coal-fired and oil-fired power generating stations and a cement plant where particulate emission concentrations ranged from 0.008 to 14 grains/SCFD and emission rates ranged from 10 to 6800 lbs/hr.

The mean coefficients of variation of particulate concentration and emission rate determinations of emissions from a foundry (ferrous metallurgy) were 45.1 and 37.7 percent, respectively. The mean particulate concentration and emission rate of this relatively low emission source were 0.0015 grains/SCFD and 2.3 lbs/hr. The greater variability in the determinations at the lower emission source results from errors in recovery, handling, and weighing the small particulate catches.

If necessary, the precision of particulate emission measurements from lower emission sources can probably be improved by increasing sample catch through a longer sampling time or a higher sampling rate, however, there are some practical and operational limitations. For example, a sampling time of approximately 10 hours would be required at Site II to collect the 11 milligram minimum filter catch recommended in the test method. Furthermore, negative weights obtained in several tests indicate that normal filter weight variations from handling may be several milligrams. Therefore, even if 11 milligrams of particulate material is collected, significant weight errors can occur. The handling error is not surprising since it is usually necessary to recover part of the in-stack flat-glass fiber filter by scraping it off the backing plate of the filter assembly. Also, a portion of the outer periphery of filter frequently sticks to the upper or lower portion of the filter body.

The alternate of sampling at a higher rate to achieve greater precision encounters operational limitations. The many components of the sampling system (two filters, four impingers, and desiccant trap) cause a pressure drop which usually restricts the sampling rate to about one cfm.

The caliber of the test data demonstrates that the proposed ASTM method is capable of producing particulate measurements with good precision even though it is frequently felt that the procedure employs fragile and complex sampling equipment and includes a multiplicity of operations. However, experience in this study has shown that the commercially available equipment can endure the test environment and that the equipment and procedural operations can be mastered by competent sampling teams.

Glassware can be handled without breakage if reasonable care is exercised but, in pretest preparations, an inordinate amount of time can be consumed in locating and correcting leaks in the 19 glass-to-glass connections (14 ball-joints and 5 taper).

The coupling of the probe and the filter/impinger box into one unit presents problems in sampling in locations with space restrictions. In these instances, disassembly may be required which introduces the possibility of sample loss or contamination from dust in the sampling area. The equipment options permitted by the proposed ASTM method can facilitate sampling, especially in tight areas.

The optional sampling arrangements were used at Site I by Laboratories A and B and at Site II by Laboratories A and D. Abnormally high probe residues were obtained by Laboratory A, Site II using a 7-foot heated Teflon® line between the probe and the filter/impinger box. Laboratory B at Site I used a similar arrangement without any apparent problems. The possibility of sample contamination suggests that sampling line materials should be carefully evaluated before use in particulate testing.

The operation of the sampling system using a nomograph permits rapid adjustments to isokinetic sampling conditions without undue demand on operator time. The control of the probe and filter box temperatures is performed essentially manually and requires frequent monitoring. Automation of the temperature control would relieve the operator from frequent temperature monitoring and frequent adjustments which may be required under certain conditions. Proper temperature control is very important, particularly in tests where sulfuric acid condensation can occur.

The study results do not yield a measure of accuracy, consequently, concerns of biases in the test method can not be completely allayed. Several investigators (15-18) have considered the problem of sulfuric acid condensation in particulate sampling systems and sulfur oxide reactions with various filter media or the particulate catch. These interactions would yield particulate measurements which are higher than the true value due to formation of sulfates.

Emissions from three sources sampled in this study contained sulfur oxides. Sites I, III, and IV contained SO_2 levels of 250, 2500, and 1500 ppm, respectively, and the respective SO_3 concentrations were about 5, 25 (estimated), and 10 ppm based on highly variable measurements. At all sites, sampling system temperatures, both probe and filter box, were maintained above the reported dew point of sulfuric acid. Examination of the test data does not provide any clear evidence that the determinations were affected by sulfur oxide condensation or reaction. However, potential errors from such reactions must be recognized in selection of filter media and operating conditions for particulate sampling of source emissions.

Another potential source of error could be the introduction of material from the stainless steel probe into the wash solutions used during sample recovery. A visual observation of probe wash solutions obtained in this study has indicated the presence of a ferric hydroxide precepetate presumably from the stainless steel probe. Similar results have been reported by Hillenbrand, et. al. (16). While the mass of the probe material may be small, relative to the total particulate catches obtained in this study, it could result in significant errors in the testing of low emission sources.

One solution to the problem is the use of an inert probe liner such as glass or Vycor®, however, fragility of the sampling probe is greatly increased. In some cases such as Site III where 15-foot probes were required, glass liners are not practical. A more favorable solution may be to locate the backup filter in-stack immediately behind the primary filter and, thereby, eliminate the need for sample collection from the probe and probe heating as well.

Examination of the backup filter catches indicates that significant thimble seal leakage occurred in several determinations e.g. Laboratory A, Site I and Laboratories A, B, and D, Site IV. Leakage may occur due to faulty gaskets or failure to sufficiently tighten the thimble in its holder. Fear of breakage may cause restraint in applying the proper pressure to seal the thimble. In other tests, it is unclear whether the backup filter catch results from thimble leakage or passage of very fine particulates, e.g. Site III data. (A considerable portion of the total catch was also found in the acetone and water washes in many tests, however, the quantity in the probe was not isolated; the probe and nozzle washes were combined.)

The inability to quantitatively collect the particulate sample in the Alundum® thimble in many tests points to the necessity for a backup filter. If fine particulates pass through the thimble or leakage occurs during sampling, collection on the backup filter still permits a valid particulate measurement. Without a backup filter e.g. as in ASTM D2928,(10) escape of particulate around or through the thimble renders the test results invalid and additional time and money must be spent on a repeat test.

An approximation of the precision of particulate measurements by ASTM D2928 can be made by statistical analysis of the thimble catch data. Based on all determinations at the three sites (I, III, and IV) where Alundum® thimbles were used, the between-laboratory standard error expressed as the coefficient of variation is about 9 percent. It should be noted that this estimate of precision does not include data on the nozzle catch collected as prescribed by D2928. Futhermore, there are differences between sampling procedures and the sampling equipment normally used for D2928 and the proposed ASTM method which could affect the precision estimate.

Collected Residue Measurements

The collected residue determinations exhibit much greater variability than the particulate measurements. The mean coefficients of variation of determinations at the four test sites range from 25.4 to 93.0 percent. In general, the variation in tests at each site is not random, but instead reflects an ordered nature with respect to laboratories. The ordered variations indicate that the results obtained with the test method are highly subject to the sampling equipment, sampling procedure, sample recovery, technique and analytical procedure employed by the individual laboratories.

The high values of Laboratory A, Site II probably result from a sampling equipment component. The laboratory used a heated Teflon® line between the probe and box filter. The high acetone wash and organic extract residue indicate that organic material may have been volatilized from the line during testing and condensed in the impinger train. (High particulate results were also obtained by Laboratory A, Site II.) The high values of Laboratory D, Site II may also be due to use of a Teflon® line, in this case, an unheated line between a heated backup filter on the end of the probe and the impinger train. The high acetone wash residues, which include a rinse of the Teflon® line, indicate that organics were removed from the tubing. Other sources of error in the test method due to equipment components could result from materials envolved from gaskets used in the thimble and backup filter.

Probably one of the most significant variables during sampling could be gas temperature in impinger train. In this study, the laboratories maintained gas temperatures of less than 70 F at the impinger train exit with a typical temperature range of 55 to 70 F. It is felt that impinger train temperature differences do not account for a significant portion of the variability observed in the results.

The area of major concern in collected residue determinations is the sample recovery and analysis. In these steps, SO_2 dissolved in the impinger solution can be readily oxidized to sulfate, which gives rise to "false particulates". The proposed ASTM method incorporates steps to eliminate SO_2 by heating the extracted aqueous impinger solution. Extraction and heating of the samples are performed as quickly as possible after sampling. Still the possibility of SO_2 oxidation exists due to dissolution of air in the samples during recovery and transfer to and from bottles. Hillenbrand(16) has reported significant SO_2 to sulfate conversion during these operations.

The sulfate analyses performed on a limited number of samples from Sites III and IV do not indicate that SO_2-to-sulfate conversion occurred during the determinations. In fact, results from Site III show less sulfate than predicted from the SO_3 which would be expected to condense in the impingers. Based on the sulfate analyses, SO_3 concentrations are calculated to be about 6 to 10 ppm, while the estimated concentration in the stack gas was at least 25 ppm. Assuming the impinger SO_3 determination is accurate, this could signify that some SO_3 is lost in the front end of the sampling train.

Using the sulfate analyses data for Site IV to calculate SO_3 concentation produces estimates in the range of 3 to 4 ppm which is reasonably close to the measured SO_3 concentration in the stack gas, 5 ppm.

On the other hand, if it is assumed that the sulfate is due to oxidation of SO_2, the percentage converted in the Site III and IV sample is only about 0.4 and 0.2 percent, respectively. In view of the low conversion determined from limited data, it appears that SO_2 "false particulate" formation can be reduced to a tolerable level. However, satisfactory performance may be highly subject to individual laboratory technique.

Other factors which may introduce errors in sample recovery and analysis include: (1) contamination of reagents, particularly organics, from storage or wash bottles (2) contamination of samples from storage bottles, and (3) contamination of samples during evaporation. For example, significant contamination of acetone can occur from improper wash bottles. A Guth wash bottle with the normal Tygon® tubing connector and rubber stopper can give blank residues of 5 to 10 mg. All glass tubes and Teflon® stoppers should be used in wash bottles to reduce blank weight and blank samples should be taken directly from the wash bottle.

Sample storage bottles should be selected to minimize contamination. Teflon® liners are required in bottle caps to eliminate dissolution of normal liners by acetone and chloroform-ether.

Contamination of samples can occur during evaporation in a normal hood in a dusty area.. If possible, samples should be evaporated in a filtered, reverse airflow, clean hood.

Summary

Based on the interlaboratory study, it is concluded that the particulate portion of the proposed ASTM test method can produce satisfactory measurements. However, measurements of collected residue using the test method appears to be subject to variations from a number of factors. The influence of these various factors must be determined and be brought under control in the procedure before reliable, interpretable collected residue measurements can be realized.

RECOMMENDATIONS

Based on the precision measures obtained in this study, the proposed test method appears acceptable for particulate determinations. However, consideration of potential problems involving reactions of stack gas components, especially sulfur oxides, with the sampling system components is recommended. The magnitude of any interferences and the specific conditions under which they occur should be assessed and, if significant, sampling conditions and sampling train components should be selected to eliminate errors.

Results obtained using the collected residue procedure show considerable variation. However, a more detrimental factor is the potential interference from SO_2 which would negate the determination of water soluble collected residue. In addition, system components and/or sample recovery and analysis operations can apparently produce high, variable organic residues. Additional study of the collected residue procedure is recommended. Ambiguities in the method must be resolved before meaningful measurements in source emissions can be achieved.

Specific recommendations and suggestions have been made by the cooperating and coordinating laboratories regarding the method as tested in this study. Since the input came from several sources, the recommendations are not always mutually compatible, however, all have been included in the following summary. Initially, suggested improvements in method documentation are given followed by recommended equipment modifications and operating procedure changes.

General Suggestions

1. A straight-forward, stepwise summary of the sampling procedure should be included in the method descriptions.
2. A compilation of all equations arranged in logical order would be helpful in the calculation of results.

Recommended Equipment Modifications

1. Permit the option of using a condenser, preferably of metal, in place of the glass impinger train when only sampling for particulates.

2. Relocate the out-of-stack back-up filter to an in-stack position to eliminate probe and filter heating and sample recovery.
3. Replace the stainless steel probe with an inert probe (glass-or Teflon®-lined) to eliminate metal probe deposits in the washings.
4. The minimum nozzle diameter recommendation (1/4") is too large for many stacks.
5. Specify the manner in which Greenburg-Smith impingers are to be modified.
6. Use all modified Greenburg-Smith impingers in train to reduce pressure drop in system.
7. Cut off center tube of the first impinger behind the filter at a point slightly above the level of 200 ml of water. This will prevent sucking-back the impinger water into the filter which occurs occasionally during leak checks.
8. Silica gel or a desiccant other than Drierite® is recommended for use at the desiccant in the moisture trap (drying tube). Drierite® tends to form a densely packed bed which restricts flow and also it is frequently carried into the check valve causing blockage. At least 200 grams of desiccant should be used.
9. A fifth modified Greenburg-Smith impinger or a similar metal trap is acceptable for use as the moisture trap (drying tube). The trap should be cooled in the ice bath.
10. In general, the use of commercially-available sampling systems and equipment should be recognized in the procedure.

Recommended Procedural Changes

1. Changes are required in text and equations in Paragraphs 5.5.1, 5.5.1.1, 5.5.1.2 and 5.5.1.3 to include use of the desiccant trap in the moisture content determination.

2. Parenthesis are missing in Equations (8) and (9).
3. Section 5.0 should include the equation for calculating Q_{STPD}.
4. Paragraph 6.2.1. Nozzle is shown in Figure 6.
5. Paragraph 6.2.2. Include the equation for estimating sample weights. See D2928-71, Equation (15).
6. Paragraph 6.2.2 and Table 5. The minimum sample weights should be reconsidered based on weighing error and weight changes in recovery and handling of filters, particularly the glass fiber type.
7. Paragraph 6.2.3. Thimble holder is shown in Figure 7.
8. Paragraph 6.2.3.2. Figures 8 and 9 show flat filter holders.
9. Heating capacity of probe should be specified in Paragraph 6.2.4, e.g. capable of maintaining the gas sample stream at a specified temperature or condition through the length of probe.
10. Gelman Type A is frequently used and should be included as an equivalent filter in Paragraph 6.2.6. Identify manufacturers since abbreviations such as MSA may not be familiar to all users.
11. Impinger train components described in Paragraphs 6.1 and 6.2.7 are not the same. All modification Greenburg-Smith impingers are recommended if impinger train is used.
12. Specify temperature operating range for collected residue impinger train in Paragraph 6.2.7. A maximum gas temperature of 70 F measured at the outlet of the last impinger is suggested.
13. Paragraph 6.2.8 and 7.3.5. At least 200 grams of desiccant in a modified Greenburg-Smith impinger or a similar metal containment is recommended, 100 g has been found to be insufficient in many cases. The trap should be maintained at ice temperature.
14. Section 7.0. The test method contains no isokinetic sampling specifications. An equation should be given to calculate the percent isokinetic sampling achieved during the test period (see Reference 13). An acceptable variation from isokinetic sampling should be stated.

15. Paragraph 7.1. The combined probe and pilot tube assembly referred to as a "Pitobe®" in 7.1 may not be familiar to all users.
16. Paragraph 7.1.3. A sampling rate of about 0.75 cfm is more consistent with the capability of commercially available sampling equipment and with the nomograph employed as a sampling aid.
17. Paragraph 7.1.3. Nozzle selection is discussed in Paragraph 6.1.1. Additional data on nozzle size selection such as that given in D2928-71, Equations (13) and (14) should be included in this paragraph for those not using a nomograph.
18. Paragraph 7.2. Sampling time should be related to the period required to obtain a minimum weight of particulate sample consistent with requirements of Paragraph 6.2.2 (amended as suggested in Item 5). Also, recognition must be given to situations which will not give minimum sample weights in a reasonable sampling time e.g. Site II of this study.
19. Drawing as shown in Figure 1 of this report would be a better representation of the particulate sampling train referred to in Paragraph 7.3.6 and Figure 13 of the method.
20. Paragraph 7.3.7. The high pressure drop in the sampling system caused by the components and sample build-up on the filters frequently requires more than 15-inch vacuum to maintain isokinetic sampling conditions. Therefore, a leak test at a higher vacuum (say 20 inches) is recommended.
21. A list of data which must be taken during the test should be included in Section 7.4 with references to appropriate forms on which to record readings. Suggested forms are given in Appendix C
22. Section 7.4 Instruction should be given on preheating the probe and maintenance of a prescribed gas temperature in the probe. Operating temperature must consider the dew point of sulfuric acid mist, if present.

23. Section 7.4.5. A sample identification system such as: H_2O wash-probe, Acetone wash-probe, etc. would be more effective than suggested numbering system.

24. Section 7.4.5. Suggest minimum volumes of water and acetone that are to be used to wash system components. Minimum volumes of acetone and water for blank analysis should be specified.

25. Paragraph 7.4.5.2. Specific instructions as to what parts are to be washed with acetone should be included e.g. internal surfaces of nozzle, in-stack filter holder, probe, and front-half of back-up filter holder. These surfaces should be brushed to assure quantitative recovery of particulate material. Acetone wash sample bottles should be glass with caps containing Teflon® inserts.

26. Paragraph 7.4.5.3. Water wash is probably not necessary if brushing is used with acetone wash.

27. Paragraph 7.4.5.5. Impingers <u>should</u> be washed with water. There should not be an option to use a water wash.

28. Comment between Paragraph 7.4.6.2 and 7.4.6.3. A caution should be included to evaporate samples in an area where they will not be contaminated, preferably in a clean hood.

29. Paragraphs 7.4.6.4 and 7.4.6.5. Evaporation of water samples at 70 F is very time consuming and increases chances for sample contamination. Evaporation to dryness on a steam bath is suggested.

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APPENDIX A

REPRINT OF ASTM

PROPOSED METHOD FOR SAMPLING STACKS FOR PARTICULATES AND COLLECTED RESIDUE SIMULTANEOUSLY

Third Draft - January 1973

PROPOSED ASTM D - - - - - - -

SAMPLING STACKS FOR PARTICULATES AND COLLECTED RESIDUE SIMULTANEOUSLY

Third Draft - January, 1973

"These proposed recommended practices have no status as an ASTM standard and are published on behalf of the sponsoring committee for information only for a maximum of two years. Comments are solicited and should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa, 19103."

SAMPLING STACKS FOR PARTICULATES AND COLLECTED RESIDUE SIMULTANEOUSLY

1.0 SCOPE

1.1 This method covers the sampling of particulates and collected residue simultaneously and is to be used where the determination of the collected residue is desired.

2.0 SIGNIFICANCE

2.1 The following procedure covers use of the impinger type of train to sample gases for particulates and collected residue simultaneously for quantitative considerations. The filter box-impinger sample train is shown in Figure 13.

3.0 DEFINITIONS

3.1 Definitions other than those following are listed in ASTM Definitions D 1356, Terms Related to Atmospheric Sampling and Analysis:

A_n	area of sampling nozzle, square feet
A_s	effective area of flue, square feet
C_m	meter correction factor, dimensionless
C_p	pitot tube correction factor, dimensionless
C_w	volume of condensate in condenser, milliliters
d_n	internal diameter of sampling nozzle, inches
D_s	internal diameter of flue, inches
E	particulate emission rate, pounds per hour
E_1	collected residue emission rate, pounds per hour
E_{in}	potential particulate emission rate at the collector inlet, pounds per hour
E_{out}	particulate emission rate at the collector outlet, pounds per hour

3.0 DEFINITIONS (CONT'D)

G_s	specific gravity of flue gas referred to air, dimensionless
h_{avg}	average velocity pressure in flue, inches of water
$\sqrt{h_{avg}}$	average of the square roots of the velocity pressures, inches of water, square root
h_n	velocity pressure at nth sampling point, inches of water
M_d	average molecular weight of flue gas, dry basis, pounds per pound mole
M_s	average molecular weight of flue gas, at flue conditions, pounds per pound mole
n	nth sampling point from center of flue
N	number of sampling points across a diameter
P_b	barometric pressure, inches of mercury
P'_m	gage pressure (suction) at meter, inches of mercury
P_m	absolute pressure at meter, inches of mercury
$P_{m(avg)}$	average absolute meter pressure, inches of mercury
P'_s	static pressure in flue, inches of water
P_s	absolute pressure in flue, inches of mercury
P_{wc}	vapor pressure of water vapor at condenser exit temperature
Q_m	sampling rate at meter conditions, cubic feet per minute
Q_n	sampling rate at nozzle at flue conditions, cubic feet per minute
Q_s	flue gas flow rate at flue conditions, cubic feet per minute.

3.0 DEFINITIONS (CONT'D)

QST P	flue gas flow rate at standard conditions, cubic feet per minute
QST PD	dry flue gas flow rate at standard conditions, cubic feet per minute
r_n	radial distance from center of flue to nth sampling point, inches
T	total sampling time, minutes
t_c	temperature at the condenser, degrees Fahrenheit
T_c	temperature at the condenser, degrees Rankine
t_m	temperature at the meter, degrees Fahrenheit
T_m	absolute temperature at the meter, degrees Rankine
$T_{m(avg)}$	average absolute meter temperature, degrees Rankine
t_s	temperature in the flue, degrees Fahrenheit
T_s	absolute temperature in the flue, degrees Rankine
u_{avg}	average flue gas velocity, during preliminary stable run, feet per minute
u_n	flue gas velocity at nth sampling point, feet per minute
u_r	flue gas velocity at reference point, feet per minute
$u_{r(avg)}$	average velocity at reference point during preliminary stable run, feet per minute
V_c	equivalent vapor volume of condensate at meter conditions, cubic feet
V_m	gas volume sampled at meter conditions, cubic feet
V_w	Volume of water vapor remaining in meter volume, cubic feet

3.0 DEFINITIONS (CONT'D)

$V_{ST\ PD}$	dry gas volume sampled at standard conditions, cubic feet
W	moisture in flue gas, volume percent
Y	particulate weight, milligrams
Y_1	collected residue weight, milligrams
Z	particulate concentration at flue conditions, grains per cubic foot
Z_1	collected residue concentration at flue conditions, grains per cubic foot
$Z_{ST\ PD}$	particulate concentration at standard conditions (dry), grains per cubic foot
$Z_{1ST\ PD}$	collected residue concentration (dry), grains per cubic foot

3.1.1 Definition of Particulate

Particulate is that material removed by the dual filtration system specified in this standard.

3.1.2 Definition of Collected Residue

Collected residue is that material collected during source sampling (after initial removal of particulates) which is retained in a condensation device or liquid collector, maintained at the temperature specified by the test procedure used, after the removal of uncombined water.

4.0 PLANNING A STACK TEST

4.1 The plan for collecting the sample requires preliminary knowledge of the process that produces the dust-laden gas stream, and consequently, the actual taking of the sample cannot be divorced from the process itself. It becomes easier to consider the whole topic as one, namely, the sample and for what purpose the sample is to be used, that is, preliminary engineering studies, economic value, regulatory control, etc.

4.1.1 The sample is only useful as it relates to the process. If further action based on the results of sampling is contemplated, the sampling plan must include full information on process feed rate, gas volumes, fuel rate, temperatures, and so forth during the period of sampling. Part of the sampling plan, therefore, will be to determine what process information should be obtained. Preliminary data in many processes can be obtained by making a material balance.

4.2 The first point of information will be to decide if the process is steady state and subject to no more than normal variation in operation, or if it is cyclic with a predictable start and stop. If the process is steady state, make arrangements with operating personnel to hold the process conditions at a particular level for sufficient time to allow the taking of several samples of whatever duration is most satisfactory. If the process is cyclic, decide whether to sample over one full cycle or whether the cycle is long enough to be broken into definable parts. It is often desirable to study parts of a cycle since an average during each part is often more meaningful than an average over the entire cycle. If the cycle is of short duration, it may be necessary to sample over several cycles in order to obtain a weighable amount of material. (See 7.2 for additional discussion on sampling time).

4.2.1 Another factor which must be taken into consideration is that some processes are seasonal, and testing may have to be performed at a time when production is at a peak level. It is essential that the sampling plan give the greatest return of information.

4.3 Planning also includes the selection of the sampling site. The physical layout of the process equipment gas cleaning equipment, fans, etc. often is forced to conform to what little space is available. The result is that the sampling site, which usually requires a working platform on top of a scaffold rising from the ground or projecting out from a roof, must be located with care. Ideally, locate a sampling site so that the velocity throughout the duct cross section follows a normal, flat parabolic distribution. A section of round flue is preferable to a rectangular flue since there tends to be less fluctuation in velocity across a round flue. In most cases, depending on the gas velocity, a uniform velocity distribution in a circular flue will occur about eight diameters downstream and two diameters upstream from any flow disturbance such as a bend, connection, change in area, visible flame, etc. (in rectangular flues, use the shortest dimension as the diameter for measuring purposes.) There are times when this arrangement is found, but more often than not compromises must be made and the sampling site is less than ideal. In such cases, the site must have the longest run of straight flue available directly upstream and as little interference from branch ducts, etc. as possible. The longest run of straight flue is often found in the discharge stack, but other locations in the system might be chosen if otherwise suitable. The intent of the sampling plan must be uppermost in mind. If the purpose is to determine the rate of particulate discharge to the atmosphere, a sampling site well upstream of the fan and stack will not necessarily produce dependable results. Heavy material often settles out in the bottom of a flue or stack before reaching the atmosphere.

4.3.1 Presuming that several straight runs of flue are available, select a vertical rather than a horizontal flue. There tends to be better dust distribution in a vertical section of flue than in a horizontal section in which the dust can be segregated by gravity even when traveling at high velocity. If dust segregation is suspected, carry out the sampling with greater care than usual, that is, sample the full area of the flue using a greater number of traverse points than would otherwise be required. (In order to assure sampling in the lower portion of the duct when the sampling is performed in a horizontal section, select the traverse axes so that one axis is vertical).

4.4 Consider other factors, such as availability of sufficient working space and the need for inserting or removing the probe, in selecting the sampling site. The probe may be somewhat lengthy and require considerable clearance from other objects. Electrical power or compressed air at about 100 psi must be available. Pay due attention to need for proper lighting, shelter for the equipment during extended stack sampling studies and need for proper safety precautions through

4.0 PLANNING A STACK TEST (CONT'D)

strength of structure, presence of guard rails, proper means of access, portection against short circuiting of electrical equipment in bad weather, presence of gas, etc. Ground all probes when sampling at electrostatic precipitators or other locations where a static charge can exist.

4.5 To perform the velocity traverses and sampling tests, install sampling ports of the size needed to accommodate the sampling equipment. Four inch nipples or couplings are usually satisfactory.

4.6 Assistance is often required to note and record process information during the test. Provide some means of communication between the operating area and the sampling site.

4.7 The purpose of testing must also be considered in selecting the sample trains. If a test for emissions is being run, any applicable train may be selected. If an efficiency test is being run, sampling trains at inlet and outlet should be the same and should use the same filtration devices.

5.0 MEASUREMENT OF FLUE GAS FLOW

5.1 No particulate sampling can be performed until gas flow has been measured. Measurement of flue gas flow includes determination of the following parameters which define the physical conditions of the gas stream: velocity, static pressure, temperature, moisture, and gas density. Methods of measuring these parameters and their limitations are described in this section.

5.1.1 The number of points within a flue at which these various parameters must be determined depends on the cross-sectional area of the flue, the location of the sampling site in regard to flow obstructions, and on the desired accuracy of the sample. See Table 1 for suggestions.

5.2 Velocity - The accurate determination of the gas velocity is one of the most important measurements, since both sampling rates and total gas flow depend on this value. Determine the average velocity in a flue by measuring velocities at separate points and taking the arithmetic average of these values.

5.2.1 Location of Sampling Points - Velocities in any flue cannot be assumed to be uniform across any large cross-sectional area. However, in any single subarea, one may assume a constant rate of change of velocity over the area with average velocity at the centroid of this area. Determine the number of points at which velocities are to be measured, and their location in accordance with commonly accepted practice when gas flow patterns are uniform. In all cases, divide the effective inside area into a number of equal areas, and measure the gas velocity at the centroid of each of these areas. In rectangular flues, divide the cross-sectional area into equal rectangular subareas as shown in Fig. 1. The number of areas to be used depends on the flow pattern and flue size. Use Table 1 to find the minimum number of areas when sampling at least eight equivalent diameters downstream from the nearest flow disturbance (see 4.3).

5.2.1.1 Though no exact rules are available, it is good practice to increase the number of sampling points when sampling less than eight diameters downstream from any flow disturbance. When only four to six diameters of straight duct are available, double the number of points used. Sampling sites less than four diameters downstream from any flow disturbance are special cases. When necessity of emission data requires sampling with less than four diameters straight duct, recognition must be given to the inability to ensure even an approach to representative sampling. Data shall include the range of velocity measurements and the selection of average velocity values and location of sample point selection.

5.2.1.2 In circular flues divide the area concentrically as shown in Fig. 2. The minimum number of areas to use is shown in Table 2 and the distance to the test point is shown in Table 3 or may be calculated from the equation below:

$$r_n = D_s \sqrt{(2n - 1)/4N} \quad (1)$$

5.2.1.3 Again, if a site less than eight diameters downstream from a flow disturbance is used, increase the number of sampling points used as previously mentioned.

5.2.1.4 Conduct traverses along two diameters at right angles to each other. When sampling must be done in an irregular-shaped flue, divide the flue into equal areas of any shape, and measure the parameters at the centroid of each area.

5.2.2 Velocity Measurement (See D 3154) - A standard or "S" type pitot tube and inclined manometer are satisfactory for measuring velocity pressures of 0.01 in. of water (equivalent to 400 ft/min at 60F) or greater. Details of a typical standard pitot tube are shown in Fig. 3. At locations where the standard pitot tube cannot be inserted into the flue, or where dust or moisture or both are present which might clog the small holes in this instrument, use a Staubscheibe pitot tube, commonly called a Type S pitot tube, shown in Fig. 4. For this latter case, use a correction factor to compensate for the inherent high reading given by the Type S pitot tube. The correction factor may be determined by comparing readings taken with a Type S pitot tube and with a standard pitot tube. (The correction factor is often supplied by the manufacturer of the Type S tube. It is usually in the order of 0.83 ± 0.02.) As stated in 5.2, the velocity is measured at specific points within the flue according to a plan determined by flue size. Marks placed on the pitot tube aid in locating the traverse points at which the velocity is to be measured.

Note 1 - A simple method for marking off the pitot tube for use in taking a velocity traverse is as follows:

(1) Thread the stabilizing plug on the pitot tube into the port to be used for the velocity traverse.

(2) Slide the pitot tube all the way into the port until the tip touches the far wall of the flue and the tip is aligned with the gas stream. Using a china marker or other suitable means, mark the pitot tube at a point immediately adjacent to the stabilizing plug.

(3) Slide the pitot tube out of the port until the tip is even with the inner wall of the flue. Again mark it at a point immediately adjacent to the stabilizing plug.

5.0 MEASUREMENT OF FLUE GAS FLOW (CONT'D)

(4) The distance between the two lines is the internal diameter of the flue (D_S). Mark the centerline halfway between these two points.

(5) Mark the traverse points on the pitot tube after referring to Table 3 or use Eq 1. (It is advisable to mark the traverse points in one manner and the centerline and end points in a different manner.)

(6) Take velocity readings only at the traverse points and not at the centerline or end points.

5.2.3 The pitot tube is used to measure the difference between the total and static pressures in a flue. This pressure differential is equal to the velocity head and is read on a suitable manometer or draft gage in inches of water. The accuracy of the velocity reading depends on the type of manometer and for this reason use an inclined manometer which reads to within 1 percent of the highest reading expected. Use care in reading any draft gage to ensure that it is properly zeroed, leveled before use, and free of leaks. Check the zero reading before and after each set of readings. Record the readings on a gas velocity data log sheet (See Table 4).

5.2.4 When the gas velocity is less than 400 ft/min, the velocity pressure is too low to permit accurate measurement with standard inclined manometers. In this case, use an ultra-sensitive micromanometer on which pressures to the nearest 0.001 in. of water can be read. If an accurate reading still cannot be obtained, use a thermo-anemometer of the hot-wire type or a calibrated vane anemometer. Use the thermo-anemometer only in clean gas streams. Use all of the highly sensitive, low-velocity measuring devices in accordance with the manufacturer's instructions. When all the above methods cannot be used for combustion products a laminar flow based on stoichiometric computation could be considered.

5.3 Temperature - Measure the gas temperature with a standard base metal thermocouple and a potentiometer. In larger flues, measure the temperature at various points as was done in measuring velocities. If possible, take temperature and velocity traverses simultaneously. Unshielded thermocouples may be used to a temperature of about 700 F. For higher temperatures, use a shielded thermocouple.

5.3.1 In small flues a standard mercury bulb thermometer inserted into the flue may be used. Carefully seal the access hole to prevent in-leakage of outside air. Allow sufficient time for the thermometer to reach equilibrium before a reading is taken. If there are frequent variations of the gas temperature with time due to process changes, a continuous recording of the temperature will prove useful.

5.4 Static Pressure - Measure the static pressure by connecting the static pressure tap of a standard pitot tube to a water gage manometer. If high static pressures are expected, use a vertical U-tube mercury-filled manometer. Calibrate and read the manometer in inches of water. The absolute pressure in the flue is equal to the atmospheric pressure plus or minus the static pressure in the flue depending on whether it is under vacuum or pressure.

$$P_s = P_b \pm (P'_s/13.6) \qquad (2)$$

The static pressure need only be determined at a single point in the flue in most cases. Check this pressure occasionally throughout the test period.

5.5 Gas Density - Gas density depends on the temperature, the absolute pressure, the moisture content, and on the composition of the gas stream.

5.5.1 Moisture Content - Determine the water content of the gas stream by passing a known volume of the gas stream through a condenser and measuring the amount of water condensed. Use the condensed water volume and the temperature of the gas leaving the condenser to determine the total moisture content. An explanation of these calculations follows:

5.5.1.1 Determine the equivalent vapor volume of the condensate at the meter:

$$V_c = (C_w/453.6)(387/18)(T_m/530)(29.92/P_m)$$

$$= 0.00268\ (C_w)(T_m/P_m) \qquad (3)$$

5.5.1.2 Determine amount of water remaining in gas stream after condenser:

$$V_w = (V_m/P_m)(P_{wc}) \qquad (4)$$

5.5.1.3 Actual percent moisture in flue gas:

$$W = [(V_c + V_w)/(V_c + V_m)](100) \qquad (5)$$

5.5.1.4 Wet- and dry-bulb temperatures may also be used to measure moisture content if the wet-bulb thermometer can be kept wet continuously and heavy dust loading does not interfere with the moisture equilibrium. Gas flow over the wet bulb must be at least 15 ft/s. Refer to a psychrometric chart to find the moisture content of the gas stream (See Fig. 5).

5.5.2 Gas Composition - An accurate determination of flue gas flow requires a knowledge of its chemical composition in addition to its moisture content. If there is reason to believe that the molecular weight of the gas must be determined by composition analysis, the particular analysis depends on the process. For most fuel combustion processes, determine the carbon dioxide (CO_2), carbon monoxide (CO), and the oxygen (O_2) content of the gas stream. Determine the nitrogen (N_2) by difference. If the sulfur dioxide (SO_2) content of the gas stream is above 1 percent, include it in the analysis. Use an Orsat apparatus to determine chemical composition, especially if the intent of the particulate sampling is to relate the particulate to the percent CO_2 or other gaseous component. Simpler devices may be used for measuring CO_2 and O_2 in combustion gas, which are not as accurate as an Orsat, but which will determine the approximate molecular weight rapidly in the field. Both methods must yield an analysis on a dry basis.

5.5.3 If the gas stream to be sampled varies with time, perform gas analyses at various time intervals to determine changes in gas composition. An integrated gas sample may be collected in a glass container or plastic bag during the test period and a single analysis performed on the collected sample.

5.5.4 Determine the specific gravity of the gas or the molecular weight or both for a typical combustion process (neglecting SO_2) as follows:

$$(\text{percent } CO_2) \times (0.44) =$$

$$(\text{percent } CO) \times (0.28) =$$

$$(\text{percent } O_2) \times (0.32) =$$

$$(\text{percent } N_2) \times (0.28) =$$

$$\text{Sum} = M_d$$

$$M_s = M_d[(100 - W)/100]+(0.18)(W) \qquad (6)$$

5.5.5 Determine the specific gravity of the gas (referred to air at standard conditions) as follows:

$$G_s = M_s/(387)(0.0749) \qquad (7)$$

5.6 Total Gas Flow

5.6.1 Stable Flow Conditions - After the various parameters have been determined, calculate the gas velocity in feet per minute (fpm) from the following:

$$u_n = (2.90)(60)(C_p)\sqrt{29.92/P_s)(1.00/G_s(h_n)(T_s)} \qquad (8)$$

In the various flue gas parameters, such as temperature, vary greatly from point to point in the duct, make a separate calculation for each point and use the arithmetic average of these velocities as the average velocity. Usually only the velocity pressure varies from point to point. In that case, factor out the other parameters in order to simplify the calculations. Average flue gas velocity is equal to these constants times the average of the square roots of the velocity pressures is in Eq. 9. (It is important to note that the average of the square roots of the velocity pressures is used. The velocity pressures cannot first be averaged and then the square root taken.)

5.0 MEASUREMENT OF FLUE GAS FLOW (CONT'D)

$$u_{avg} = (2.90)(60)(C_p)[\sqrt{29.92/P_s)(1.00/G_s)(T_s}][(\sqrt{h_{avg}})] \quad (9)$$

The flue gas flow rate in cubic feet per minute is then equal to the product of the inside cross-sectional area of the flue and the average velocity.

$$Q_s = (u_{avg})(A_s) \quad (10)$$

Determine the flue gas flow rate at standard conditions:

$$Q_{stp} = (Q_s)(530/T_s)(P_s/29.92) \quad (11)$$

5.6.2 Changing Flow Conditions - If the entire flow pattern changes moderately during the test period, monitor this change by measuring the flow at a single point and relating this flow to the total stack flow obtained during a fairly stable period. Determine the point of average velocity during stable flow conditions and locate a fixed pitot tube at this point for reference during the period of changing flow. The average velocity across a flue is equal to the average velocity at the reference point times the ratio of the average velocity across the flue during the stable run divided by the average velocity at the reference point during the stable run.

$$u_{avg} = (u_r)[(u)_{avg}/(u_r)_{avg}] \quad (12)$$

6.0 SAMPLING TRAIN (Refer to Figure 13)

6.1 The sampling train for collecting particulate matter and collected residue from a gas stream flowing through a stack or flue consists of the following interconnected elements:

(1) Sampling nozzle of proper dimensions and design.

(2) Particulate collector (par 6.2.2) in a stainless steel holder if required.

6.0 SAMPLING TRAIN (CONT'D)

(3) Stainless steel probe for extending the thimble holder and nozzle into the flue, heated if required.

(4) High vacuum connecting hose with smooth inner wall should be used where required and should be heated where necessary.

(5) Heated filter.

(6) 2-500cc Greenberg-Smith Impingers each containing 100cc of distilled water preceeded and followed by one 500cc empty gas wash bottle, all in an ice bath for removal of collected residue.

(7) Drying tube.

(8) Vacuum pump with controls.

(9) Dry gas meter.

(10) Orifice meter.

All the foregoing elements should be sized for a sampling rate of 0.8 to 1.2 SCFM at isokinetic conditions.

6.2 Elements of the Sampling Train

6.2.1 Nozzles - The first part of the sampling equipment to encounter the dust- or moisture-laden gas stream is the nozzle. In order to extract a uniform sample of gas and particulate matter, use a nozzle of predetermined and definite diameter. The minimum inlet diameter recommended is ¼ in. The size may increase to any diameter depending upon the collection equipment, the velocity in the flue, and the amount (weight) of sample required. Use a nozzle of such size that isokinetic flow can be maintained. Figure 7 shows drawings of typical nozzles. The leading edge of the nozzle should be sharp and tapered.

6.2.2 Particulate Collector - The guiding principle in selecting the particulate collector is to obtain a sample sufficient in weight to be far in excess of the normal handling and other errors brought about by the conditions of sampling. Find the proper collector in Table 5.

6.2.3 Particulate Collector Holder

6.2.3.1 Alundum Thimbles - a stainless steel holder for Alundum thimbles is shown in Figure 8. The overall diameter has been kept to a minimum to facilitate insertion of the entire holder through a relatively small sampling port. The holder provides a method for clamping the thimble firmly in position with its lip pressed against a soft asbestos gasket. The gasket sealing together the components of the holder is made of relatively hard asbestos material. Such holders and the Alundum thimbles can withstand temperatures approaching 1000°F. Alundum thimbles with glass fiber lining meet all sampling conditions for 100 mg or more.

6.2.3.2 Flat Filter Holders - A variety of holders for flat, round filters are available in a wide range of sizes. In general, these filter holders use the filter material itself when clamped into position, to provide the function of a gasket. (See Figs. 9a and 9b.) These holders usually contain a porous medium such as a wire

6.0 SAMPLING TRAIN (CONT'D)

screen or sintered stainless steel as a filter support. In general, such holders are not suitable for high-temperature operations. Special precautions must be taken to prevent loss of collected material when changing filters.

6.2.3.3 Packed Glass Tube - A glass tube such as shown in Figure 10, packed with a glass wool or fiber glass material makes an excellent collecting device where the gasses are wet. It is suitable for all temperature applications but great care must be used to avoid breakage.

6.2.4 Probes

A heated probe is used to extend the thimble holder and nozzle into the stack to the proper position. Its diameter must be sufficient to provide adequate stiffness for support at the greatest distance within the stack. Type 316 or 18-8 stainless steel or equivalent should be used because of the requirement that it should be washed after each use and to prevent contamination of the sample.

6.2.5 Vacuum Hose

The probe and filter assembly should be as close as possible, but when required may be connected with a heated smooth bore Teflon hose. (If filter holder assembly is directly coupled to the probe, the heated hose will not be needed.)

6.2.6 Filter Assembly

A glass fiber filter (MSA 1106 BH) or equivalent should be located outside the breeching in a flat filter holder with a heating system capable of maintaining the temperature of the sample gas above 250 F or its acid dew point, whichever is higher, but not to exceed stack gas temperature. The purpose of this filter is to act as a back-up to the particulate collector in the dry filtration system. Use of this filter will preclude loss of an acceptable test due to leakage around, or breakage of, the particulate collector inside the breeching.

6.2.7 Impinger Assembly

A condenser system consisting of two 500cc modified Greenberg-Smith impingers each filled with 100cc of distilled water flanked by two 500cc empty gas wash bottles used to condense moisture and other condensible materials. All bottles should be connected in series and immersed in an ice bath.

6.2.8 Drying Tube

A drying tube containing 100 grams Drierite, silica gel or an equivalent dessicating agent is used to collect any remaining moisture in the sample gases.

6.2.9 High vacuum hose capable of holding a vacuum of at least 15 inches of mercury is used for connecting the balance of the apparatus to the pump.

6.2.10 An air tight vacuum pump with coarse and fine flow controls is used to draw gas sample.

6.2.11 Volume Meter

A volume meter is needed for measuring total sample flow. A calibrated dry gas test meter is the most

6.0 SAMPLING TRAIN (CONT'D)

satisfactory totalizing volume meter available for source test work. Calibrate the meter prior to use and determine a meter correction factor (C_M) if necessary.

6.2.12 Rate Meter

A calibrated orifice meter (Figure 11) is used to indicate the approach of sampling rate to isokinetic conditions, after all variables such as moisture etc. have been accounted for.

6.2.13 A calibrated thermocouple and a calibrated "S" type pitot tube are attached to the probe so that the sensing portion of each is adjacent to the sampling nozzle.

6.2.14 Thermometers (thermocouples) and pressure gages (manometers) of suitable accuracy are required to determine gas conditions at specific points as shown in Figure 13.

7.0 PROCEDURE

7.1 Calculation of the Proper Sampling Rate

Calculations cannot be carried out until the velocity traverse described in 5.2 has been completed. Sampling must be performed isokinetically. If the velocity of the gas is changed as it enters the sampling nozzle, mechanical separation of the coarse particles will occur which will give erroneous sampling results.

Where a Pitobe is used, the nomograph supplied with this instrument may be used to determine the isokinetic flow for each point during sampling.

7.0 PROCEDURE (CONT'D)

Where the null (balanced draft) method is used, the isokinetic sampling rate is maintained by keeping the draft gauge at the null point.

7.1.1 The rate and volume meters for measuring the gas sample measure the gas at conditions of temperature, pressure, and moisture content which are different than those in the flue. Therefore, calculate the sampling rate at the meter for each sampling point before starting the test and record on the log the required rate. The flue gas conditions are known from the information obtained during the velocity traverse. If these conditions are not constant, the change will be noted on the pitot tube draft gauge or the balanced draft gauge. The sampling rate can be corrected by adjusting the sampling rate controls to give a corresponding change in the orifice meter draft gauge or the balanced draft gauge. For the preliminary test, estimate the meter conditions. In subsequent tests use the meter conditions from the previous test.

7.1.2 Calculate the sampling rate at the meter as follows:

$$Q_m = (U_n)(A_n)(T_m/T_s)(P_s/P_m)[V_m/(V_m + V_c)] \qquad (13)$$

7.1.3 Select a nozzle size as described in 6.2.2 which will provide a meter sampling rate between 0.8-1.2 cubic feet per min for isokinetic conditions at the nozzle. The quantity and fineness of the dust in the stack gas effects the sampling rate by increasing the pressure drop as the test progresses. Charts relating sampling rate with stack and meter conditions can be prepared for the range of conditions expected.

7.0 PROCEDURE (CONT'D)

7.2 Total Sampling Time

The total sampling time is egual to the number of points to be sampled times the sample duration at each point. Use the same points for sampling which were used for the velocity traverse. Use a sample duration at any point of no less than 5 min under steady conditions. If conditions permit, use a sampling duration longer than 5 min and a total sampling time of at least 1 h because of the improved reliability of the test result.

7.3 Assembling the Sampling Train

7.3.1 After the proper nozzle and particulate collector have been selected, assemble the sampling train. Use TFE-fluorocarbon tape (¼ in. wide) to lubricate the threads on all connections in the train unless the temperature will exceed 500 F (260C), which then requires the use of a powdered graphite lubricant. Take extreme care to ensure that no tape or graphite contaminates the thimble, probe, filter, the assembly comprising the nozzle, particulate collector, and probe. Assemble the particulate collector holder without a collector in place and mark the probe with the same traverse points used for conducting the velocity traverse as discussed in 5.2.2. The sampling program is carried out by locating each traverse mark in turn at the flue wall and sampling for the time selected. Sample only at the traverse points.

7.3.2 Place a clean, weighed particulate collector in the particulate collector holder and tighten securely, noting carefully the seat against the gaskets. Mark the end of the sampler to indicate the direction of the nozzle tip.

7.3.3 A previously dried and weighed filter is placed in the filter holder and the openings sealed (6.2.6).

7.3.4 The impingers must be laboratory cleaned and dried after which the openings are sealed.

7.3.5 The drying tube is filled with approximately 100 grams of Drierite (or equivalent) which has been dried to a constant weight and the weight recorded. The tube shall be identified and the openings sealed.

7.3.6 Assemble the complete train as shown on Fig. 13 after removing the seals from the openings.

7.3.7 Check the entire sampling train for leaks by plugging the nozzle and pulling a 15-inch mercury vacuum. A leakage rate of no more than 0.02 CFM at the meter is acceptable. This should be repeated at the beginning and end of each test.

7.4 Performing the Test

After sampling rates have been calculated and the train assembled and checked, the test itself can be performed.

7.4.1 Scrape the inside of the sampling port free of dust before each day's testing. Close the control valve on the meter and insert the sampler into the flue to the first traverse point, with the sampling nozzle pointed downstream in the direction of gas flow.

Note 2 - When sampling hot gases, start at the traverse point farthest away from the port and move the sampler out as the test progresses. This allows at least part of the probe to cool and makes handling of the sampler at the conclusion of the test more convenient. A pair of asbestos gloves is useful for handling hot samplers and pitot tubes.

It is advisable to allow the nozzle, particulate collector and its holder, filter and its holder to preheat so that moisture present in the gases does not condense in the filter during the initial part of the sampling. In very hot flues, the Alundum thimble holder can expand while the gaskets can shrink, thus causing the thimble to loosen and allow the gases to bypass the thimble. In this case, it may be necessary to preheat the thimble holder in the stack, remove it and re-tighten the thimble. While the particulate collector and filter are preheating, record the initial meter reading, the numbers of the particulate collectors and filter, and other such data on the sampling data log-sheet (See Table 6).

7.4.2 When starting the test, turn the sampler so that the nozzle is facing in the upstream direction, turn on the pump at once, open the control valve and start the stop-watch. Note the time and record it on the log-sheet. Adjust the control valve until the proper sampling rate is obtained. Adjust the sampling rate for every point, and maintain the isokinetic rate by continuous observation and adjustment. Record the meter volume, pressure, and temperature as well as the condenser temperature for every point.

7.4.2.1 When sampling at one point has been completed, move the sampler to the next point as quickly as possible. Close the control valve only when transferring the sampler from one sample port to the other. Exclude the time required to transfer the sampler from one port to another from the total sampling time.

7.4.3 At the completion of the test, close the control valve on the meter, turn off the pump, turn the particulate collector holder so that the sampling nozzle is facing downstream and record the final gas volume and time. Remove the holder carefully from the flue, making certain that the nozzle does not scrape dust from the inside of the port. Keep the nozzle elevated at all times so that none of the sample is lost.

7.4.4 Extreme care should now be taken that none of the sample is lost or contaminated. The sampler assembly should be sealed at the nozzle and downstream end of the probe or high vacuum hose. The drying tube should be resealed at both ends. The impinger-filter box should be sealed at both ends. Remove all sampling train components carefully to the field laboratory for sample recovery.

7.4.5 Sample Recovery

7.4.5.1 Remove particulate collector from holder and place in its container. Brush all dust from the nozzle and holder and add to the dust in the particulate collector (container No. 1).

7.4.5.2 Wash all internal surfaces up to the filter with C.P. acetone. Determine the volume of the liquid and place in a clean labeled bottle (container No. 2).

7.0 PROCEDURE (CONT'D)

7.4.5.3 If the material being sampled contains inorganic salts, the same surfaces should be washed with distilled water, the liquid volume determined, and the liquid placed in a clean labeled bottle (container No. 7).

7.4.5.4 Transfer the filter and any loose material from the filter holder to the tared, covered dish (container No. 3).

7.4.5.5 Record the volume of water in the impingers and place in another clean labeled bottle (container No. 4). Wash impingers with distilled water if the material sampled contains inorganic salts. Measure the volume of liquid and add to the bottle above (container No. 4).

7.4.5.6 Wash impingers with C.P. acetone, determine the liquid volume, and place in a clean labeled bottle (container No. 5).

7.4.6 Sample Preparation and Analysis

The preparation in paragraphs 7.4.6.1 and 7.4.6.2 must be made shortly after sampling, with no intervening transport or storage.

7.4.6.1 After the samples are recovered, the impinger liquid and water washing, if any, (container No. 4) must be treated to reduce oxidation of SO_2 to SO_3 which may occur. The first step is to extract any organics from the impinger liquid. Place the impinger liquid and water rinse, if any, (container No. 4) in a separatory funnel and treat with three (3) 25 ml. portions of chloroform.

7.0 PROCEDURE (CONT'D)

Complete the extraction with three (3) 25 ml. portions of ethyl ether. Combine the ether and chloroform extracts into a clean labeled bottle (container No. 6).

7.4.6.2 The impinger liquid from 7.4.6.1 is boiled until the volume has been reduced about 25%. The remaining liquid is returned to container No. 4 for transport to the Laboratory.

The remaining analysis may be done after the samples have been transported back to the Laboratory or stored.

7.4.6.3 The acetone rinse liquid from the dry filtration system (container No. 2) must be evaporated at 70 F, dessicated to a constant weight, and weighed to the nearest 0.1 mg.

7.4.6.4 The wash water from the dry filtration system, if any, (container No. 7) must be evaporated at 70 F in normal atmosphere, dessicated to a constant weight, and weighed to the nearest 0.1 mg. (Boiling of the sample would remove organics).

7.4.6.5 The impinger liquid from 7.4.6.2 (container No. 4) is boiled, preferably in a steam bath, almost to dryness. This remaining material is then transferred to a tared dish, dessicated to a constant weight, and weighed to the nearest 0.1 mg.

7.4.6.6 The impinger acetone rinse liquid (container No. 5) is transferred to a tared dish, evaporated at 70 F, dessicated to a constant weight, and weighed to the nearest 0.1 mg.

7.4.6.7 The chloroform and ether extractions (container No. 6) are transferred to a tared dish, evaporated at 70 F, dessicated to a constant weight, and weighed to the nearest 0.1 mg.

7.4.6.8 Blanks should be run on all liquids used in the above procedures.

7.5 Weighing and Handling Procedures

7.5.1 Number the filter on the smooth side (a stamp with rubber stamp ink is useful for this purpose) and heat in a laboratory drying oven for 2 hours at 215 F (102 C). After removal from the oven, immediately place the filters in individual, petri dishes for cooling to room temperature in a dessicator. After cooling, remove the filters one at a time, and weigh to the nearest 0.1 mg. Transport the weighed filters in covered petri dishes to the holders.

7.5.2 After a filter has been used for sampling, return it to the covered petri dish (sample side up) for transportation back to the laboratory. If the flue being sampled contains very hot gases, allow the filter to cool in the holder before it is transferred to a petri dish. Take care that none of the collected material is lost during transportation back to the laboratory. Reweigh the used filters using the previously described heating and weighing procedures (7.5.1).

7.5.3 Sand the lip and outside of the new Alundum thimbles, wash in distilled water, fire at 1000 F for 1 h, cool, and store until needed.

7.0 PROCEDURE (CONT'D)

Note 3 - Sand the lip of the Alundum thimble using fine sandpaper. Care must be taken to sand the edge to remove loose material and to make a flat surface in one plane normal to the long axis of the thimble. If high points or thin edges are created, the seat against the gasket will be uneven and when the holder is tightened the thimble may crack.

7.5.4 When preparing the Alundum thimble or packed glass tube for use, number the outside of the Alundum thimbles, or the inside of the packed glass tube ground-glass joint, with pencil. Clean the outside of the packed tubes thoroughly and place the thimbles or packed tubes in uncapped glass jars and heat overnight at 215 F (102 C) (8-oz glass jars have been found suitable for Alundum thimbles). Remove the jars from the oven, immediately cap them and allow the jars and thimbles to cool to room temperature. Place the thimble or packed tube in a previously weighed weighing bottle, cover, and weigh to the nearest 0.1 mg. Return the thimble or packed tube to the jar and re-cap the jar.

7.5.5 Weigh the filters, particulate collectors, in a laboratory on an analytical balance capable of weighing to the nearest 0.1 mg.

7.5.6 Transport the Alundum thimbles or packed glass tubes to and from the site in plastic jars or in glass jars lined with crushed aluminum foil or other suitable material to prevent the thimbles or packed tubes from striking against the inside of the jar. Take care that the thimble is not chipped or cracked in transit and that none of the sample is lost. If

7.0 PROCEDURE (CONT'D)

the flue gas being sampled is very hot, allow the thimble to cool in the holder. After the thimble or packed tube is cool, place it in its transport container. Clean the outside of the packed tube before heating and weighing. Reweigh the thimbles or packed tubes using the previously described heating and weighing procedure.

Note 4 - Under most conditions, Alundum thimbles may be cleaned for reuse by the following procedure: brush out the collected sample, boil the thimbles for 2 h in hydrochloric acid (1 + 1), remove the thimbles, rinse off excess acid, boil twice in distilled water, fire at 1000 F (538 C) for 1 h, cool, and store until needed.

7.6 Sample Weights Determination

7.6.1 The sources of various samples which have been obtained by this method can be briefly summarized as follows:

Source	Paragraphs
Particulates	
1. Particulate Collector	7.4.5.1, 7.5.5
2. Particulate Collector holder, probe, and vacuum hose dust	
a. Acetone wash	7.4.5.2, 7.4.6.3
b. Water wash (inorganic salts)	7.4.5.3, 7.4.6.4
3. Filter particulate	7.4.5.4, 7.5.5
Collected Residue	
4. Impingers	

7.0 PROCEDURE (CONT'D)

Source	Paragraphs
Collected Residue	
4. Impingers (Cont'd)	
a. Impinger liquid and water washing	7.4.5.5, 7.4.6.2, 7.4.6.5
b. Impinger acetone washings	7.4.5.6, 7.4.6.6
c. Organic extraction	7.4.6.1, 7.4.6.7

7.6.2 Determine the particulate sample weights by subtracting the tare weights from the gross weights of the particulate collector (7.5.5) and filter (7.5.5). Add to this the material from paragraphs 7.4.6.3 and 7.4.6.4 adjusted to remove any weight contributed by the liquid used (7.4.6.8).

7.6.3 Determine the collected residue by adding the residues from 7.4.6.5, 7.4.6.6 and 7.4.6.7 after adjusting them to remove any weight contributed by the liquid used (7.4.6.8).

8.0 CALCULATIONS OF PARTICULATE AND COLLECTED RESIDUE CONCENTRATIONS, EMISSION RATES, AND COLLECTION EFFICIENCIES

8.1 After the test has been completed the results must be reported. Separately express the particulate and collected residue concentrations in grain per cubic foot of dry gas (gr/Scfd).

8.2 Determine the weight of the samples (Y) and (Y_1) as shown in 7.6. Calculate the gas volume sampled (meter volume) adjusted to standard conditions dry by using the following equation:

$$\mathrm{VST\ PD} = (V_m - V_w)(C_m)\ (530/T_{mavg})(P_{mavg}/29.92) \qquad (14)$$

8.0 (CONT'D)

8.3 Determine the particulate concentration:

$$Z_{STPD} = (Y)(0.01543)/V_{ST\ PD} \qquad (15)$$

8.3.1 Determine the collected residue concentration:

$$Z_{1ST\ PD} = (Y_1)(0.01543)/V_{ST\ PD} \qquad (16)$$

8.4 Calculate the particulate emission rate:

$$E = (Z_{ST\ PD})(Q_{ST\ PD})(60)/7000 \qquad (17)$$

8.4.1 Calculate the collected residue emission rate:

$$E_1 = (Z_{1ST\ PD})(Q_{ST\ PD})(60)/7000 \qquad (18)$$

8.5 Determine the particulate collection efficiency (in percent) of the collector:

$$\text{Collection efficiency} = [(E_{in}-E_{out})/E_{in}]X100 \qquad (19)$$

TABLE 1 Minimum Number of Sub Areas for Rectangular Flues

Inside Cross-Sectional Area of Flue, ft²	Minimum Number of Test Points
1[a] to 2	4
Over 2 to 12	6 to 24
Over 12	Over 24

[a] In-stack sampling equipment is not recommended for flues smaller in cross-sectional area than 1 ft².

TABLE 2 Minimum Number of Equal Areas for Velocity Measurements in Circular Flues

Flue Diameter, in.	Minimum Number of Equal Areas
12[a] to 24	3
Over 24 to 48	4
Over 48 to 72	5
Over 72	6 or more

[a] In-stack sampling equipment is not recommended for flues smaller than 12 in. in diameter.

APPENDIX

A1. The following tables (A1 and A2) have been included for the convenience of the reader.

TABLE A1 Vapor Pressures of Water, in. Hg

Temperature, Deg F	0	1	2	3	4	5	6	7	8	9
−20	0.0126	0.0119	0.0112	0.0106	0.0100	0.0095	0.0089	0.0084	0.0080	0.0075
−10	0.0222	0.0209	0.0199	0.0187	0.0176	0.0168	0.0158	0.0150	0.0142	0.0134
−5	0.0376	0.0359	0.0339	0.0324	0.0306	0.0289	0.0275	0.0259	0.0247	0.0233
0	0.0376	0.0398	0.0417	0.0441	0.0463	0.0489	0.0517	0.0541	0.0571	0.0598
10	0.0631	0.0660	0.0696	0.0728	0.0768	0.0810	0.0846	0.0892	0.0932	0.0982
20	0.1025	0.1080	0.1127	0.1186	0.1248	0.1302	0.1370	0.1429	0.1502	0.1567
30	0.1647	0.1716	0.1803	0.1878	0.1955	0.2035	0.2118	0.2203	0.2292	0.2383
40	0.2478	0.2576	0.2677	0.2782	0.2891	0.3004	0.3120	0.3240	0.3364	0.3493
50	0.3626	0.3764	0.3906	0.4052	0.4203	0.4359	0.4520	0.4686	0.4858	0.5035
60	0.5218	0.5407	0.5601	0.5802	0.6009	0.6222	0.6442	0.6669	0.6903	0.7144
70	0.7392	0.7648	0.7912	0.8183	0.8462	0.8750	0.9046	0.9352	0.9666	0.9989
80	1.032	1.066	1.102	1.138	1.175	1.213	1.253	1.293	1.335	1.378
90	1.422	1.467	1.513	1.561	1.610	1.660	1.712	1.765	1.819	1.875
100	1.932	1.992	2.052	2.114	2.178	2.243	2.310	2.379	2.449	2.521
110	2.596	2.672	2.749	2.829	2.911	2.995	3.081	3.169	3.259	3.351
120	3.446	3.543	3.642	3.744	3.848	3.954	4.063	4.174	4.289	4.406
130	4.525	4.647	4.772	4.900	5.031	5.165	5.302	5.442	5.585	5.732
140	5.881	6.034	6.190	6.350	6.513	6.680	6.850	7.024	7.202	7.384
150	7.569	7.759	7.952	8.150	8.351	8.557	8.767	8.981	9.200	9.424
160	9.652	9.885	10.12	10.36	10.61	10.86	11.12	11.38	11.65	11.92
170	12.20	12.48	12.77	13.07	13.37	13.67	13.98	14.30	14.62	14.96
180	15.29	15.63	15.98	16.34	16.70	17.07	17.44	17.82	18.21	18.61
190	19.01	19.42	19.84	20.27	20.70	21.14	21.59	22.05	22.52	22.99
200	23.47	23.96	24.46	24.97	25.48	26.00	26.53	27.07	27.62	28.18
210	28.75	29.33	29.92	30.52	31.13	31.75	32.38	33.02	33.67	34.33
220	35.00	35.68	36.37	37.07	37.78	38.50	39.24	39.99	40.75	41.52
230	42.31	43.11	43.92	44.74	45.57	46.41	47.27	48.14	49.03	49.93
240	50.84	51.76	52.70	53.65	54.62	55.60	56.60	57.61	58.63	59.67
250	60.72	61.79	62.88	63.98	65.10	66.23	67.38	68.54	69.72	70.92
260	72.13	74.36	74.61	75.88	77.16	78.46	79.78	81.11	82.46	83.83
270	85.22	86.63	88.06	89.51	90.97	92.45	93.96	95.49	97.03	98.61
280	100.2	101.8	103.4	105.0	106.7	108.4	110.1	111.8	113.6	115.4
290	117.2	119.0	120.8	122.7	124.6	126.5	128.4	130.4	132.4	134.4
300	136.4	138.5	140.6	142.7	144.8	147.0	149.2	151.4	153.6	155.9
310	158.2	160.5	162.8	165.2	167.6	170.0	172.5	175.0	177.5	180.0
320	182.6	185.2	187.8	190.4	193.1	195.8	198.5	201.3	204.1	206.9
330	209.8	212.7	215.6	218.6	221.6	224.6	227.7	230.8	233.9	237.1
340	240.3	243.5	246.8	250.1	253.4	256.7	260.1	263.6	267.1	270.6
350	274.1	277.7	281.3	284.9	288.6	292.3	296.1	299.9	303.8	307.7
360	311.6	315.5	319.5	323.5	327.6	331.7	335.9	340.1	344.4	348.7
370	353.0	357.4	361.8	366.2	370.7	375.2	379.8	384.4	389.1	393.8
380	398.6	403.4	408.2	413.1	418.1	123.1	428.1	433.1	438.2	443.4
390	448.6	453.9	459.2	464.6	470.0	475.5	481.0	486.6	492.2	497.9
400	503.6	509.3	515.1	521.0	526.9	532.9	538.9	545.0	551.1	557.3

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TABLE A2 Miscellaneous Constants

0.0749 = weight of one cubic foot of dry air at standard conditions, pounds
13.6 = specific gravity of mercury
18 = molecular weight of water
28 = molecular weight of carbon monoxide and nitrogen
29.92 = atmospheric pressure at sea level, in. Hg
32 = molecular weight of oxygen
44 = molecular weight of carbon dioxide
387 = volume of a pound mole of a gas at standard conditions, cubic feet
453.6 = number of grams in one pound
530 = standard temperature, degrees Rankine
7000 = number of grains in one pound

TABLE 3 Equal Area Zones for Velocity Traverses in Round Ducts

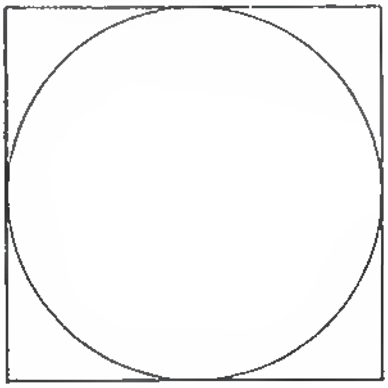
Duct Inside		No. of Equal Zones	Area of Each Zone, ft²	Radius to Traverse Point, in.							
Diameter, in.	Area ft²			Point 1	Point 2	Point 3	Point 4	Point 5	Point 6	Point 7	Point 8
8	0.3491	2	0.1746	2	3½						
10	0.5454	2	0.2725	2½	4⅜						
12	0.7854	2	0.3925	3	5¼						
		3	0.2618	2½	4¼	5½					
14	1.069	2	0.534	3½	6						
		3	0.356	2⅞	5	6⅜					
15	1.227	2	0.6134	3⅝	6½						
		3	0.409	3	5⅜	6⅞					
16	1.396	2	0.7085	4	7						
		3	0.465	3¼	5⅝	7¼					
18	1.767	2	0.883	4½	7⅞						
		3	0.589	3¾	6⅜	8¼					
20	2.182	3	0.727	4⅛	7⅛	9¼					
		4	0.535	3⅝	6⅛	7⅞	9⅜				
22	2.640	3	0.880	4½	7¾	10					
		4	0.66	3⅞	6¾	8⅝	10¼				
24	3.142	3	1.047	4⅞	8½	11					
		4	0.785	4¼	7⅞	9½	10¼				
26	3.687	3	1.229	5⅜	9¼	12					
		4	0.922	4⅝	8	10¼	12⅛				
28	4.276	3	1.425	5⅜	9⅞	12¾					
		4	1.07	5	8⅝	11	13⅛				
30	4.909	4	1.227	5⅜	9¼	11⅞	14				
		5	0.982	4⅝	8¼	10⅝	12½	14¼			
32	5.585	4	1.396	5⅝	9¾	12⅝	14⅞				
		5	1.117	5	8¾	11⅜	13⅜	15¼			
36	7.069	4	1.767	6⅜	11	14¼	16¾				
		5	1.416	5⅝	9⅞	12¾	15	17⅛			
42	9.621	4	2.405	7½	12¾	16⅝	19⅝				
		5	1.924	6½	11½	14⅞	17½	19⅞			
48	12.51	4	3.13	8½	14⅝	19	22⅜				
		5	2.50	7½	13⅛	17	20	22⅞			
		6	2.085	7	12	15½	18⅜	20¾	23		
54	15.9	5	3.18	8½	14¾	19⅛	22⅝	25⅝			
		6	2.65	7¾	13½	17½	20⅝	23¼	25⅞		
60	19.63	5	3.93	9½	16⅜	21¼	25⅛	28½			
		6	3.27	8¾	15	19⅜	22⅞	25⅞	28¾		
66	23.76	5	4.75	10⅜	18⅛	23⅜	27⅝	31¼			
		6	3.96	9⅝	16½	21⅜	25¼	28½	31⅝		
72	28.27	5	5.65	11⅜	19¾	25½	30⅛	34⅛			
		6	4.71	10½	18	23¼	27½	31¼	34½		
78	33.18	6	5.53	11¼	19½	25¼	29⅞	33⅞	37⅜		
		7	4.74	10⅜	18	23⅜	27⅝	31¼	34⅝	37⅝	
84	38.48	6	6.41	12¼	21	27⅛	32⅛	36⅜	40⅜		
		7	5.50	11¼	19½	25⅛	29¾	33⅝	37¼	40½	
90	44.18	6	7.36	13⅛	22½	29⅛	34⅜	39	43¼		
		7	6.31	12	20⅞	26⅞	31⅞	36⅛	39⅞	43⅜	
96	50.27	6	8.38	14	24	31	36⅝	40⅝	46		
		7	7.18	12⅞	22¼	28¾	34	38½	42½	46¼	
108	63.61	6	10.60	15⅝	27	34⅞	41¼	46¾	51¾		
		7	9.09	14⅜	25	32¼	38¼	43¼	47⅞	52	
120	78.54	6	13.09	17⅜	30	38¾	45⅞	52	57½		
		7	11.22	16	27¾	35⅞	42⅜	48⅛	53⅛	57⅞	
		8	9.82	15	26	33½	39⅝	45	49¾	54⅛	58⅛
132	95.03	6	15.84	19⅛	33	42⅝	50¼	57⅛	63¼		
		7	13.57	17⅝	30½	39½	46⅝	52⅞	58½	63⅝	
		8	11.88	16½	28⅝	36⅞	43⅝	49½	54¾	59½	63⅞
144	113.10	6	18.85	20⅞	36	46½	55	62⅜	69		
		7	16.16	19¼	33⅜	43	50⅞	57¾	63¾	69⅜	
		8	14.14	18	31⅛	40¼	47⅝	54	59¾	64⅞	69¾

TABLE 4 Velocity Traverse

Test No. ______________
Location: ______________
____
Type Pitot Tube: ______________
Date: __________ Time: ______
Calc. By: ______________

Point, n	Position, in.	Reading h_n, in. H_2O Run 1	Reading h_n, in. H_2O Run 2	h_n Average	$\sqrt{h_n}$	u_n, fpm
Total		XXX		XXX		
Average		XXX		XXX		

Stack Dimensions: ______________ Radius: __________ Temp.: __________ Static Pressure: __________
Barometric Pressure: ______________



Equal Area Zones for Velocity Traverse
% of the flue radius from center to test point

Point from Center	2	3	4	5	6
1	50.0	41.2	35.8	31.2	29.2
2	87.6	70.6	61.0	54.6	50.0
3		91.2	79.0	71.0	64.6
4			93.4	83.6	76.4
5				95.6	86.6
6					96.0

TABLE 5 Particulate Collectors Recommended for Use in Sampling Conditions Indicated

Condition No.	Expected Sample Weight		Flue Temperature			Liquid Droplets Present		Collector Recommended (The figure in parentheses is the minimum sample weight recommended)
	<100 mg	>100 mg	<200 F	200 to 300 F	300 to 800 F	Yes	No	
1	x		x			x		Versapor[a] (24 mg)
2	x			x		x		Versapor[a] (56 mg)
3	x				x	x		packed tube[c] (20 mg)
4	x		x				x	glass fiber[b] (11 mg) Versapor[a] (24 mg)
5	x			x			x	glass fiber[b] (11 mg) Versapor[a] (56 mg)
6	x				x		x	glass fiber[b] (11 mg)
7		x	x			x		packed tube[c] (20 mg)
8		x		x		x		packed tube[c] (20 mg)
9		x			x	x		packed tube[c] (20 mg)
10		x	x				x	Alundum thimble[d] (100 mg)
11		x		x			x	Alundum thimble[d] (100 mg)
12		x			x		x	Alundum thimble[d] (100 mg)

The following have been found satisfactory for this purpose:

[a] = Versapor filter 6429 supplied by Gelman Instrument Co., 2 in. diameter.

[b] = Glass fiher filter Type A supplied by Gelman Instrument Co., 2 in. diameter.

[c] = See 6.2.3.3 (tentative).

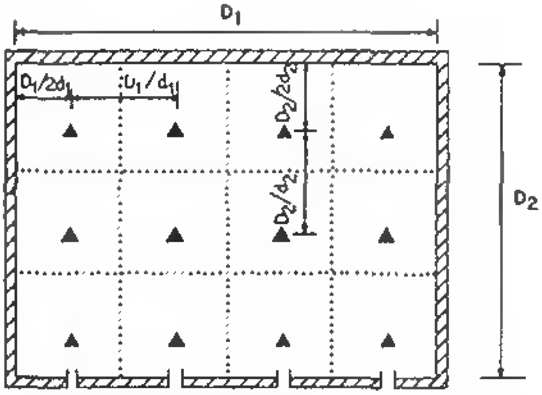
[d] = RA 360 Norton (5).

TABLE 6 Source Sampling Data

Type filter: ____________
Filter No.: ____________
Condensed water: ______ ml

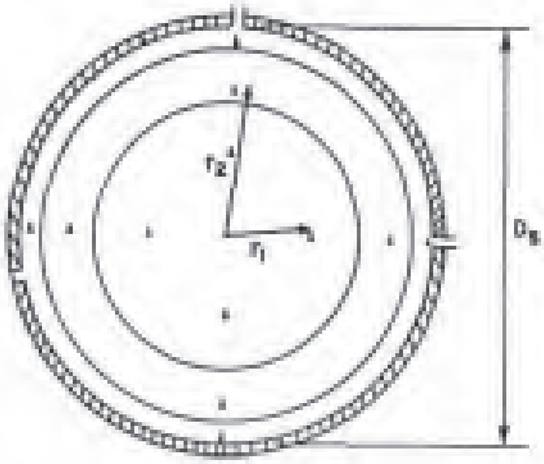
Test No.: ____________
Location: ____________
____
Date: ____________
Time: ____________
Collector: ____________

Point	Time, min	Meter Data					Absolute Pressure, $P_b - P'_m$	Velocity Pressure at "N" h_n, in. H_2O	$\sqrt{h_n}$	Velocity at Nozzle, u_n, fpm	Desired Flow at Meter, cfm	Stack Temperature, deg F
		Reading, ft³	Volume per time period ft³	Meter Temperature, dry bulb, deg F	Meter Temperature, wet bulb, deg F	Meter Gage Vacuum Pressure, in. Hg P'_m						
Total		XXX						XXX				



d_1—number of areas across flue width
d_2—number of areas across flue perpendicular to width

FIG. 1 Cross Section of Rectangular Flue Divided into Twelve Equal Areas with Traverse Points Located at the Center of each Area.



The location and number of traverse points for a flue of a given diameter can be determined by referring to Table 3 or Eq 1.

FIG. 2 Cross Section of Circular Flue Divided into Three Concentric Equal Areas, Showing Location of Traverse Points.

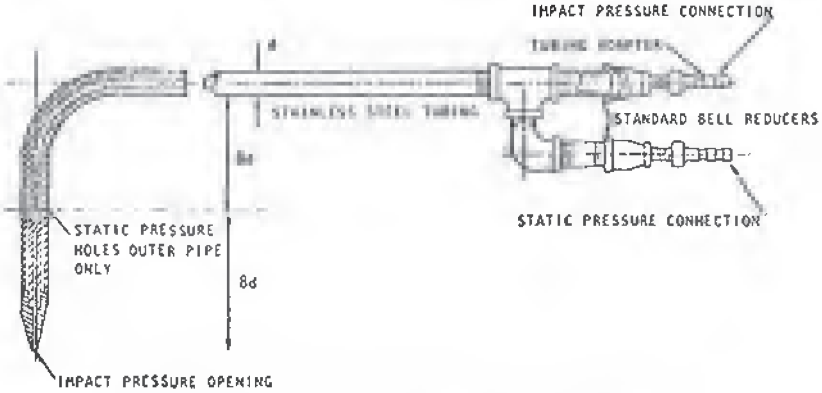


FIG. 3 Approximate Standard Pitot Tube Details.

FIG. 4 Type S Pitot Tube.

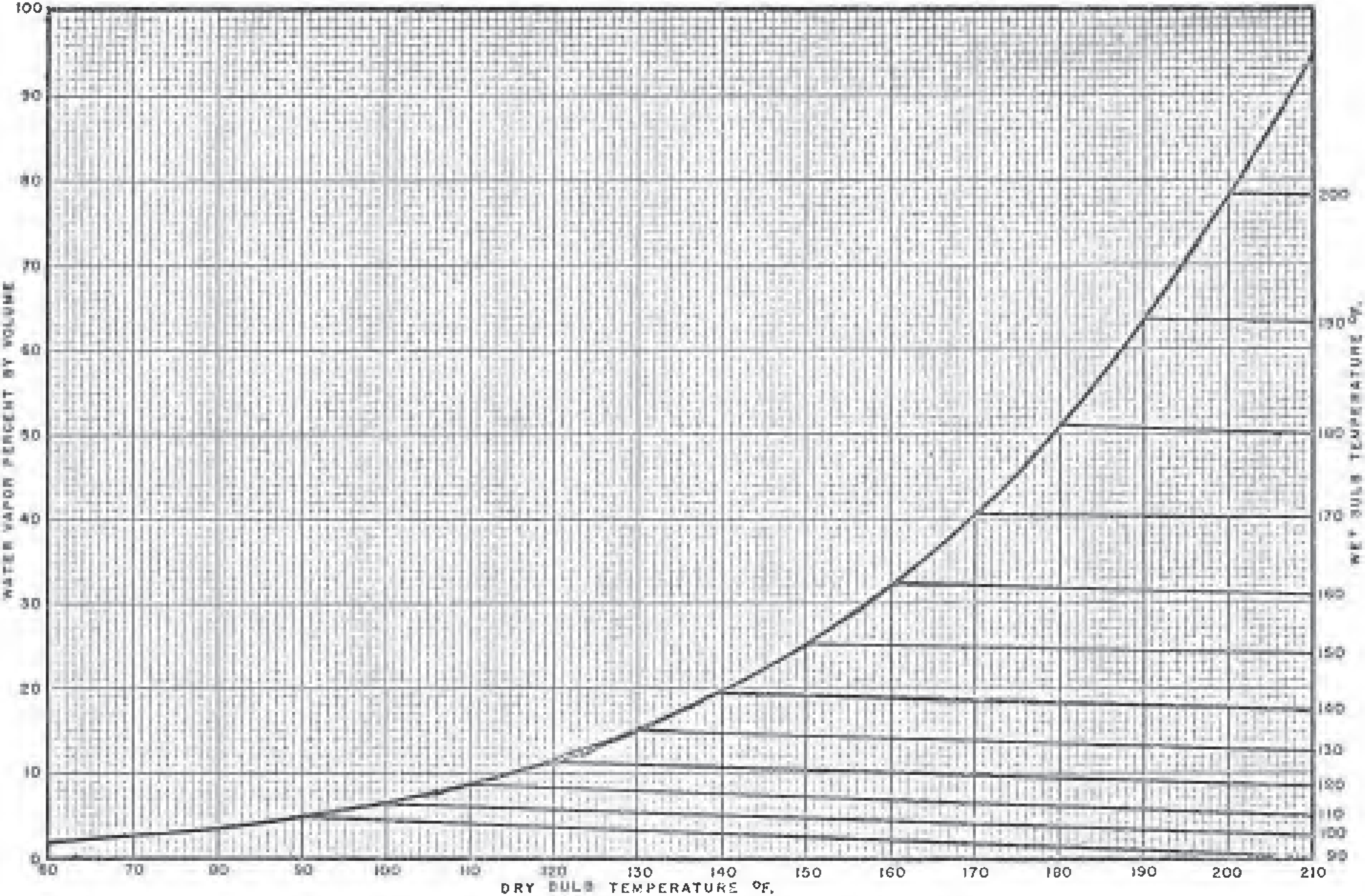
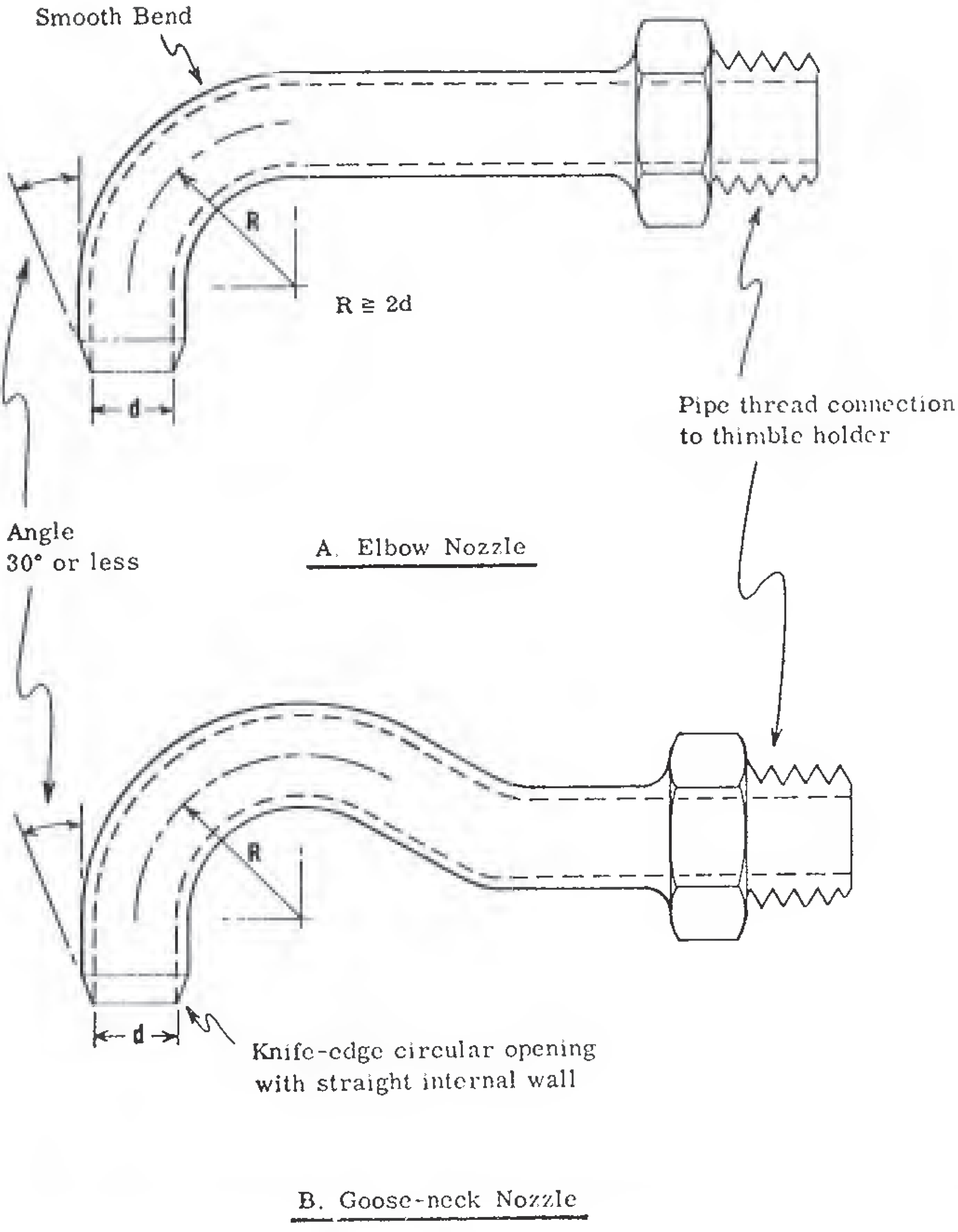


FIG. 5 High-Temperature Psychometric Chart for Air-Water Vapor Mixtures at 1 atm (29.921 in. Hg).



A. Elbow Nozzle

B. Goose-neck Nozzle

FIG. 6 Typical Sampling Nozzles.

FIG. 7 Typical Holders for Alumdum Thimbles.

FIG. 8 Typical Holder for Flat, Round Filters.

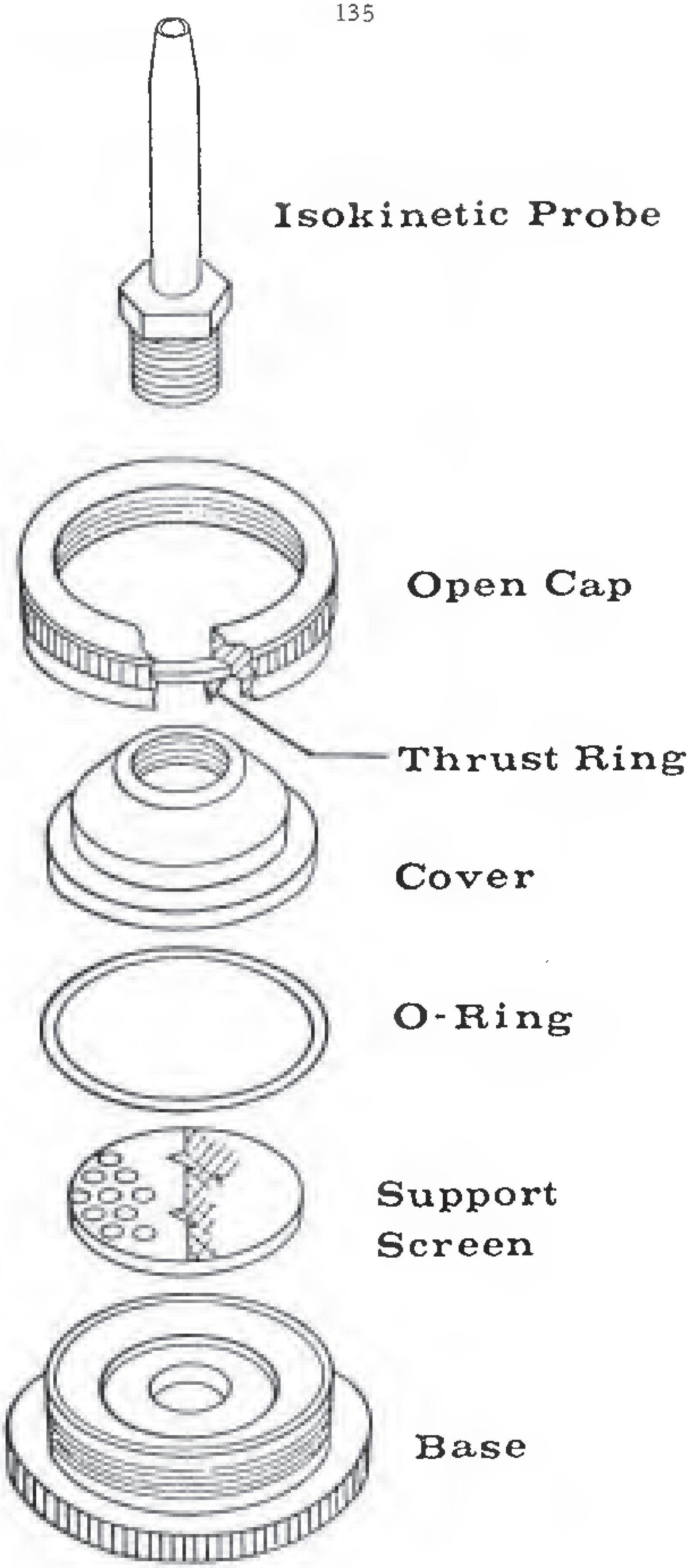


FIG. 9 Exploded Diagram of Holder for Flat, Round Filters.

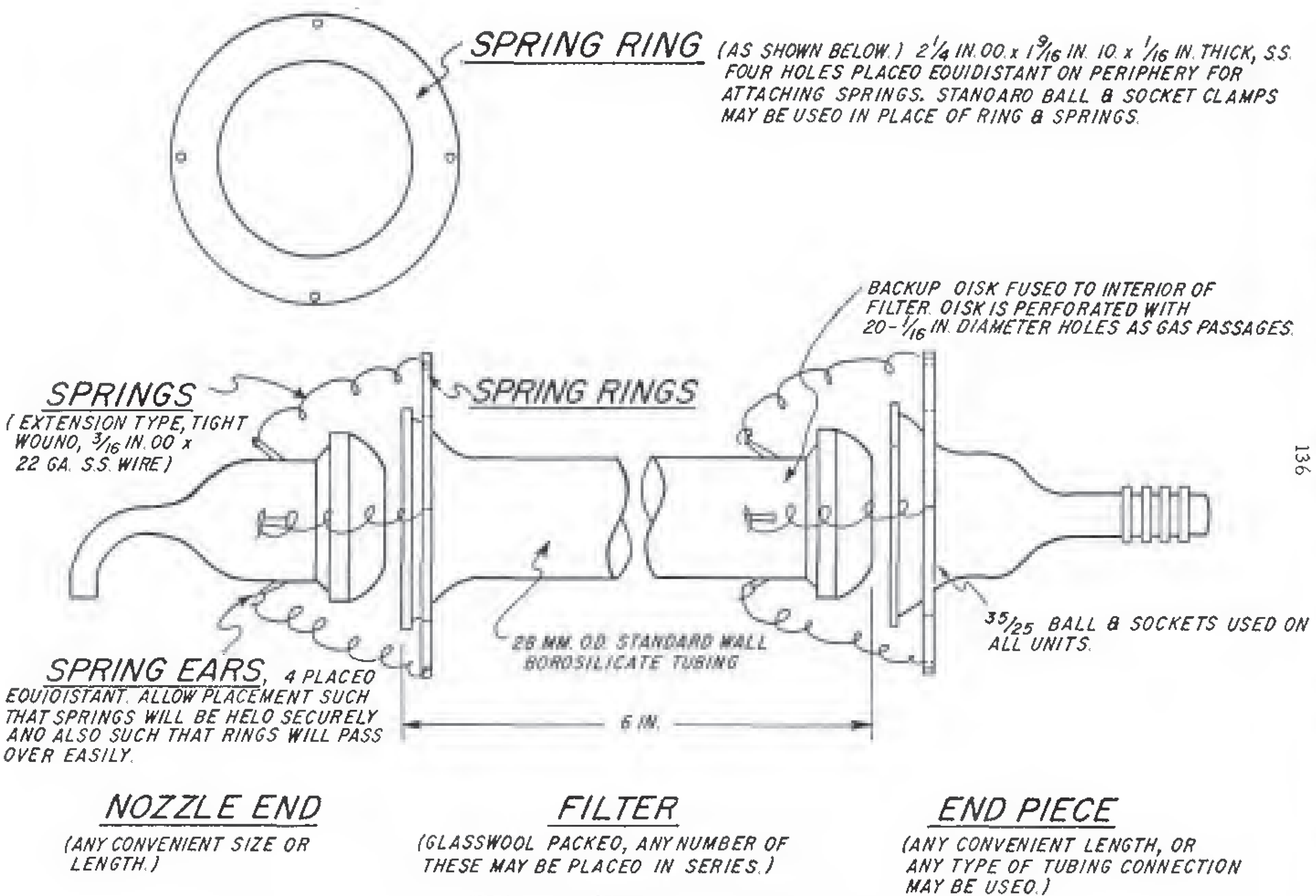


FIG. 10 Glass Wool Filter Assembly (Exploded View).

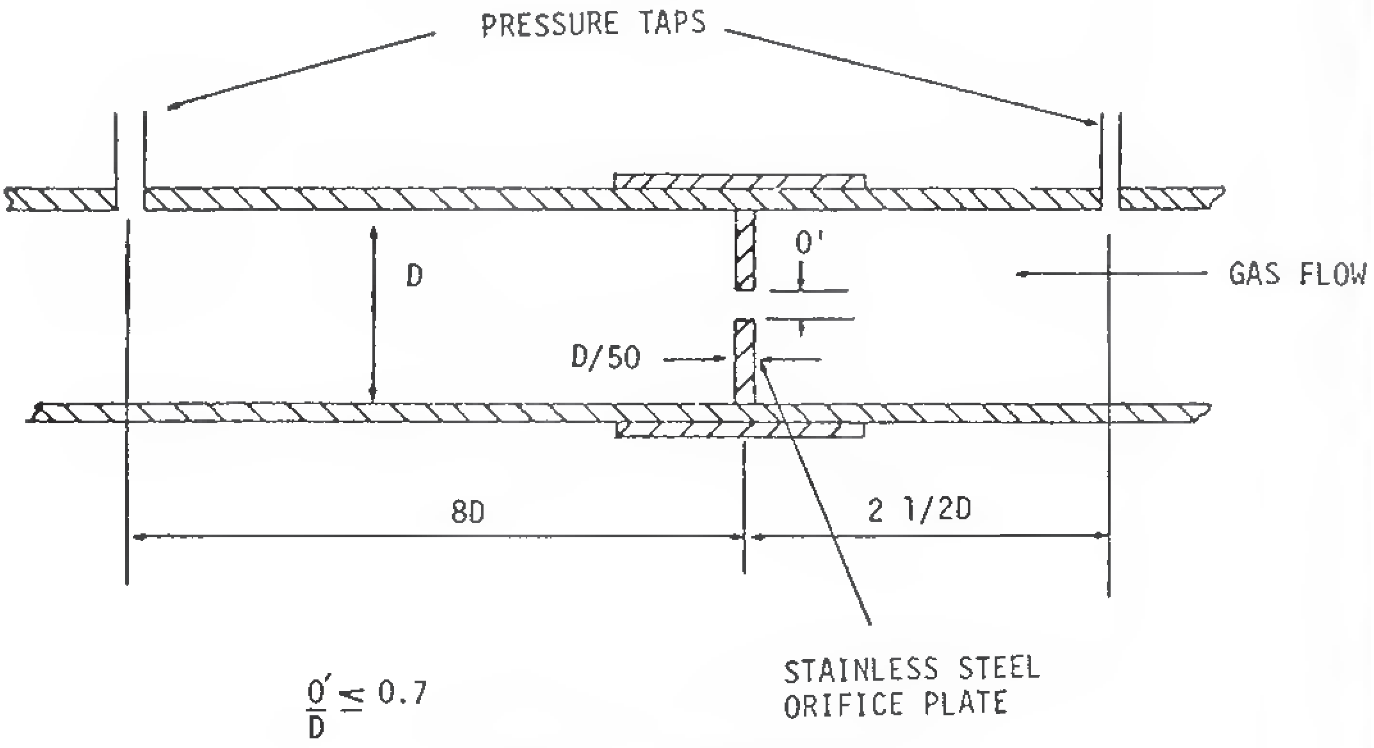


FIG. 11 Orifice Meter.

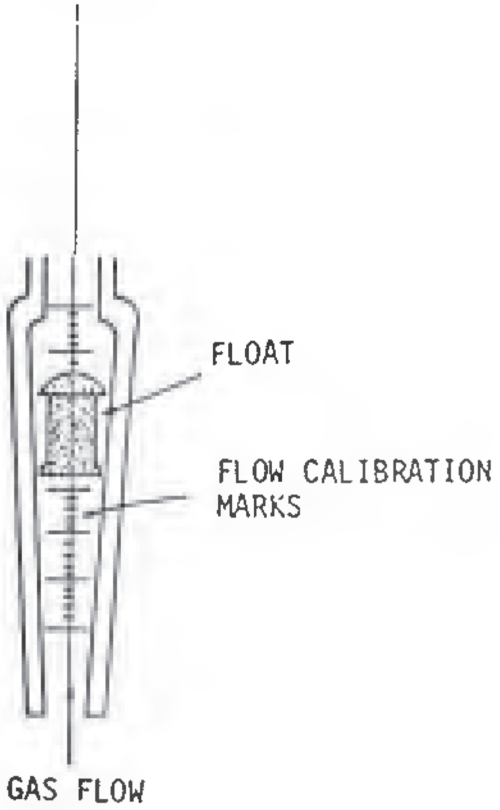
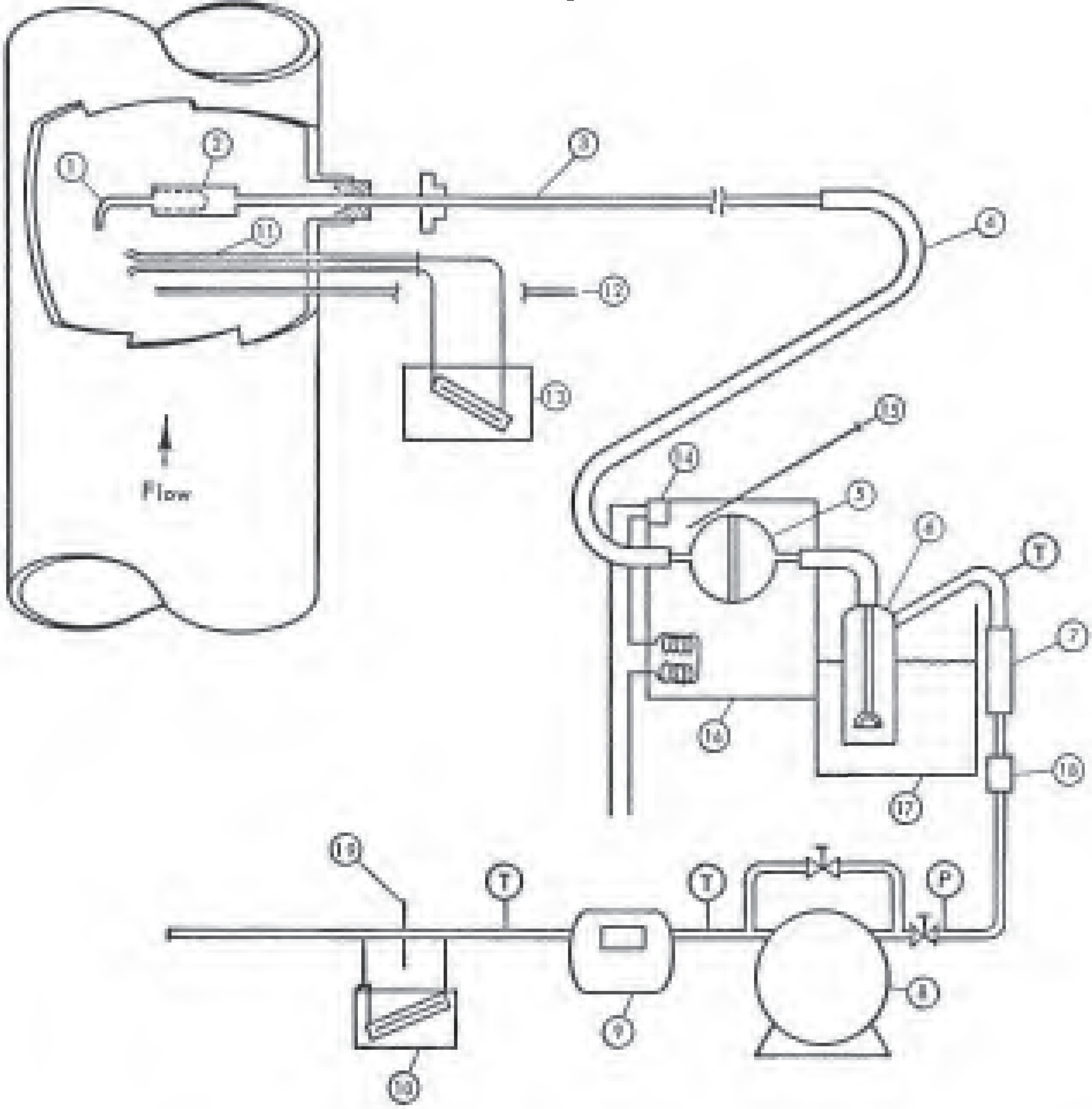


FIG. 12 Rotameter.



T Temperature measurement

P Pressure measurement

1. Nozzle
2. Thimble holder and thimble
3. Probe
4. High vacuum line
5. Filter holder and filter
6. Impinger (s)
7. Drying tube
8. Air tight vacuum pump
9. Gas meter
10. Manometer
11. S-type pitot tube
12. Thermocouple
13. Manometer
14. Thermoswitch
15. Thermometer
16. Heated box
17. Ice bath
18. Quick disconnect
19. Orifice meter

FIGURE 13 SAMPLING TRAIN FOR COLLECTABLE RESIDUE

APPENDIX B

PRACTICAL APPLICATIONS OF BETWEEN-LABORATORY STANDARD ERROR MEASURES DERIVED FROM THE THRESHOLD STUDY

PRACTICAL APPLICATIONS OF BETWEEN-LABORATORY STANDARD ERROR MEASURES DEPRIVED FROM THE THRESHOLD STUDY

The relationship developed in this report for estimating the between-laboratory standard error are useful as a means of quantifying uncertainty associated with the measurement process for the test method. In particular, they allow for the calculation of confidence intervals which represent the best estimate of the range in which the true value being measured lies. For example a 95 percent confidence interval for the true measure would be calculated as $m \pm 1.96\ s$, where s is estimated from the appropriate regression equation reported herein, and m is the best estimate of the true measure obtained from the test method.

As an illustration, if any single laboratory were measuring particulate concentrations and obtained a value of 4.350 grains/SCFD, the between laboratory standard error would be estimated as

$$\begin{aligned}\hat{s} &= -0.0003 + 0.060\ m\\ &= -0.0003 + 0.060\ (4.350)\\ &= 0.261 \text{ grains/SCFD.}\end{aligned}$$

A 95 percent confidence interval for the measurement of particulate concentration by any laboratory would be estimated as the range

$$\begin{aligned}m \pm 1.96\ \hat{s} &= 4.350 \pm 1.96\ (0.261)\\ &= (3.838,\ 4.862).\end{aligned}$$

Thus if a large number of laboratories had made measurements of particulate concentration at the same time, we would expect that 95 percent of these measurements would be within the range of 3.838 to 4.862 grains/SCFD, given the sampling conditions at the time that the actual measurement was made.

As a further illustration, suppose three laboratories had made simultaneous measures of emission rate, and obtained values of 975, 867, and 903 lbs/hr. The arithmetic average of these determinations is 915 lbs/hr. The best estimate of the between laboratory standard error is

$$\begin{aligned}\hat{s} &= 0.290 + 0.067\ (915)\\ &= 61.595 \text{ lbs/hr.}\end{aligned}$$

A 95 percent confidence interval for the measurement of emission rate by any laboratory is estimated as $m \pm 1.96\hat{s} = 915 \pm 1.96\ (61.595)$

$$= (794.3,\ 1035.7).$$

The interval from 794.3 to 1035.7 lbs/hr represents the range in which 95 percent of the simultaneous determinations of emission rate by any of a large number of laboratories would be expected to fall, given the sampling conditions at the time of actual measurement.

The estimated between-laboratories standard error relationships can also be useful in determining conformance source performance requirements. For example, suppose a laboratory determines that the particulate concentration is 0.021 grains/SCFD, using the test method. Because of the inherent variability between laboratories, another laboratory may determine that the concentration is above 0.021 and still another laboratory may have determined that the concentration is below 0.021 grains/SCFD. Suppose that a requirement is established that the particulate concentration in the emissions does not exceed 0.020 grains/SCFD. Given the actual determination of 0.021, what is the probability that the determination exceeds the limit, or equivalently, what percent of determinations by a large number of laboratories would exceed the limit? The best information available is that laboratory determinations are distributed around 0.021 with a standard error of S_T (between-laboratory) $= -0.0003 + 0.060\ (0.021)$

$$= 0.001 \text{ grains/SCFD.}$$

The probability that any laboratory's determination will exceed the 0.020 grains/SCFD level is calculated as

$$P\ (X \geq 0.020) = P\ \left(\frac{X-m}{S_T \text{ (between-laboratory)}} \geq \frac{0.020-0.021}{0.001}\right)$$

$$= P\ (Z \geq -1.000)$$

where Z is a standardized normal variate. From tables of the normal distribution,

$$P(Z \geq -1.000) = 0.8413 \quad .$$

Thus the probability that any laboratory determination will exceed the standard is 0.84, or equivalently, given a large number of laboratories making determinations, 84 percent of these laboratory determinations would have resulted in determinations in excess of 0.02 grains/SCFD. This percentage reflects the certainty with which it can be stated that a particular level, in this case 0.02 grains/SCFD, has been exceeded. In some instances, greater certainty may be desired before judging that a determination exceeds a limiting value. For example a 90 percent probability may be desired, so that the likelihood of wrongfully declaring a determination in excess of a limit is small, in this case 10 percent.

Alternatively several laboratories may make concurrent determinations, in which case the probability of any laboratory's determination exceeding a limit could be calculated under any hypothesized value for the true concentration. Using the binomial distribution, the parameter "p" would be calculated as above for the true concentration. If three laboratories were making simultaneous determinations, the probability of <u>at least</u> one laboratory exceeding the standard is calculated as

$$P^* = \sum_{i=1}^{m} \binom{n}{i} p^i (1-p)^{n-i} = \sum_{i=1}^{3} \binom{3}{i} (0.84)^i (0.16)^{3-i}$$

This is equivalent to the complement of the probability that no laboratory determination exceeds the limit, ie,

$$\begin{aligned} P &= 1.00 - \binom{3}{0} (0.84)^0 (0.16)^3 \\ &= 1.00 - (1)(1.00)(0.004) \\ &= 0.996 \; . \end{aligned}$$

Thus if three laboratories are making determinations simultaneously, and the true concentration is at 0.021 grains/SCFD, it is almost certain that at least one laboratory's determination would be greater than 0.2 grains/SCFD.

---

* $\binom{n}{i}$ = number of ways of selecting i items from n items

$$= \frac{n!}{i!\,(n-i)!} \; .$$

APPENDIX C

SUGGESTED FORMS FOR RECORDING AND CALCULATING PARTICULATE AND COLLECTED RESIDUE SAMPLING DATA

FIELD DATA

PLANT ____________
DATE ____________
SAMPLING LOCATION ____________
SAMPLE TYPE ____________
RUN NUMBER ____________
OPERATOR ____________
AMBIENT TEMPERATURE ____________
BAROMETRIC PRESSURE ____________
STATIC PRESSURE, (P_s) ____________
FILTER NUMBER (s) ____________

PROBE LENGTH AND TYPE ____________
NOZZLE I.D. ____________
ASSUMED MOISTURE, % ____________
SAMPLE BOX NUMBER ____________
METER BOX NUMBER ____________
METER $\Delta H_{@}$ ____________
C FACTOR ____________
PROBE HEATER SETTING ____________
HEATER BOX SETTING ____________
REFERENCE Δp ____________

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY ________ MINUTES

TRAVERSE POINT NUMBER	SAMPLING TIME, min / CLOCK TIME (24-hr CLOCK)	GAS METER READING (V_m), ft^3	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
				DESIRED	ACTUAL		INLET $(T_{m\ in})$, °F	OUTLET $(T_{m\ out})$, °F			

COMMENTS:

EPA (Dur) 235
4 72

ANALYTICAL DATA

PLANT ____________________

DATE ____________________

SAMPLING LOCATION ____________________

SAMPLE TYPE ____________________

RUN NUMBER ____________________

SAMPLE BOX NUMBER ____________________

CLEAN-UP MAN ____________________

COMMENTS:

FRONT HALF

LABORATORY RESULTS

ACETONE WASH OF NOZZLE, PROBE, CYCLONE (BYPASS), FLASK, FRONT HALF OF FILTER HOLDER	CONTAINER ________	____________ mg
FILTER NUMBER ________ ________ ________ ________ ________ ________	CONTAINER ________	____________ mg
	FRONT HALF SUBTOTAL	____________ mg

BACK HALF

IMPINGER CONTENTS AND WATER WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER	CONTAINER ________	____________ mg
	ETHER-CHLOROFORM EXTRACTION	____________ mg
ACETONE WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER	CONTAINER ________	____________ mg
	BACK HALF SUBTOTAL	____________ mg
	TOTAL WEIGHT	____________ mg

MOISTURE

IMPINGERS

FINAL VOLUME ________ ml

INITIAL VOLUME ________ ml

NET VOLUME ________ ml

SILICA GEL

FINAL WEIGHT ________ g ________ g ________ g

INITIAL WEIGHT ________ g ________ g ________ g

NET WEIGHT ________ g ________ g ________ g

TOTAL MOISTURE ____________ g

EPA (Dur) 231
4/72

Stack Test Using EPA Methods 2, 3, 4, & 5

Stack Dia. = ______________ Ft. Cp = ______________

Stack Area = A = ______________ Sq. Ft.

Nozzle Dia. = ______________ Inches

Nozzle Area An = ______________ Sq. Ft.

Meter Volume Vm = ______________ Cu. Ft.

Barometer Pb = ______________ "Hg $Ps = Pb \pm \frac{Ps'}{13.6} =$ ______________ "Hg

$\Delta H_{AVG} =$ ______________ "H_2O $Pm = Pb + \frac{\Delta H_{AVG}}{13.6} =$ ______________ "Hg

$(\sqrt{\Delta P})_{AVG} =$ ______________

Meter Temp. Tm = ______________ °R.

Stack Temp. Ts = ______________ °R.

$Vm_{std} = (17.71)\ (Vm) \left(\frac{Pm}{Tm}\right) =$ __________ Cu. Ft.

$Vw_{std} = (.0474)\ (Vlc) =$ __________ Cu. Ft.

$Bwo = \left(\frac{Vw_{std}}{(Vm_{std} + Vw_{std})}\right) (100) =$ ______ %

GAS ANALYSIS

COMPONENT	VOL. FRACT.	X	MOL. WT.	=	MW FRACTION
CO_2		X	44	=	
O_2		X	32	=	
CO		X	28	=	
N_2		X	28	=	

SUM = Md = ______________ lb./lb mole

$Ms = Md\ (1 - Bwo) + 18\ Bwo =$ ______________ lb/lb. mole

$Gs = \frac{Ms}{28.99} =$ ______________

$\%\ EA = \frac{(\%O_2) - 0.5\ (\%CO)}{0.264\ (\%N_2) - (\%O_2) + 0.5\ (\%CO)} \times 100 =$ ______________ %

TEST NUMBER________

Sheet 2 of 3

$$V_s = (85.48)\ (C_p)\ (\sqrt{\Delta P})_{avg} \sqrt{\frac{T_s}{P_s\ M_s}} = \_\_\_\_\_\_\_\_\_\_\_\_\ \text{F.P.S.}$$

$$(\text{F.P.S.})\ (60) = \_\_\_\_\_\_\_\_$$

$$Q_s = 3600\ (1-B_{wo})\ (V_s)\ (A) \left(\frac{530}{T_s}\right) \left(\frac{P_s}{29.92}\right) = \_\_\_\_\_\_\_\_\_\_\_\_\ \text{CFH @ STPD}$$

$$C'_s = (.0154) \left(\frac{M_n}{V_{m\ std}}\right) = \_\_\_\_\_\_\_\_\_\_\_\_\ \text{gr./SCF}$$

$$C_s = (2.205 \times 10^{-6}) \left(\frac{M_n}{V_{m\ std}}\right) = \_\_\_\_\_\_\_\_\_\_\_\_\ \text{lb/SCF}$$

$$I = \frac{(T_s)\ (1.667)\ \left[(.00267)\ (V_{lc}) + \left(\frac{V_m}{T_m}\right)\ (P_m)\right]}{V_s\ P_s\ A_n} = \_\_\_\_\_\_\_\_\ \%$$

NOTE: Acceptable results : if $90\% \leq I \leq 110\%$, the results are acceptable, otherwise, reject the results and repeat the test.

	WEIGHT OF PARTICULATE COLLECTED			
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN	
G. F. Filter			g	
Alundum Thimble			g	
Acetone Wash			g	
		$(\times 10^3)$ Mn = TOTAL =	mg	

CONDENSIBLES COLLECTED

Zw = ____________ mg

	VOLUME OF LIQUID WATER COLLECTED	
	IMPINGER VOLUME ml.	SILICA GEL WEIGHT g.
FINAL		
INITIAL		
LIQUID COLLECTED		

Imp. Vol. Col. + H_2O in Sil. Gel. = Vlc = ______ ml.

TEST # ____________

Sheet 3 of 3

ADDITIONAL REPORTING METHODS FOR EPA STACK TEST

1. Mass Flow Rate =

$d = \frac{(Md)\quad(Ps)}{(21.85)\quad(Ts)}$ = ____________ lb/ft^3

$(3600)\quad(Vs)\quad(A)\quad(d)$ = ____________ LBS GAS/HR.

---

2. Particulate Concentration

C's = ____________ gr/scf (from Sheet 2)

$\frac{(C's)\quad(Qs)}{7000}$ = ____________ LBS/HR (Particulates)

$\frac{\text{LBS/HR}}{(.001)\quad(\text{Lbs Gas/Hr.})}$ = ____________ LBS/1000# GAS

$\frac{\text{LBS/HR}}{\text{Feed Rate}\quad(\text{TPH})}$ = ____________ $\frac{\text{LB}}{\text{Ton of}}$

---

3. Condensibles Concentration

$Zs = (2.205 \times 10^{-6})\ \frac{(Zw)}{(Vm\ std)}$ = ____________ LBS/SCF

$Z's = (.0154)\ \frac{(Zw)}{Vm\ std}$ = ____________ gr/SCF

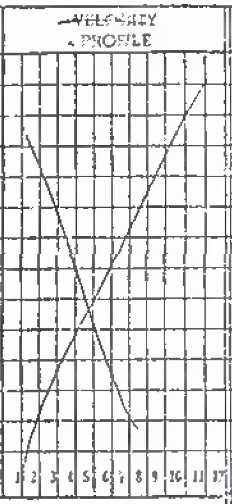
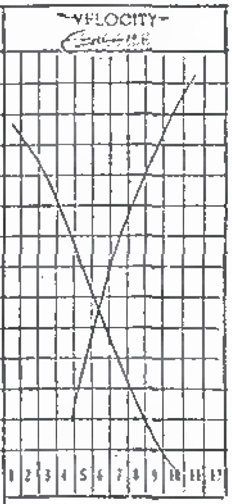
$\frac{(Z's)\quad(Qs)}{7000}$ = ____________ LBS/HR (Condensibles)

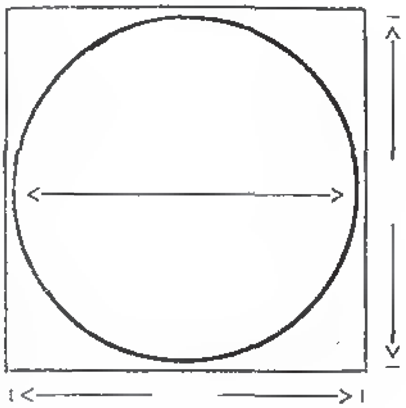
$\frac{\text{LBS/HR}}{(.001)\quad(\text{LBS Gas/Hr.})}$ = ____________ LBS/1000# GAS

$\frac{\text{LBS/HR}}{\text{Feed Rate}\quad(\text{TPH})}$ = ____________ LBS/TON OF FEED

GAS VOLUME DATA SHEET

Dep't. ______________ Location ______________ Date ______________
Test by ______________ Sheet No. ____ of ____ Sheets Test No. ______________

	H In.w.g.	$\sqrt{H}$	VELOCITY PROFILE		H In.w.g.	$\sqrt{H}$	VELOCITY PROFILE
							
Total				Total			
				Totals			
				Average			



Barom. P_b = ______ "Hg
Ambient Air ______ °F

Stack Area ______ Sq. Ft.
Dry Bulb t_d = ______ °F
Wet Bulb t_w = ______ °F
Dew Point t_c = ______ °F
Wt. Fract. H_2O ______
Pitot Correction Factor F_s = ______

Stack Temp. ______ °F + 460 = T_s = ______ °R
Stack Diff. Pressures
$\Delta P = \pm$ ______ " w.g. (0.0734) = $\pm$ ______ "Hg
Stack Abs. Press. $P_s = P_b \pm \Delta P$ = ______ "Hg

$$\frac{\text{Wt } H_2O}{18} = \text{\_\_\_\_\_\_ Mols.;} \quad \frac{\text{Mols of } H_2O}{\text{Mols. of } H_2O + 0.0345} = \frac{\text{\_\_\_\_\_\_}}{\text{\_\_\_\_\_\_} + 0.0345} = \text{\_\_\_\_\_\_ Vol. Fract. } H_2O^*$$

Gas Analysis (Moisture Correction Factor, Km = 1 − Vol. Fract. H_2O)

Conponent		Vol. Fract. ×	Km ×	Mol. Wt. =	MW. Fraction. (Stack Cond.)
Moisture			1.000	18 =	
Carbon Dioxide	D.B.			44 =	
Oxygen	D.B.			32 =	
Carbon Monoxide	D.B.			28 =	
Nitrogen	D.B.			28 =	
MW = Average Molecular Wt. =					

$$\text{Density of Gas Referred to Air} = G = \frac{\text{Avg. Mol. Wt.}}{28.95} = \text{\_\_\_\_\_\_}$$

$$\text{Average Velocity, } V_s = 174\, F_s \sqrt{\frac{29.92}{P_s} \times \frac{1.00}{G} \times T_s}\ \sqrt{H} = \text{\_\_\_\_\_\_ FPM}$$

$$\text{Volume, (cond.), } V_o = \text{\_\_\_\_\_\_ FPM} \times \text{\_\_\_\_\_\_ Sq. Ft.} = \text{\_\_\_\_\_\_ CFM}$$

$$\text{Volume, (70°F), } V_{std} = \text{\_\_\_\_\_\_ CFM} \times \frac{530}{T_s} \times \frac{P_s}{29.92} = \text{\_\_\_\_\_\_ SCFM}$$

$$W_g = \frac{V_{std}\,(MW)}{379} = \text{\_\_\_\_\_\_ Lbs. Gas/Min.;} \quad W_{H_2O} = W_g \times \text{Wt. Fract. } H_2O = \text{\_\_\_\_\_\_ Lbs. } H_2O \text{ Per Min.}$$

*Basis: One Lb. of Dry Air

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

(Phenol Disulfonic Acid Procedure)

USING ASTM METHOD D 1608-60

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

ASTM DATA SERIES PUBLICATION DS 55-S8

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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, 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 source emissions. 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), dustfull (D 1739-70), total sulfation (D 2010-65), particulate matter (D 1704-61), and lead (D 3112) in the atmosphere (1-5)[*].

Methods for the measurement of the relative density of black smoke (D 3211-73T) (6), oxides of nitrogen (D 1608-60), sulfur oxides (D 3226-73T), and particulates and collected residue (proposed method) in source emissions were evaluated in Phase 2 of Project Threshold. Evaluation of a pitot tube method (D 3154-72) (7) for determining the average velocity in a duct was also performed in conjunction with the particulates and collected residue tests.

The interlaboratory "round-robin" approach 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 is responsible for providing personnel and equipment, assembling apparatus, sampling and analyzing collected samples either on-site

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[*] References are given on Page 90.

or at their 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 oxides of nitrogen (commonly called "NO_x) in pilot plant and actual source emissions using ASTM Method D 1608-60 (8).

SUMMARY OF RESULTS

Statistical analysis of 637 oxide of nitrogen (NO_x) determinations in flue gas from a pilot plant furnace and 92 NO_x determinations in industrial combustion source emissions using ASTM D 1608-60 produced the following results.

- The between-laboratory component of variance (reproducibility) of NO_x determinations over the concentration range of about 20 to 2000 ppm NO_2 as estimated from the pilot plant tests may be expressed by the equation

  $$\hat{S}_B = 2.21 \sqrt{m} - 1.18$$

  where $\hat{S}_B$, the between-laboratory component of variance, and m, the mean NO_x concentration are given in ppm NO_2.
- The within-laboratory component of variance (repeatability) of NO_x determinations over the concentration range of about 20 to 2000 ppm NO_2 as estimated from the pilot plant tests may be expressed by the equation

  $$\hat{S}_W = 1.52 \sqrt{m} - 4.21$$

  where $\hat{S}_W$, the within-laboratory component of variance, and m, the mean NO_x concentration are given in ppm NO_2.
- The mean between-laboratory standard error, S_T (between-laboratory)* determined from field tests at an oil-fired power plant and cement kiln at flue gas concentrations in the range of 90 to 260 ppm NO_2 is 14.5 ppm. The mean between-laboratory standard error obtained from the field data is less than the comparable

---

* S_T (between-laboratory) $= -\sqrt{\hat{S}_B^2 + \hat{S}_W^2}$

standard error measure calculated from the pilot plant estimates of the between- and within-laboratory components of variance.

- Solutions containing known quantities of potassium nitrate were supplied to each laboratory for analysis with the samples obtained from the pilot plant and site tests. The measure of between-laboratory standard error of the D 1608-60 analytical procedure expressed as the coefficient of variation ranged from 3.3 to 16 percent based on standard solutions containing 0.455 to 7.75 mg NO_2 (equivalent to about 126 to 2134 ppm NO_2). Assuming that the variability in the standards analyses is representive of the test samples, as much as 78 percent of the estimated total variation in the pilot plant tests and as much as 71 percent of the estimate total variation in one of the field tests can be attributed to the nitrate analysis procedure. The mean differences between the experimentally determined and true standard values show statistically significant negative bias occurred in the nitrate determinations at higher concentration levels.
- Pilot plant tests in which known spikes over the range of about 200 to 1400 ppm nitric oxide 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 two spike concentration ranges, ≤ 700 and >700, for the purpose of testing for bias as a function of NO_x concentration.
- On the average, the accuracy of NO_x determinations in which the sample flasks were shaken every 20 minutes and transferred after two hours was not significantly different than results obtained with the usual overnight absorption period.
- Based on comparison of typical determinations, ASTM D 1608-60 yields sample volume determinations which are slightly higher than the values obtained using the Federal Register, Method 7 procedure. Based on this difference alone, the ASTM Method results in NO_x determination which are, on the average, about 2.5 percent lower (based on the ASTM values) than the F.R., Method 7 results.

EXPERIMENTAL PROGRAM

ASTM Test Method D 1608-60

ASTM Method D 1608-60 describes equipment and procedures for the instantaneous determination of oxides of nitrogen concentration (excluding nitrous oxide) in combustion source emissions. A grab sample of the gaseous effluent is withdrawn into an evacuated flask containing a solution of hydrogen peroxide and sulfuric acid. The oxides of nitrogen are oxidized to nitrate which is reacted with phenol disulfonic acid to produce a yellow compound whose absorbance is measured with a spectrophotometer. The nitrate concentration in the sample is determined by comparison of the absorbance with a calibration curve prepared from solutions containing known quantities of nitrate ion.

The method is reported to be applicable to determination of NO_x concentrations above about five parts per million (as $NO2$). Results are calculated in parts per million as NO_2*.

A copy of ASTM D 1608-60 is reproduced in Appendix A of this report.

As a part of the Project Threshold Program, Dr. R. H. Johns, ASTM Research Associate, National Bureau of Standards, conducted a study of the conversion of nitric oxide to nitrate in the absorption step of the phenol disulfonic acid procedure. The results of Dr. Johns' study are reported in Appendix B.

Apparatus

With exception of the sampling flask size and design, the apparatus described in the Test Method was used for performance of all tests. Two liter (2000 ml) round-bottom glass flasks with a standard taper 24/40 female neck were used for sampling in place of the one liter size specified in the method. The flasks were fitted with a three-way stopcock, one arm of which was connected to the sampling probe and the other to the evacuation-purge-pressure measurement system.

A diagram of the typical sampling system as used in the tests is shown in Figure 1. Heated, borosilicate glass probes about four feet in length were used for field sampling and short sections (about 8 to 12 inches) of insulated Teflon tubing were used in the pilot plant tests.

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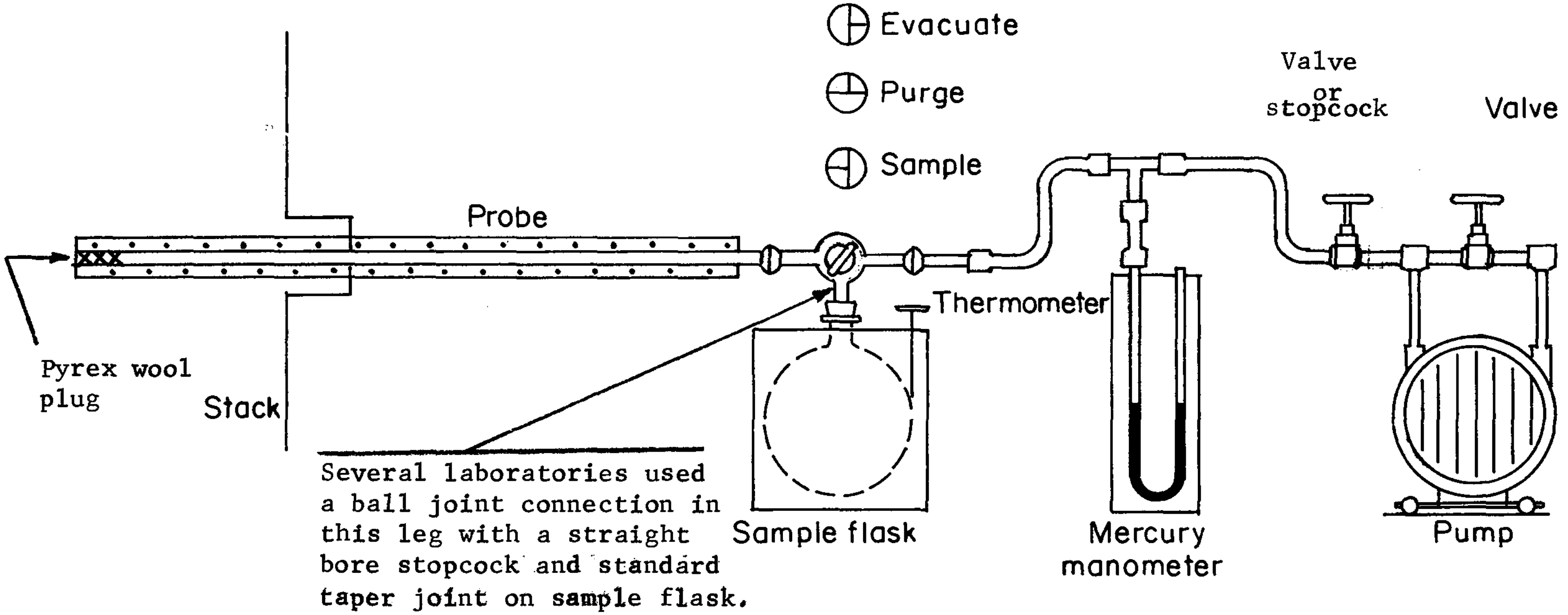
* Parts per million of NO_2 may be converted to milligrams per cubic meter of pounds per cubic foot by multiplying by 1.90 or 1.19×10^{-7}, respectively.



Several laboratories used a ball joint connection in this leg with a straight bore stopcock and standard taper joint on sample flask.

FIGURE 1. DIAGRAM OF TYPICAL SAMPLING APPARATUS USED FOR DETERMINATION OF OXIDES OF NITROGEN BY ASTM D 1608-60

Pilot Plant Tests

Tests of the oxides of nitrogen content of flue gases from the Battelle multifuel furnace using ASTM D 1608-60 were made by ten cooperating laboratories during two-three day periods in consecutive weeks, with six laboratories sampling in the first test period and four sampling in the second test period. The furnace was operated during Day 1 of each test period on natural gas and on Days 2 and 3 on fuel oil with burner settings, furnace temperatures, and fuel nitrogen additions selected to produce a range of NO_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 nitric oxide. Spiking increased the level of nitrogen oxides above that of the unspiked stream to permit study of the method over a wider concentration range and to estimate the accuracy of the method from measurements of the difference in concentration in simultaneous samples taken from the spiked and unspiked sample manifold. 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 either natural gas on the first day of each three-day period and No. 2 fuel oil on the second and third days. It has a refractory lined cylindrical combustion chamber about 15 inches in diameter and 90 inches long. It is enclosed by a steel airtight outer shell. Versatile air controls and a special burner design permit simulation of conditions which occur in firing these fuels in a full-scale combustion furnace. Figure 2 is a schematic drawing the setup for firing fuel oil. The similar setup for firing natural gas differed only in the use of a flow meter for measuring the fuel input rate of the gas fuel. Figure 3 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 NO_x TESTS

		Flue Gas Comp., %		Max Furnace	Flue Gas Temp, F[(a)]	
Fuel	Firing Rate	CO_2	O_2	Temp, F	U	S
Natural Gas	200-400 CFH	10-15	0.8-2.0	2500-2850	400-450	410-460
#2 Fuel Oil	1.5-3.0 GPH	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 nitric oxide (Matheson, C.P.) which produced a known concentration increase of NO_x in the flue gas taken from the spiked loop.

Figure 4 is an overhead view of the sampling system and Figure 5 is a dimensioned sketch from approximately the same aspect as Figure 4. 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 through the center of

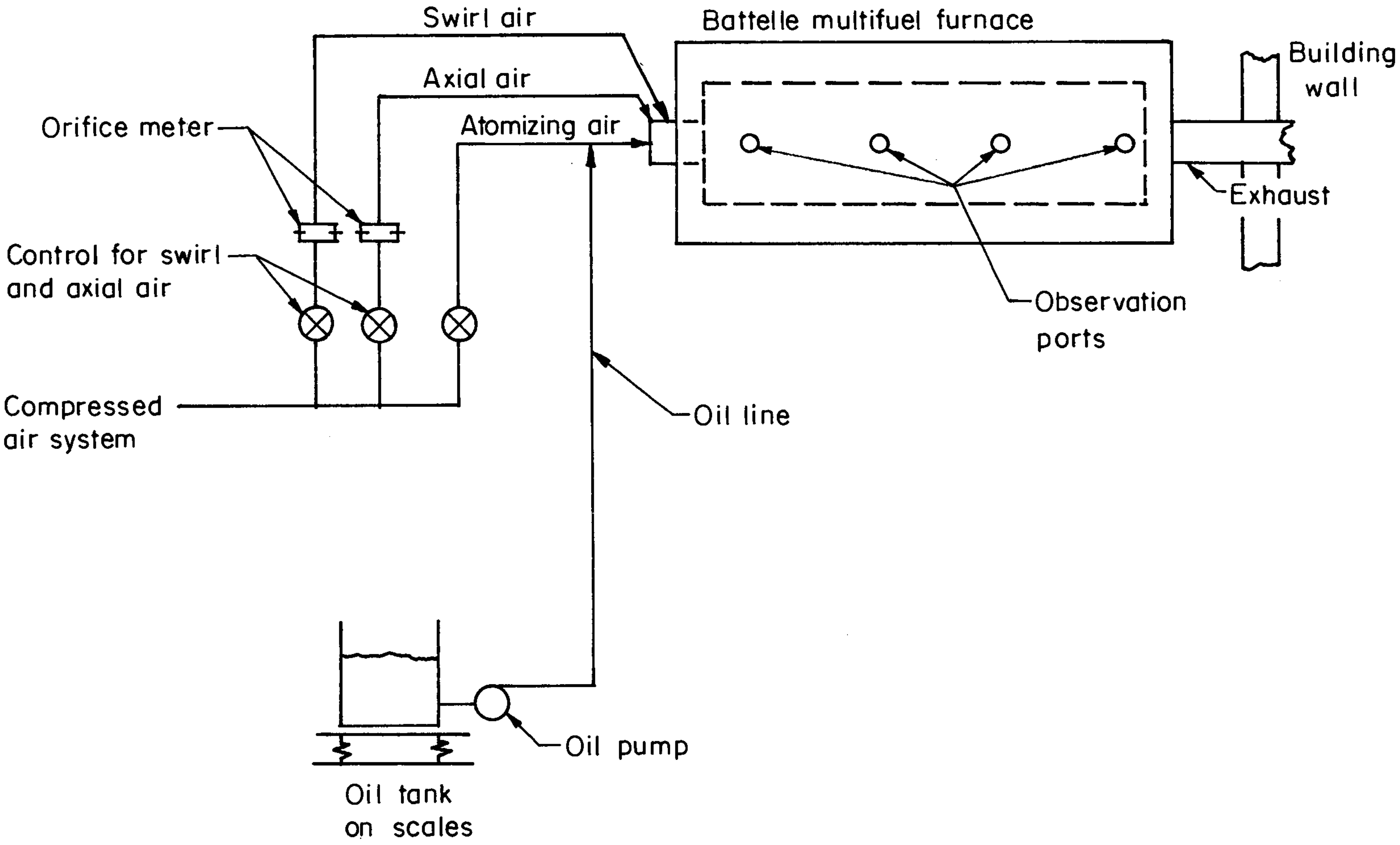


FIGURE 2. SCHEMATIC DIAGRAM OF THE BATTELLE MULTIFUEL FURNACE ARRANGED FOR FIRING WITH FUEL OIL

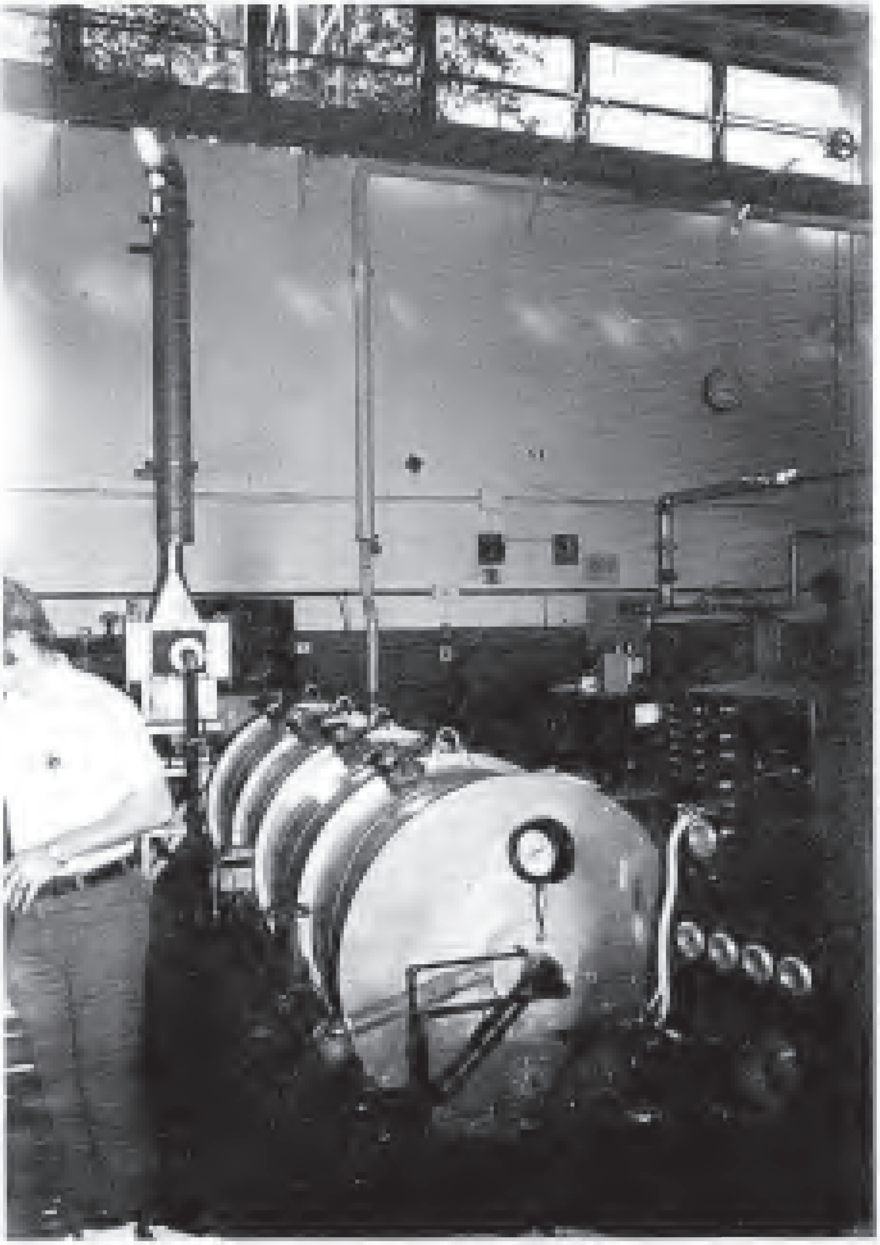


FIGURE 3. MULTIFUEL FURNACE SETUP FOR GENERATING FLUE GASES FROM COMBUSTION OF NATURAL GAS OR FUEL OIL

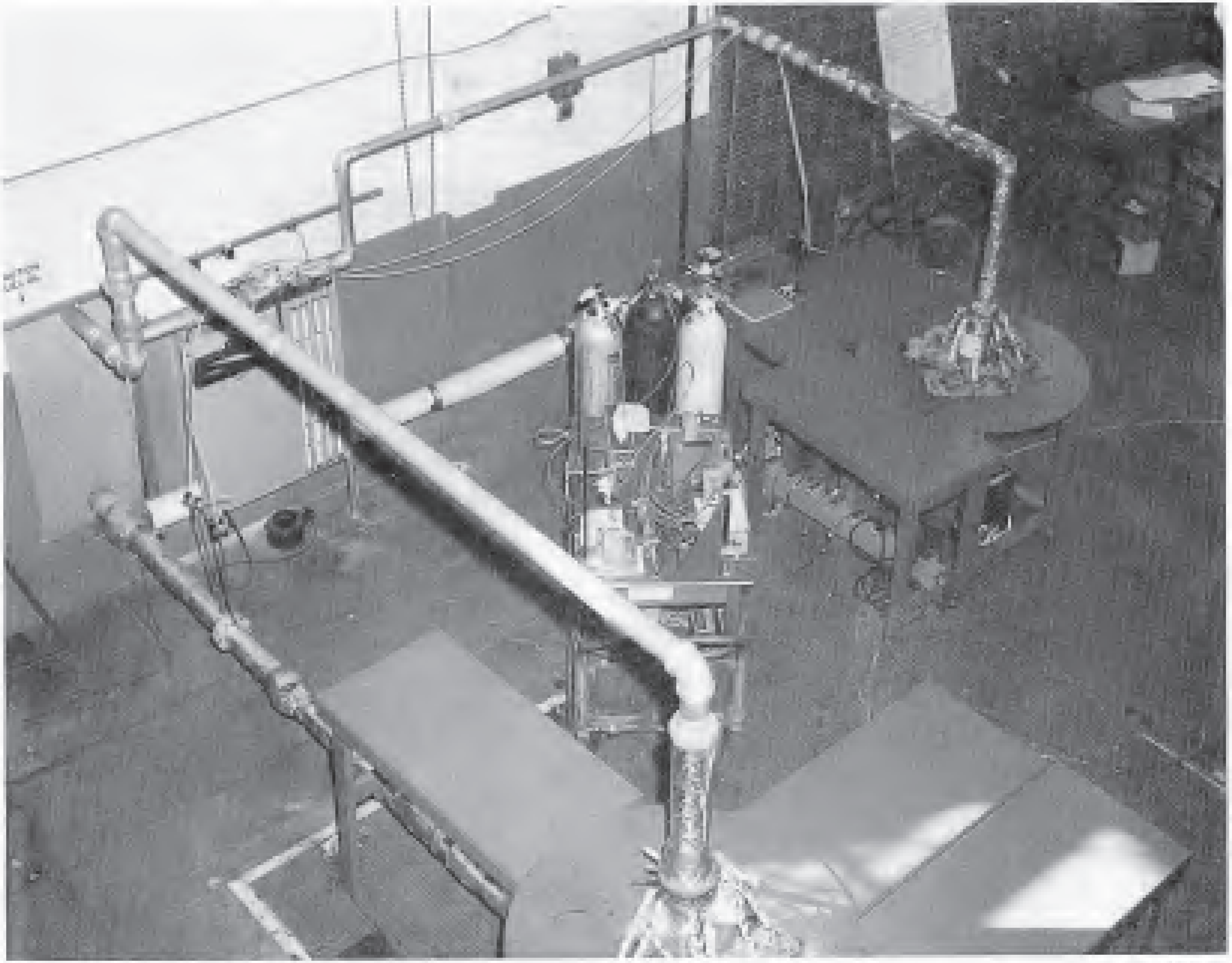


FIGURE 4. OVERHEAD VIEW OF SAMPLING SYSTEM

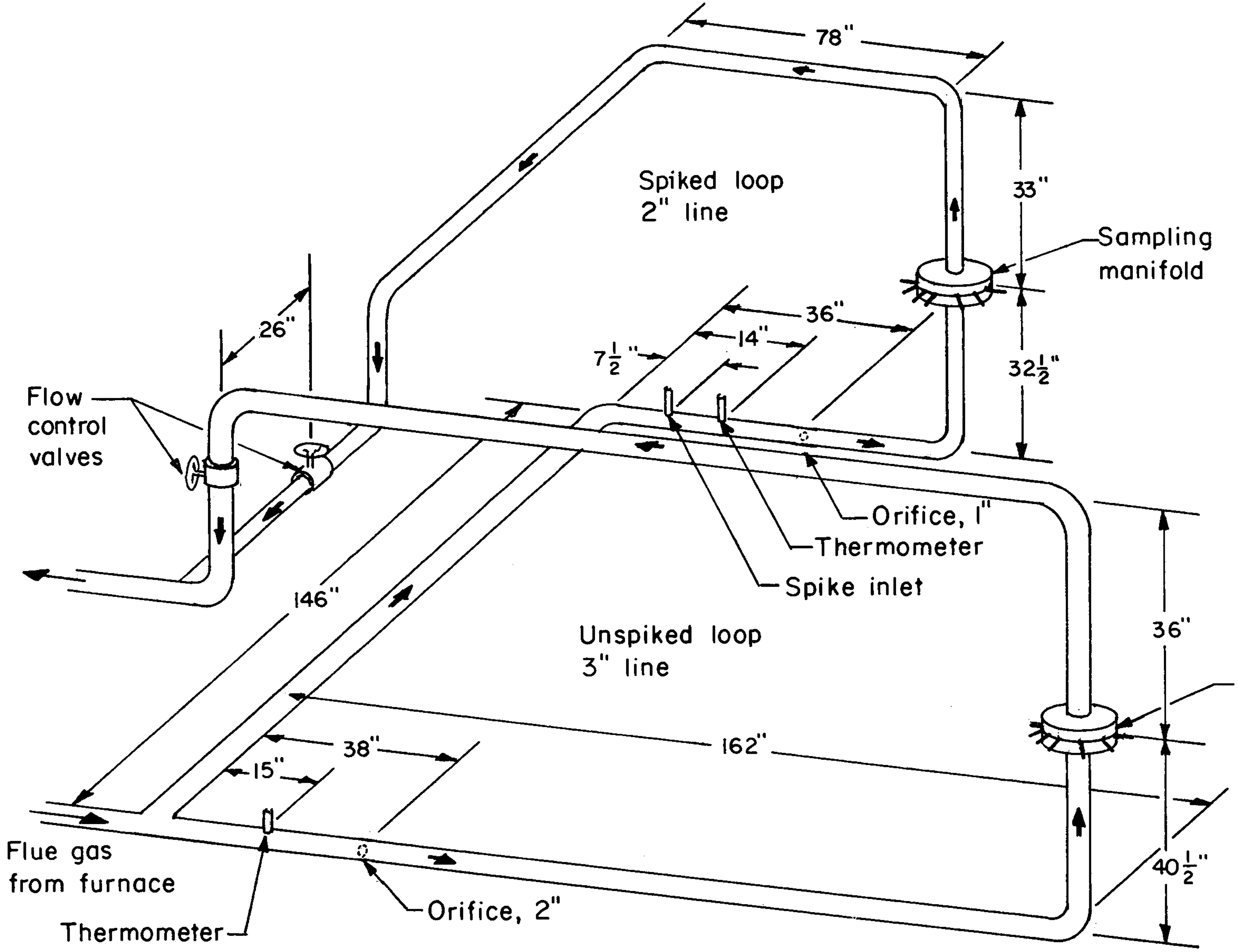


FIGURE 5. DIMENSIONED SKETCH OF SAMPLING SYSTEM

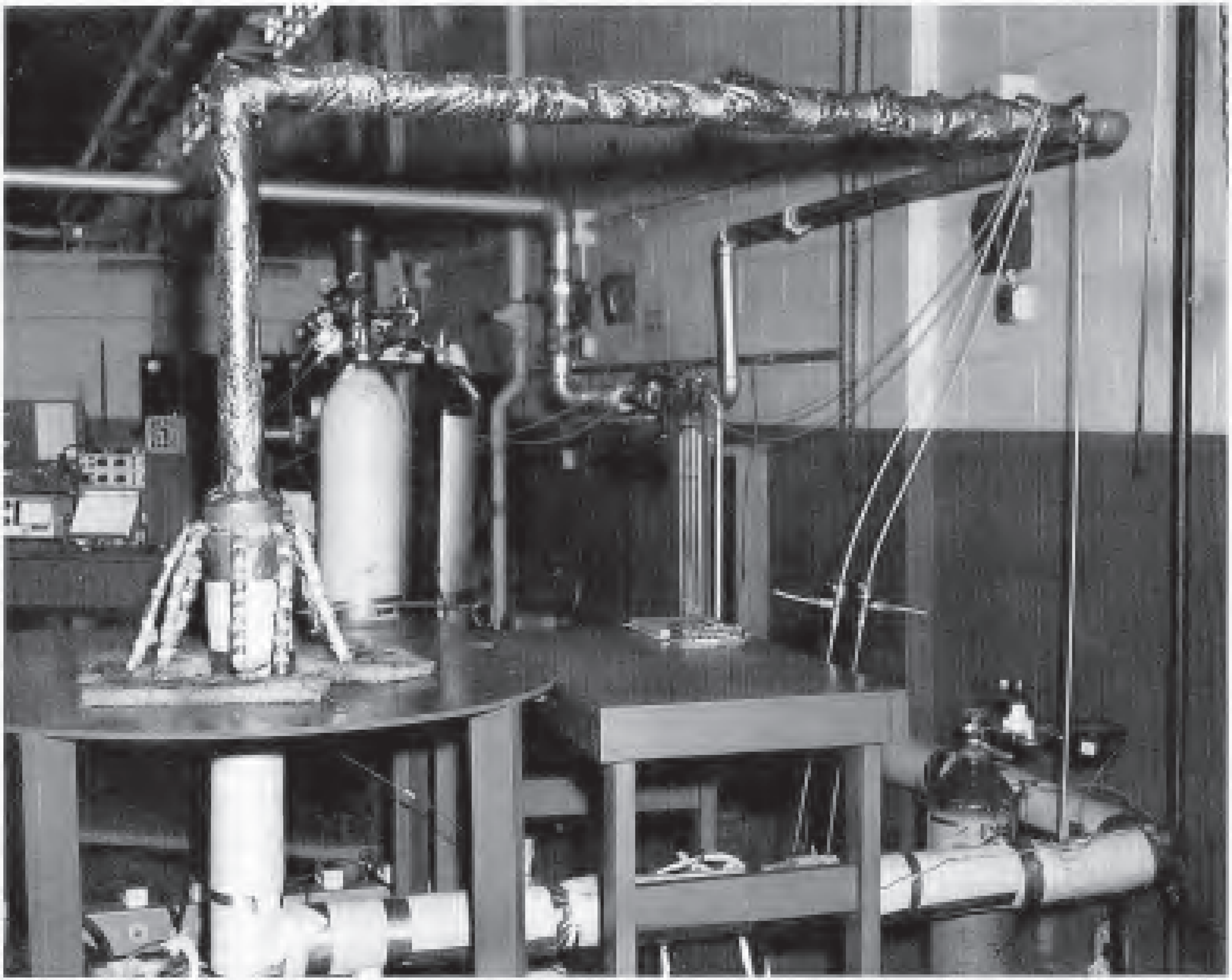


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FIGURE 6. CLOSE-UP VIEW OF SPIKED SAMPLE LOOP

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 carried the individual samples to the sampling flask 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 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. There was some difficulty with condensate at these tips during the first day of sampling until the sample streams were allowed to flow continuously to keep the flexible tubing hot between samples. These connectors were also wrapped with glass and asbestos tape insulation in the spiral pattern visible in the photograph.

Figure 6 is a closeup view of the spiked-sample loop with sampling table and flexible connectors in the foreground; a cylinder of nitric oxide 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 described in the following section. In the background behind the sampling table is a partial view of the monitoring instruments which were used to measure the concentrations of NO_x in both loops during the sampling sessions to be certain that the furnace was generating approximately the desired amount of nitrogen oxides, and that the gas streams were properly equilibrated before sampling proceeded.

Spiking Procedure

A gaseous spike of nitric oxide was injected into the flowing stream of flue gas from a cylinder of the gas which assayed 99.23 percent pure. The impurities were determined in the Battelle analytical laboratory by mass spectrometry and gas-liquid chromatography procedures, as follows: carbon dioxide, 0.08 percent; nitrogen, 0.36 percent; and nitrous oxide, 0.44 percent. The flow rate of the spiking gas was controlled by metering 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. A 1/16-inch flexible Teflon 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 7. The precision gauge had a mirror background to avoid parallax errors in reading the pointer, and a scale divided into tenths of a pound.

Four metering orifices were used to control addition of the nitric oxide spikes. The characteristics of the orifices are given in Table 2. The orifices were specially fabricated from watch jewels having bore diameters of 0.06 to 0.14 mm which covered the range from 75 to 500 ml of gas per minute from a 15-psig source. Calibration of the metering orifices was performed gravimetrically. 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 7. Gas pressure was adjusted to 15 psig and the entire assembly was placed on a

TABLE 2. CHARACTERISTICS OF METERING ORIFICES USED FOR NITRIC OXIDE SPIKES

Orifice Diameter, mm	Metering Rate, grams NO/second[(a)]
0.06	0.001464
0.08	0.002349
0.12	0.004751
0.14	0.006468

(a) At 15 psig

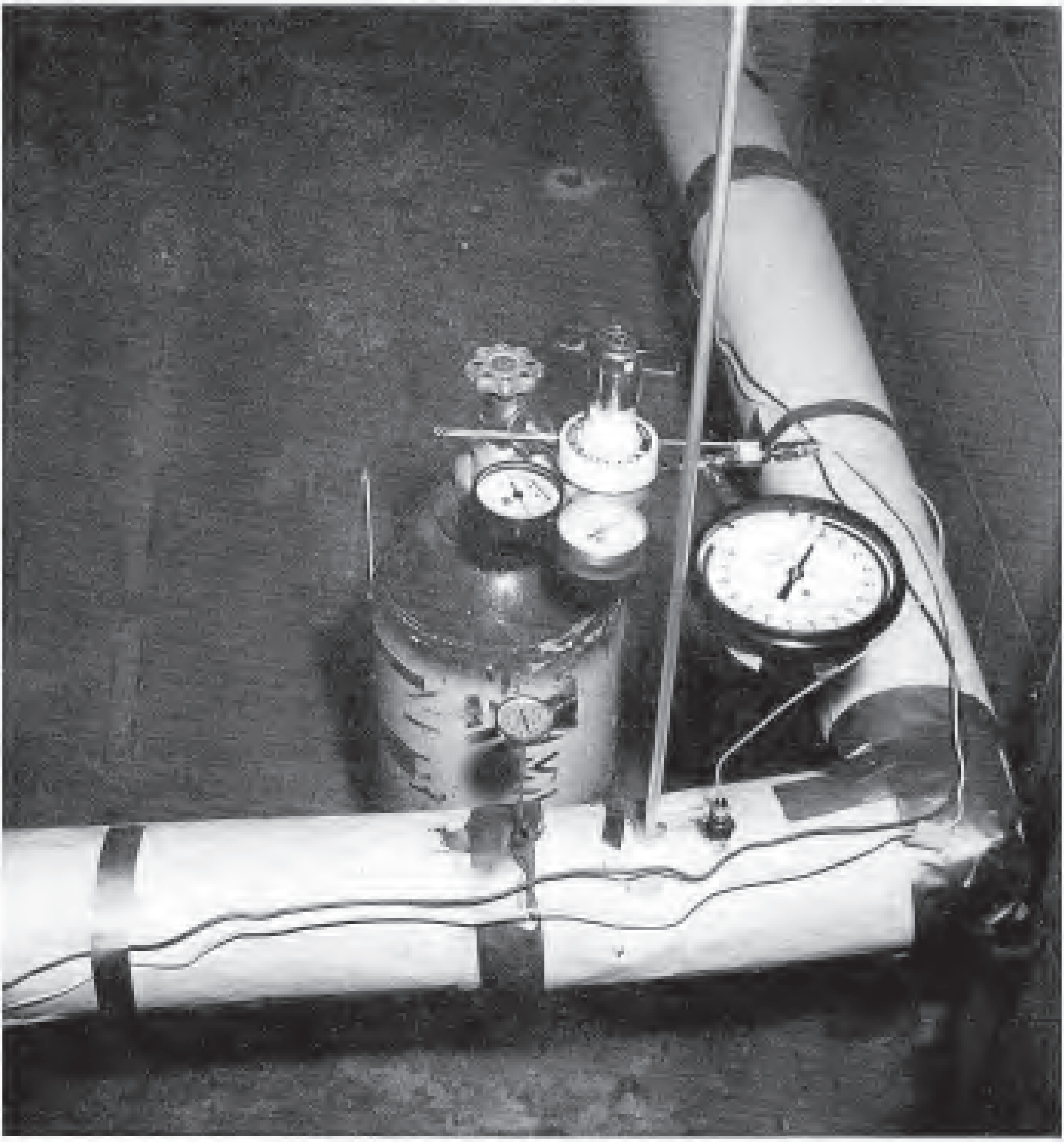

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FIGURE 7. DETAIL OF SPIKE INJECTION SYSTEM

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 nitric oxide during the tests was performed by Dr. R. H. Johns, ASTM Research Associate at the National Bureau of Standards.

Sampling Procedure

The sampling procedure followed precisely the instructions prescribed by the printed Method D 1608, although the coordinating laboratory selected certain options which are left to the choice of the analyst by the method. Each laboratory brought its own supply of 2-liter round bottom Pyrex flasks fitted with a T-bore stopcock closure. The three legs of the stopcock were fitted with two spherical 12/5 connections on the horizontal legs and one male 24/40 tapered ground glass connection on the vertical leg to fit the corresponding glass joint of the collecting flask. Because each laboratory was required to have about 20 such assemblies, an adapter was permitted incorporating a single stopcock with a 2-mm bore and with 24/40 male and female tapered joints to be interposed between the flask neck and the 24/40 tapered connector of the T-bore stopcock. Some laboratories had difficulty in purchasing enough of the T-bore assemblies to fit all the sampling flasks. The single stopcock adapter permitted the assembly to be reused while the samples were being held in the flasks during the period of absorption of the NO_x by the reagent. Each laboratory supplied its own evacuating equipment and manometer to measure the vacuum in the flasks immediately before their use for sampling. Flasks were evacuated to incipient boiling of the reagent, valved off from the pump, and the flask pressure recorded. All flasks were reevacuated and the new pressure recorded if there were a delay in taking the sample after the initial evacuation.

In preparation for sampling the flasks were attached to the glass ball joint connectors at the tips of the flexible connectors at each sampling port, and the bore of the stopcock was turned to flush the sample stream through the sampling line and stopcock. On signal the T-bore barrel was turned to divert the stream into the evacuated flask; this allowed the flask to fill to system pressure. Each laboratory always drew two simultaneous samples according to an assigned pattern: both from the same sampling loop, or one sample from each loop. The pattern is described in the next section. The first few tests showed that the withdrawal of twelve simultaneous samples (by six laboratories) from the spiked line caused a perturbation in the flow in the spiked line. This indicated that the maximum flow capacity was being reached or approached. Although the volumetric rate in the line and its inventory of well-mixed spiked flue gas were somewhat affected by simultaneous samples, the analyses did not show any real change in spiking level. Thereafter, samples from both lines were taken sequentially by each laboratory at 10-second intervals. This procedure eliminated all flow disturbance in the sampling loops.

The overnight absorption period specified for the sealed flask after sample collection may be substituted by an option in the method calling for shaking the flask every twenty minutes for two hours, after which the absorbing solution may be removed for analysis. This option was used for 10 of 15 daily pairs of samples so that the flasks used early in the day could be cleaned and reused later the same day.

When the absorption period was completed after either two hours with shaking or overnight, the internal pressure, barometric pressure, and ambient temperature were measured before the flask was opened. A 15-ml aliquot was withdrawn with a pipette from the solution in the flask and was transferred to a stoppered glass or polyethylene bottle for return to the home laboratory and subsequent analysis. This procedure was an option which was permitted to conserve time in a tight test schedule. Quantitative transfer of the total sample would have required rinsing and draining the flask. Later quantitative transfer with rinsing was required to remove the aliquot from the bottle for analysis.

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 NO_x in actual samples over a wide range of NO_x concentrations derived from natural combustion of nitrogen compounds in the fuel or nitrogen in the combustion air, and by the spiking process of adding nitric oxide to the flue gas. Table 3 shows the target pattern of operations that was developed in planning the statistical pattern. Five operating variables were used in controlling the amount of NO_x between about 150 ppm and 2150 ppm. These variables included two types of fuel, two fuel rates to vary the furnace temperature, appropriate amounts of excess air for each fuel, low-nitrogen fuel oil and the same oil doped with nitrogen-containing pyridine, and appropriate spiking rates with nitric oxide to cover the total range for which the test method was expected to be valid. The test pattern outlined in the first column of Table 3 shows 14 daily blocks. Each block constituted a pair of samples taken by each laboratory during one sampling period which extended over approximately 15 seconds. Table 4 shows the actual sequence of sampling achieved during three days of each test week. It was found expedient on occasion to reverse the order of the daily blocks because of delays caused by equipment malfunctions or for convenience in equilibrating the furnace and sampling system after a change in operating conditions. Almost the whole planned series was completed successfully, except for the omission of one half-day group during the first week.

During each test block, the NO_x concentration was monitored with an Envirometrics 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 SO_2 in addition to NO_x.

Field Tests

Measurement of oxides of nitrogen in flue gas were performed in field tests at four sites; an oil-fired power plant, a coal-fired power plant, a cement plant and a foundry. Descriptions of the emission sources and the field test procedures are given in the following sections. The NO_x levels in the foundry emissions were well below the lower limit of applicability of the method. Therefore, description of the foundry and the results have not been included in this report.

TABLE 3. TARGET PATTERN OF SPIKE CONCENTRATIONS
FOR PILOT PLANT TESTS OF ASTM D 1608-60

DAILY BLOCKS No.	Positions				DAY (1) Gas (zero N&S)	DAY (2) High Fuel Rate	DAY (3) Low Fuel Rate
1	Each lab: Two spiked samples	Lo Spike	Undoped Fuel Oil	One Fuel Rate All Day (High or Low) For Oil	Nitrogen Oxides Tests		
2	Each lab: One spiked, one unspiked				Blocks 2, 5, 9, 12 - Allow absorption flasks to stand overnight; all other blocks, shake each 20 min., transfer 2 hr.		
3	Each lab: One spiked, one unspiked				Blocks 1-7 Fuel rate = 200CFH Excess air 5-10% Target NO_x: 150-200 ppm	Blocks 1-14 3 GPH No. 2 oil 12% excess air	Blocks 1-14 1-1/2 GPH No. 2 oil 12% excess air
4	Each lab: Two unspiked						
5	Each lab: One spiked, one unspiked	Hi Spike			Blocks 1-3 NO_x spike 247 ppm Target total NO_x = 450 ppm	Blocks 1-7 Undoped fuel < 0.01% N Target NO_x = 600 ppm	Blocks 1-7 Undoped fuel < 0.01% N Target NO_x = 150-200 ppm
6	Each lab: One spiked, one unspiked						
7	Each lab: Two spiked samples				Blocks 5-7 NO_x spike 420 ppm Target total NO_x = 600 ppm	Blocks 1-3 NO_x spike 420 ppm Target total = 1020 ppm	Blocks 1-3 NO_x spike 247 ppm Target total = 450 ppm
8	Each lab: Two spiked samples	Lo Spike	Doped Fuel Oil (N or S)		Blocks 8-14 Fuel rate = 400CFH Excess air 5-10% Target NO_x = 600 ppm	Blocks 5-7 NO_x spike = 800 ppm Target total NO_x = 1400 ppm	Blocks 5-7 NO_x spike 420 ppm Target total NO_x = 600 ppm
9	Each lab: One spiked, one unspiked					Blocks 8-14 Doped fuel 0.8% N as pyridine Target NO_x = 900 ppm	Blocks 8-14 Doped fuel 0.8% N as pyridine Target NO_x = 500 ppm
10	Each lab: One spiked, one unspiked				Blocks 8-10 NO_x spike 420 ppm Target total NO_x = 1020 ppm		
11	Each lab: Two unspiked					Blocks 8-10 NO_x spike 800 ppm Target total NO_x = 1700 ppm	Blocks 8-10 NO_x spike 247 ppm Target total NO_x = 750 ppm
12	Each lab: One spiked, one unspiked	Hi Spike			Blocks 12-14 NO_x spike 800 ppm Target total NO_x = 1400 ppm		
13	Each lab: One spiked, one unspiked					Blocks 12-14 NO_x spike 1250 ppm Target total NO_x = 2150 ppm	Blocks 12-14 NO_x spikes 800 ppm Target total NO_x = 1300 ppm
14	Each lab: Two spiked samples						

TABLE 4. NO_x SAMPLES TAKEN DURING PILOT PLANT TESTS

Date, 1972	Hours	Week No.	Day No.	Sequence of Samples by Block Number
Oct. 9	p.m.	1	1	1 thru 7
Oct. 10	a.m.	1	1	8 thru 14
Oct. 10	p.m.	1	2	1 thru 6
Oct. 11	a.m.	1	2	7 thru 14
Oct. 11	p.m.	1	3	1 thru 7 (Blocks 8-14 omitted)
Oct. 16	a.m.	2	1	8 thru 14
Oct. 16	p.m.	2	1	1 thru 7
Oct. 17	a.m.	2	2	1 thru 7
Oct. 17	p.m.	2	2	8 thru 14
Oct. 18	a.m.	2	3	8 thru 14
Oct. 18	p.m.	2	3	1 thru 7

Test Site Descriptions

The characteristics of the three test sites at which ASTM D 1608-60 was evaluated are summarized in Table 5.

Site I

The eight 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 operated under steady-state conditions at full load capacity.

The oxides of nitrogen 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.

Site II

A total of 16 tests were conducted at Site II, a large coal-fired electrical generating station. The station has two units which have 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 oxide of nitrogen 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. NO_x concentrations during the test series were in the range of about 300 to 400 ppm.

Site III

Test Site III is a dry process portland cement manufacturing plant. At the Site, 16 tests were conducted using two different stacks carrying emissions from 10-ft diameter by 154-ft long cement kilns.

Tests 1 through 8 and 9 through 16 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.

TABLE 5. 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 Rage	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_2O 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.

Sampling Procedure

Sampling at each field site was performed as prescribed in the Test Method using the apparatus shown in Figure 1. Borosilicate glass probes about four feet in length were used to withdraw the stack gas samples. The probes were heated to at least 250 F to prevent condensation of moisture. A glass wool plug was inserted in the probe at the inlet end to remove particulates.

The sampling flasks (2 liter) were evacuated and pressures measured just prior to sampling. The probe and stopcock tubing was purged with the stack gas for about one minute prior to sampling. Purging was performed by the various laboratories both by suction bulbs and vacuum pumps. Sampling was performed concurrently, on signal, immediately after termination of the purging period.

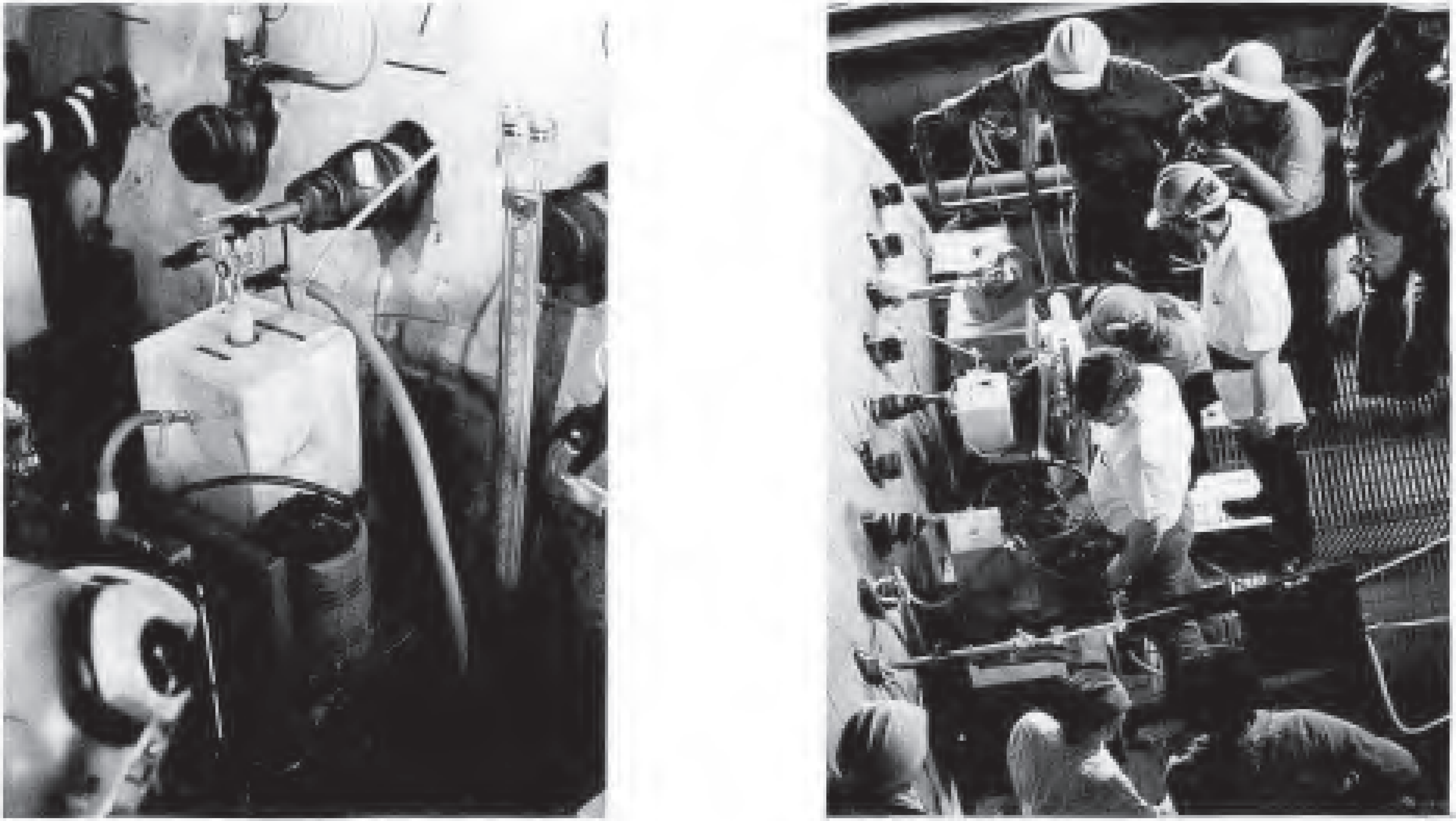
The absorbent solution used in field tests at Site I was prepared as described in Paragraph 6.1 of the Test Method. The solutions used at Sites II and III were prepared as described in Note 1. After sampling, the flasks containing the absorbent solution and gas samples were allowed to stand overnight. The flask contents were then quantitatively transferred to glass or polyethylene bottles for return to the respective laboratories for subsequent analysis.

The photograph a. in Figure 8 shows the typical sampling arrangement used in the field tests. The photograph b. in the figure shows four teams performing concurrent sampling at one of the test sites.

Test Patterns

Site I tests were performed with the four different laboratories taking all samples from the same sampling port. All tests were performed on the same day over a time period of about one and one-half hours. Site II tests included four different laboratories who moved in the pattern shown in Table 6, such that all laboratories obtained a total of four samples at each of the four sampling ports. Tests 1 through 8 were performed over a 70 minute period on one day and Tests 9 through 16 were completed during a 40 minute period on the following day.

A total of six different laboratories participated in the Site III tests. Concurrent sampling was performed by groups of four laboratories in the pattern shown in Table 7. Tests 1 through 8 were performed during a 40 minute period on Monday of the first test week and Tests 9 through 16 were completed over a 45 minute period on the following Monday, the first day of the second test week.



a.

b.

FIGURE 8. PHOTOGRAPHS SHOWING TYPICAL SAMPLING SYSTEM ARRANGEMENT (a.) AND CONCURRENT SAMPLING PROCEDURE (b.) AT FIELD TEST SITES

TABLE 6. SAMPLING PATTERN FOR NO_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 7. SAMPLING PATTERN FOR NO_x TESTS AT FIELD SITE III

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

In the tests at Site II and III, the sampling probes remained stationary and the remainder of the sampling systems were moved from port-to-port in completing the test patterns.

Analysis of Standard Nitrate Solutions

A series of solutions containing known quantities of nitrate 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 ASTM D 1608-60 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
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 NITROGEN OXIDE TESTS

Statistical Measures

The experimental program was designed and conducted to provide measures of the precision and accuracy of ASTM Method D 1608-60.

Measure of Precision

ASTM Method D 2906-70T(9) 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:

<u>Single-operator standard error</u>

S_T (single-operator) = $(S_S^2/_n)^{1/2}$

<u>Within-laboratory standard error</u>

S_T (within-laboratory) = $[S_W^2+(S_S^2/_n)]^{1/2}$

<u>Between-laboratory standard error</u>

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. (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 NO_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 NO_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, and further examples of the interpretation and usage of these estimates are presented in an appendix.

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 exceed by the absolute difference of two randomly selected test results only about 5 percent of the time in repeated experiments, e. g. Mandel(10). Others use less quantitatively oriented definitions, e.g. Davies(11). The usage in this report can be directly applied to statements of precision, as outlined in ASTM Method D 2906-70T and E 177(12), and is consistent with the usage in other Project Threshold reports.

The field site tests of D 1608-60 provide an estimate of between-laboratory standard error, S_T(between-laboratory), for the determination of NO_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 NO_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 NO_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 systemic difference or error which is called bias.

The accuracy of NO_x measurements by D 1608-60 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 nitric oxide. 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 1608-60 in accordance with the pattern given in Table 3 are summarized in Tables 8 through 13. All oxide of nitrogen values are reported as parts per million of NO_2 (ppm NO_2). Sample volumes were determined and volume calculations performed as described in Federal Register, Method 7(13). In Method 7, the flask pressure is measured prior to sampling and in D 1607-60 the initial pressure is assumed to be equal to the vapor pressure of water at the flask temperature. A comparison of results obtained by the two method is presented later in this report.

The data in Tables 8 through 11 give the results of duplicate determinations of NO_x in the pilot plant flue gas by the cooperating laboratories. Spiking with nitric oxide was used for some pairs of samples (Tables 8 and 10) to provide measurements at higher NO_x levels. Tables 8 and 9 present the results obtained by six cooperating laboratories, coded A through F, during the first week of tests and Tables 10 and 11 contain the second week test data. Four laboratories, coded G through J, participated in the second week of testing, however Laboratory I values are not reported in these or following tables since they were derived from an invalid calibration curve. (Absorbance versus concentration deviated significantly from a linear relationship). The data in Tables 8 through 11 were used to generate the estimates of between-laboratory and within-laboratory precision of NO_x measurements using D 1608-60.

Tables 12 and 13 present the 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 nitric oxide. The laboratories' estimates of the 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". The data in Tables 12 and 13 provide the basis for the estimate of the accuracy of the Test Method.

The data in Table 12 for Blocks 2, 5, 9, and 12 differ in the experimental process from that in Table 13 for Blocks 3, 6, 10, and 13, in the manner in which the absorption flasks were handled. Other steps of the test method were

TABLE 8. RESULTS OF PILOT PLANT NO_x DETERMINATIONS FOR BLOCKS IN WHICH LABORATORIES OBTAINED DUPLICATE SPIKED SAMPLES (FIRST WEEK)

(Results in ppm NO_2)

Week	Day	Block	Lab	Sample 1	Sample 2	Week	Day	Block	Lab	Sample 1	Sample 2
1	1	1	A	(a)	(a)	1	3	7	A	271	265
			B	382	357				B	357	450
			C	19(b)	155(b)				C	367	313
			D	390	307				D	412	359
			E	450	402				E	275	257
			F	429	509				F	446	433
1	2	1	A	537	504	1	1	8	A	1032	992
			B	664(b)	718(b)				B	1039	1056
			C	394	480				C	974	980
			D	527	556				D	1120	1010
			E	531	472				E	815(b)	817(b)
			F	523	426				F	1148(b)	1117(b)
1	3	1	A	136(b)	146(b)	1	2	8	A	1431(b)	1026(b)
			B	236	219				B	970	1139
			C	233	248				C	819(b)	1036(b)
			D	244	271				D	1160	1210
			E	220	209				E	1196	1170
			F	284	252				F	1163	1195
1	1	7	A	(a)	(a)	1	1	14	A	1331	1316
			B	473	548				B	(d)	(d)
			C	492	464				C	1124	1032
			D	569	538				D	1100	1124
			E	(c)	442				E	714(b)	(c)
			F	590	592				F	1342	1396
1	2	7	A	(d)	(d)	1	2	14	A	(e)	1209(b)
			B	819	858				B	1533	1592
			C	326(b)	702(b)				C	1445(b)	1413(b)
			D	884	832				D	1550	1560
			E	701(b)	637(b)				E	1567	1588
			F	867	832				F	1720(b)	1785(b)

(a) Incorrect volume of absorbent used.
(b) Rejected as outlying data.
(c) Sample leaked in transit to analytical laboratory.
(d) Flask leaked during sampling.
(e) Sample contaminated with tap water.

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

(Results in ppm NO_2)

Week	Day	Block	Lab	Sample 1	Sample 2
1	1	4	A	(a)	(a)
			B	231	190
			C	210	209
			D	193(b)	242(b)
			E	(c)	130(b)
			F	211	209
1	2	4	A	469	384
			B	456	431
			C	405(b)	230(b)
			D	461	491
			E	297(b)	292(b)
			F	469	510
1	3	4	A	(d)	29
			B	50	42
			C	41	39
			D	35	31
			E	16	25
			F	22	17
1	1	11	A	316	268
			B	484	513
			C	394	212(b)
			D	469	494
			E	210(b)	265(b)
			F	494	462
1	2	11	A	395	353
			B	529	449
			C	427	434
			D	458	478
			E	358	413
			F	436	435

(a) Incorrect volume of absorbent used.
(b) Rejected as outlying data.
(c) Sample leaked in transit to analytical laboratory.
(d) Sample spilled.

TABLE 10. RESULTS OF PILOT PLANT NO$_x$ DETERMINATIONS FOR BLOCKS IN WHICH LABORATORIES OBTAINED DUPLICATE SPIKED SAMPLES (SECOND WEEK)

(Results in ppm NO$_2$)

Week	Day	Block	Lab	Sample 1	Sample 2	Week	Day	Block	Lab	Sample 1	Sample 2
2	1	1	G	112(a)	245(a)	2	1	8	G	786	830
			H	538	519				H	889	878
			I						I		
			J	466	476				J	766	766
2	2	1	G	696	759	2	2	8	G	1549	1550
			H	710	681				H	1596	1628
			I						I		
			J	658	610				J	1390	1510
2	3	1	G	380	377	2	3	8	G	467	475
			H	(b)	347				H	389	399
			I						I		
			J	314	297				J	439	422
2	1	7	G	443	412	2	1	14	G	1201	1240
			H	580	293(a)				H	1311	1256
			I						I		
			J	562	594				J	(c)	1160
2	2	7	G	1017(a)	1049(a)	2	2	14	G	2086	2002
			H	1247	1364				H	2026	1963
			I						I		
			J	1180	1370				J	1920	1880
2	3	7	G	496	498	2	3	14	G	992	988
			H	455	463				H	1036	920
			I						I		
			J	423	443				J	907	873

(a) Reject as outlying data.
(b) Sample spilled.
(c) Stopcock opened, sample lost.

TABLE 11. RESULTS OF PILOT PLANT NO_x DETERMINATIONS FOR BLOCKS IN WHICH LABORATORIES OBTAINED DUPLICATE UNSPIKED SAMPLES (SECOND WEEK)

(Results in ppm NO_2)

Week	Day	Block	Lab	Sample 1	Sample 2
2	1	4	G	204	199
			H	237	207
			I		
			J	221	160
2	2	4	G	396	378
			H	287	252
			I		
			J	363	(a)
2	3	4	G	152	164
			H	122	120
			I		
			J	45(b)	(c)
2	1	11	G	473	450
			H	444	474
			I		
			J	418	448
2	2	11	G	747	730
			H	846	839
			I		
			J	686	525
2	3	11	G	294	311
			H	291	321
			I		
			J	291	293

(a) Flask leaked prior to sampling.
(b) Rejected as outlying data.
(c) Final pressure was not measured.

TABLE 12. RESULTS OF PILOT PLANT NO_x DETERMINATIONS FOR BLOCKS IN WHICH LABORATORIES OBTAINED CONCURRENT SPIKED AND UNSPIKED SAMPLES (OVERNIGHT ABSORPTION)

(Results in ppm NO_2)

Week	Day	Block	Lab	Spiked Sample	Unspiked Sample	Esimated Spiking Conc.	True Spiking Conc.	Difference Percentage Of True
1	1	2	A	(a)	(a)	--	--	--
			B	357	161	196	237	-17.3
			C	207(b)	162	--	237	--
			D	483	215	268	237	13.1
			E	401	51(b)	--	237	--
			F	463	232	231	237	-2.5
1	1	5	A	(a)	(a)	--	--	--
			B	597	176	421	366	15.0
			C	299(b)	189	--	366	--
			D	596	271	325	366	-11.2
			E	175(b)	54(b)	--	366	--
			F	638	224	414	366	13.1
1	1	9	A	1209(b)	433	--	360	--
			B	1154(b)	511	--	360	--
			C	766	108(b)	--	360	--
			D	1145(b)	--	--	--	--
			E	802	388	414	360	15.0
			F	1222(b)	489	--	360	--
1	1	12	A	1074	501	573	729	-21.4
			B	1355	584	771	729	5.8
			C	1131	213(b)	--	729	--
			D	1228	518	710	729	-2.6
			E	704(b)	249(b)	--	729	--
			F	1412	535	877	729	20.3
2	1	2	G	563	324	239	228	4.8
			H	600	325	275	228	20.6
			I	--	--	--	--	--
			J	430	118(b)	--	228	--
2	1	5	G	685	304	381	367	3.8
			H	733	308	425	367	15.8
			I	--	--	--	--	--
			J	644	124(b)	--	367	--
2	1	9	G	893	472	421	375	12.3
			H	825	503	322	375	-14.1
			I	--	--	--	--	--
			J	846	448	398	375	6.1
2	1	12	G	1125	530	595	763	-22.0
			H	1158	492	666	763	-12.7
			I	--	--	--	--	--
			J	1190	484	706	763	-7.5

TABLE 12. (Continued)

Week	Day	Block	Lab	Spiked Sample	Unspiked Sample	Esimated Spiking Conc.	True Spiking Conc.	Difference Percentage Of True
1	2	2	A	(c)	(c)	--	--	--
			B	761	500	261	370	-29.5
			C	169(b)	147(b)	--	370	--
			D	737	345	392	370	5.9
			E	580(b)	198(b)	382	370	--
			F	807	365	442	370	19.5
1	2	5	A	1264	500	764	746	2.4
			B	1259	413	846	746	13.4
			C	1006	392	614	746	-17.7
			D	1293	561	732	746	-1.9
			E	980	451	529	746	-29.1
			F	1299	564	735	746	-1.5
1	2	9	A	1169	371	798	738	8.1
			B	1114	439	675	738	-8.5
			C	1096	404	692	738	-6.2
			D	1190	421	769	738	4.2
			E	976	386	590	738	-20.1
			F	857(b)	350	--	738	--
1	2	12	A	1585	510	1075	1021	5.3
			B	1499	385	1114	1021	9.1
			C	1315	421	894	1021	-12.4
			D	1565	424	1141	1021	11.8
			E	898(b)	403	--	1021	--
			F	1692	447	1245	1021	21.9
2	2	2	G	689	345	344	364	-5.5
			H	605	299	306	364	-15.9
			I	--	--	--	--	--
			J	627	305	322	364	-11.5
2	2	5	G	1112	416	696	754	-7.7
			H	1194	390	804	754	6.6
			I	--	--	--	--	--
			J	1280	478	802	754	6.4
2	2	9	G	1300	784	516	772	-33.2
			H	1516	796	720	772	-6.7
			I	--	--	--	--	--
			J	1330	609	721	772	-6.6
2	2	12	G	2093	873	1220	1021	19.5
			H	2128	1315(b)	--	1021	--
			I	--	--	--	--	--
			J	1830	782	1048	1021	2.6

TABLE 12. (Continued)

Week	Day	Block	Lab	Spiked Sample	Unspiked Sample	Estimated Spiking Conc.	True Spiking Conc.	Difference Percentage Of True
1	3	2	A	184	57	127	232	-45.3
			B	316	70	246	232	6.0
			C	265	67	198	232	-14.7
			D	274	62	212	232	-8.6
			E	282	46	236	232	1.7
			F	342	92	250	232	7.8
1	3	5	A	336	59	277	361	-23.3
			B	381	52	329	361	-8.9
			C	254(b)	66	188	--	--
			D	422	52	370	361	2.5
			E	348	42	306	361	-15.2
			F	460	60	400	361	10.8
2	3	2	G	367	149	218	232	-6.0
			H	343	148	195	232	-15.9
			I	--	--	--	--	--
			J	277	148	129	232	-44.4
2	3	5	G	543	236	307	366	-16.1
			H	469	147	322	366	-12.0
			I	--	--	--	--	--
			J	482	137	345	366	-5.7
2	3	9	G	558	326	232	238	-2.5
			H	470	211	259	238	8.8
			I	--	--	--	--	--
			J	478	262	216	238	-9.2
2	3	12	G	1041	297	744	754	-1.3
			H	1063	272	791	754	4.9
			I	--	--	--	--	--
			J	921	238	683	754	-9.4

(a) Incorrect volume of absorbent used.
(b) Rejected as outlying data.
(c) Leak occurred during sampling.

TABLE 13. RESULTS OF PILOT PLANT NO_x DETERMINATIONS FOR BLOCKS IN WHICH LABORATORIES OBTAINED CONCURRENT SPIKED AND UNSPIKED SAMPLES (2 HOUR ABSORPTION)

(Results in ppm NO_2)

Week	Day	Block	Lab	Spiked Sample	Unspiked Sample	Estimated Spiking Conc.	True Spiking Conc.	Difference Percentage Of True
1	1	3	A	(a)	(a)	--	--	--
			B	463	213	250	233	7.3
			C	485	206	279	233	19.7
			D	486	230	256	233	9.9
			E	418	81(b)	--	233	--
			F	427	168	259	233	11.2
1	1	6	A	(a)	(a)	--	--	--
			B	471	63(b)	--	372	--
			C	498	192	306	372	-17.7
			D	515	207	308	372	-17.2
			E	344(b)	152	--	372	--
			F	559	103	456	372	22.6
1	1	10	A	1138(b)	468	--	360	--
			B	1068(b)	455	--	360	--
			C	1014	475	539	360	49.7
			D	615	434	181	360	-49.7
			E	783	282(b)	--	360	--
			F	1253(b)	421	--	360	--
1	1	13	A	1121	558	563	719	-21.7
			B	1364	584	780	719	8.5
			C	1098	465	633	719	-12.0
			D	1067	424	643	719	-10.6
			E	676(b)	286(b)	--	719	--
			F	1322	501	821	719	14.2
2	1	3	G	448	278(b)	--	230	--
			H	410	286(b)	--	230	--
			I	--	--	--	--	--
			J	403	160	243	230	5.7
2	1	6	G	336(b)	117	--	365	--
			H	558	282(b)	--	365	--
			I	--	--	--	--	--
			J	593	103	490	365	34.2
2	1	10	G	865	473	392	376	4.3
			H	909	496	413	376	9.8
			I	--	--	--	--	--
			J	854	481	373	376	-0.8

TABLE 13. (Continued)

Week	Day	Block	Lab	Spiked Sample	Unspiked Sample	Estimated Spiking Conc.	True Spiking Conc.	Difference Percentage Of True
2	1	13	G	1282	459	823	763	7.9
			H	1266	491	775	763	1.6
			I	--	--	--	--	--
			J	1150	368	782	763	2.5
1	2	3	A	619	258	361	371	-2.7
			B	788	227	561	371	51.2
			C	404(b)	305	--	371	--
			D	620	(c)	--	--	--
			E	513	(d)	--	--	--
			F	709	291	418	371	12.7
1	2	6	A	986	417	569	760	-25.1
			B	946	422	524	760	-31.1
			C	1045	316	729	760	-4.1
			D	1130	363	767	760	0.9
			E	(d)	273	--	--	--
			F	1238	298	940	760	23.7
1	2	10	A	917	360	557	750	-25.7
			B	1182	455	727	750	-3.1
			C	602(b)	386	--	750	--
			D	1160	416	744	750	-0.8
			E	1022	391	631	750	-15.9
			F	1108	284	824	750	9.9
1	2	13	A	(e)	(e)	--	--	--
			B	1499	398	1101	1023	7.6
			C	1397	447	950	1023	-7.1
			D	1574	453	1121	1023	9.6
			E	1767	440	1327	1023	29.7
			F	1744	345	1399	1023	36.8
2	2	3	G	767	427	340	385	-11.7
			H	815	382	433	385	12.5
			I	--	--	--	--	--
			J	708	401	307	385	-20.3
2	2	6	G	1216	472	744	787	-5.5
			H	1314	459	855	787	8.6
			I	--	--	--	--	--
			J	1270	454	816	787	3.7
2	2	10	G	1582	844	738	754	-2.1
			H	1448	774	674	754	-10.6
			I	--	--	--	--	--
			J	1450	791	659	754	-12.6

TABLE 13. (Continued)

Week	Day	Block	Lab	Spiked Sample	Unspiked Sample	Estimated Spiking Conc.	True Spiking Conc.	Difference Percentage Of True
2	2	13	G	1949	730	1219	1013	20.3
			H	2098	586(b)	--	1013	49.3
			I	--	--	--	--	--
			J	1940	793	1147	1013	13.2
1	3	3	A	185	42	143	226	-36.7
			B	480(b)	72	--	226	--
			C	263	60	203	226	-10.2
			D	277	35	242	226	7.1
			E	190	(d)	--	--	--
			F	324	69	255	226	12.8
1	3	6	A	302	12	290	364	-20.3
			B	375	43	332	364	-8.8
			C	361	32	329	364	-9.6
			D	350	42	308	364	-15.4
			E	211(b)	(d)	--	--	--
			F	472	48	424	364	16.5
2	3	3	G	381	138	243	232	4.7
			H	(f)	130	--	--	--
			I	--	--	--	--	--
			J	304	38(b)	--	232	--
2	3	6	G	476	94	382	371	3.0
			H	340	51	289	371	-22.1
			I	--	--	--	--	--
			J	436	57	379	371	2.2
2	3	10	G	537	274	263	232	13.4
			H	479	269	210	232	-9.5
			I	--	--	--	--	--
			J	445	246	199	232	-14.2
2	3	13	G	894	279	615	747	-17.7
			H	918	316	602	747	-19.4
			I	--	--	--	--	--
			J	905	218	687	747	-8.0

(a) Incorrect volume of absorbent used.
(b) Rejected as outlying data.
(c) Stopcock turned wrong direction during sampling.
(d) Sample leaked in transit to analytical laboratory.
(e) Sample contaminated with tap water.
(f) Sample spilled.

performed the same in all blocks. In the former case, the absorption flasks were allowed to stand overnight while in the latter series of blocks, the flask were shaken every 20 minutes and were transferred after 2 hours. An overnight absorption period was used for all blocks in which either two spiked or two unspiked samples were taken. In the accuracy analysis, the results for these two Test Method options are compared to determine whether they might contribute to any bias in the determinations.

The data in Tables 8 through 11, which were used for estimates of between- and within-laboratory variance were examined for outliers using several criteria. One of these was the Studentized range test (14) 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. A second criteria used to detect outliers considered the contribution of each observation to the group's total sum of squares of deviations about the group mean. Although this method did not explicitly test for statistically significant outliers, it provided a screening device which identified observation which contributed a relatively high percentage of the total sum of squares of deviation about the group mean.

The data in Tables 12 and 13 which were used for the accuracy analysis, also were examined for outliers. One criteria for identifying outliers was based upon the estimated spike value from the observations. This estimated spike value was obtained as the difference between the determinations for the spiked and unspiked sample. A percentage difference was calculated using the true known spike value as base. The frequency distribution of observed percentage differences was determined and 95 percent cut off limits were established for this distribution. Any determinations outside these limits were flagged as outliers.

Visual scans of the data were sufficient to identify which observations within a group resulted in the tests for outliers being significant. Further confirmation of these outliers were made using the single sample test procedures (15) based upon Table 1 of ASTM E 178.

A summary of the number and distribution of outlying values is given in Table 14. One hundred and twenty-one determinations were lost due to experimental errors; 84 by one laboratory due to an erroneous calibration curve. Of the remaining 756 determination, 82 were declared to be outliers, and excluded due to probable errors in the experimental process and/or recording of data.

Field Tests

Tables 15, 16, and 17 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 samples were taken by four laboratories. Sample volume measurements and calculations were performed as described in Federal Register, Method 7.

The data from Sites I and III show reasonably good agreement among concurrent samples while Site II exhibits considerable variation. It is believed that the variation results from actual concentration differences at the various sampling ports due to factors which are discussed later in the report. Consequently, the Site II data were excluded from further statistical treatment. Site I and Site III test data were examined for outlying values using Dixon's Criterion(14). Four of the 24 tests (96 determinations) performed at the two sites were determined to contain one outlying value. The outliers could not be attributed to any recognized error in sampling or 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) were the data collected in blocks 1, 4, 7, 8, 11, and 14 of the pilot plant tests. These blocks 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 procedures outlined in Brownlee.(16) Basically, this

TABLE 14. SUMMARY OF DATA REJECTED AS OUTLYING

Sample Type	Determinations	Outlying Values
Both Spiked		
1st week	120	24
2nd week	96	5
Both Unspiked		
1st week	60	10
2nd week	48	1
One Spiked and One Unspiked		
Overnight Absorption		
1st week	120	20
2nd week	96	3
2-Hr absorption		
1st week	120	13
2nd week	96	6
Totals	756	82

TABLE 15. RESULTS OF NO_x DETERMINATIONS AT FIELD TEST SITES USING ASTM METHOD D 1608-60

Site	Laboratory	Test Number	Port Number	Oxides of Nitrogen Concentration ppm NO_2
I	A	1	7	183
	B		9	180
	C		5	150
	D		3	197
I	A	2	7	184
	B		9	185
	C		5	157(a)
	D		3	185
I	A	3	7	180
	B		9	176
	C		5	189
	D		3	182
I	A	4	7	187
	B		9	183
	C		5	186
	D		3	176

(a) Rejected as outlying data based on Dixon's Criterion.

TABLE 15. (Continued)

Site	Laboratory	Test Number	Port Number	Oxides of Nitrogen Concentration ppm NO_2
I	A	5	7	181
	B		9	187
	C		5	127 (a)
	D		3	185
I	A	6	7	186
	B		9	188
	C		5	185
	D		3	195
I	A	7	7	191
	B		5	183
	C		9	176
	D		3	191
I	A	8	7	182
	B		5	172
	C		9	190
	D		3	198

(a) Rejected as outlying data based on Dixon's Criterion

TABLE 16a RESULTS OF NO_x DETERMINATIONS AT FIELD TEST SITES USING ASTM METHOD D 1608

Site	Laboratory	Test Number	Port Number	Oxides of Nitrogen Concentration ppm NO_2
II	A	1	2	495
	B		1	76
	C		4	309
	D		3	484
II	A	2	2	534
	B		1	85
	C		4	437
	D		3	498
II	A	3	3	462
	B		2	126
	C		1	318
	D		4	570
II	A	4	3	521
	B		2	389
	C		1	313
	D		4	573

TABLE 16. (Continued)

Site	Laboratory	Test Number	Port Number	Oxides of Nitrogen Concentration ppm NO_2
II	A	5	4	590
	B		3	372
	C		2	274
	D		1	94
II	A	6	4	533
	B		3	325
	C		2	330
	D		1	209
II	A	7	1	136
	B		4	389
	C		3	241
	D		2	345
II	A	8	1	188
	B		4	394
	C		3	309
	D		2	717

TABLE 16. (Continued)

Site	Laboratory	Test Number	Port Number	Oxides of Nitrogen Concentration ppm NO_2
II	A	9	2	613
	B		1	139
	C		4	277
	D		3	405
II	A	10	2	528
	B		1	151
	C		4	428
	D		3	13
II	A	11	3	422
	B		2	548
	C		1	338
	D		4	634
II	A	12	3	482
	B		2	399
	C		1	327
	D		4	573

TABLE 16. (Continued)

Site	Laboratory	Test Number	Port Number	Oxides of Nitrogen Concentration ppm NO_2
II	A	13	4	417
	B		3	298
	C		2	297
	D		1	182
II	A	14	4	430
	B		3	397
	C		2	320
	D		1	209
II	A	15	1	241
	B		4	459
	C		3	283
	D		2	492
II	A	16	1	235
	B		4	462
	C		3	350
	D		2	617

TABLE 17. RESULTS OF NO_x DETERMINATIONS AT FIELD TEST SITES USING ASTM METHOD D 1608

Site	Laboratory	Test Number	Port Number	Oxides of Nitrogen Concentration ppm NO_2
III	A	1	1	233
	B		3	262
	C		2	255
	D		4	220
III	A	2	1	220
	B		3	260
	C		2	236
	D		4	226
III	A	3	2	250
	B		4	248
	C		3	243
	D		1	257
III	A	4	2	261
	B		4	240
	C		3	260
	D		1	264

TABLE 17. (Continued)

Site	Laboratory	Test Number	Port Number	Oxides of Nitrogen Concentration ppm NO_2
III	A	5	3	227
	B		1	252
	C		4	233
	D		2	233
III	A	6	3	224
	B		1	258
	C		4	223
	D		2	243
III	A	7	4	224
	B		2	255
	C		1	197
	D		3	240
III	A	8	4	199
	B		2	244
	C		1	180
	D		3	218

TABLE 17. (Continued)

Site	Laboratory	Test Number	Port Number	Oxides of Nitrogen Concentration ppm NO_2
III	A	9	4	178
	E		2	177
	C		3	166
	F		1	86 (a)
III	A	10	4	128
	E		2	122
	C		3	129
	F		1	120
III	A	11	1	137
	E		3	127
	C		4	118
	F		2	89
III	A	12	1	133
	E		3	128
	C		4	120
	F		2	113

(a) Rejected as outlying data based on Dixon's Criterion

TABLE 17. (Continued)

Site	Laboratory	Test Number	Port Number	Oxides of Nitrogen Concentration ppm NO_2
III	A	13	2	172
	E		4	153
	C		1	153
	F		3	11 (a)
III	A	14	2	155
	E		4	139
	C		1	165
	F		3	98
III	A	15	3	117
	E		1	100
	C		2	88
	F		4	127
III	A	16	3	122
	E		1	115
	C		2	103
	F		4	130

(a) Rejected as outlying data based on Dixon's Criterion.

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 18. From this table, it can be seen that an estimate of within-laboratory precision, S_W, is given by

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

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

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

where

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

TABLE 18. 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 Labs	$\sum_{i=1}^{k} n_i - k$	$\sum_{i=1}^{k} \sum_{j=1}^{n_i} (X_{ij}-\bar{X}_{i.})^2$	S_1^2	σ_B^2
Total	$\sum_{i=1}^{k} n_i - 1$	$\sum_{i=1}^{k} \sum_{j=1}^{n_i} (X_{ij}-\bar{X}_{..})^2$		

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

The results of this statistical analysis are presented in Tables 19 and 20. Table 19 presents the estimates of between- and within-laboratory components of variance for each block of simultaneous determinations of duplicate spiked samples, and Table 20 gives the corresponding data for duplicate unspiked samples. The statistical summaries presented in Tables 19 and 20 do not include the data points which were rejected as outliers.

Figure 9 is a scattergram of the block statistics, presenting a plot of between-laboratory component of variance, $\hat{S}_B$, (reproducibility) versus the square root of the mean NO_x concentration, $\sqrt{m}$.

A least-squares regression equation of the form $\hat{S}_B = b\sqrt{m} + a$ was fitted to the data points in Figure 9 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 $\hat{S}_B = 2.21\sqrt{m} - 1.18$ is obtained as an estimate of the true regression curve $s = \beta\sqrt{m} + \alpha$. The standard deviation of the residuals about the regression line is found to be 16.9 ppm. The regression accounts for approximately 56 percent of the variability in reproducibility estimates. This curve summarizes the estimate of the between-laboratory component of variance (reproducibility) over the concentration range of about 20 to 2000 ppm NO_2 obtained from the pilot plant tests.

Separate least-squares analyses of the data in the concentration ranges of < 600 ppm NO_2 and >600 ppm NO_2 were performed. The resulting least-squares curves (S_B versus $\sqrt{m}$) did not vary significantly from the relationship

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* 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 250, an upper limit of the reproducibility estimate.

TABLE 19. BETWEEN-LABORATORY AND WITHIN-LABORATORY PRECISION FOR DETERMINATIONS OF DUPLICATE SPIKED SAMPLES

Week	Day	Block	No. of Labs	No. of Measmts.	Mean NO_x Conc., ppm	Between-Lab Std. Dev(S_B), ppm	CV, %	Within-Lab Std. Dev(S_W), ppm	CV %
1	1	1	4	8	403.3	50.4	12.5	45.0	11.2
		7	5	9	523.1	50.8	9.7	30.4	5.8
		8	4	8	1025.4	25.5	2.5	41.9	4.1
		14	4	8	1220.6	144.3	11.8	39.0	3.2
1	2	1	5	10	495.0	23.4	4.7	47.1	9.5
		7	3	6	848.7	(a)	(a)	30.1	3.6
		8	4	8	1150.4	45.2	3.9	64.0	5.6
		14	3	6	1565.0	(a)	(a)	25.9	1.7
1	3	1	5	10	241.6	18.8	7.8	15.5	6.4
		7	6	12	350.4	67.7	19.3	35.2	10.1
2	1	1	2	4	499.8	39.9	8.0	10.7	2.2
		7	3	5	518.2	90.9	17.5	22.3	4.3
		8	3	6	819.2	58.1	7.1	18.5	2.3
		14	3	5	1233.6	51.4	4.2	33.7	2.7
2	2	1	3	6	685.7	40.8	6.0	34.4	5.0
		7	2	4	1290.3	(a)	(a)	111.6	8.7
		8	3	6	1537.2	73.4	4.8	50.7	3.3
		14	3	6	1979.5	65.6	3.3	45.9	2.3
2	3	1	3	5	343.0	40.3	11.8	8.6	2.5
		7	3	6	463.0	31.6	6.8	8.8	1.9
		8	3	6	431.8	38.0	8.8	8.7	2.0
		14	3	6	952.7	42.0	4.4	49.4	5.2

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

TABLE 20. BETWEEN-LABORATORY AND WITHIN-LABORATORY PRECISION FOR DETERMINATIONS OF DUPLICATE UNSPIKED SAMPLES

Week	Day	Block	No. of Labs	No. of Measmts.	Mean NO_x Conc., ppm	Between-Lab Std. Dev(S_B),ppm	CV, %	Within-Lab Std. Dev(S_W),ppm	CV %
1	1	4	3	6	210.0	(a)	(a)	16.8	8.0
		11	5	9	432.7	88.9	20.6	24.5	5.7
1	2	4	4	8	458.9	13.7	3.0	36.11	7.9
		11	6	12	430.4	39.0	9.1	31.1	7.2
1	3	4	6	11	31.6	10.5	33.4	4.4	13.8
2	1	4	3	6	204.7	(a)	(a)	27.8	13.6
		11	3	6	451.2	7.4	1.6	19.7	4.4
2	2	4	3	5	335.2	66.1	19.7	19.7	5.9
		11	3	6	728.8	109.2	15.0	66.2	9.1
2	3	4	2	4	139.5	25.8	18.5	6.1	4.4
		11	3	6	300.2	(a)	(a)	14.1	4.7

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

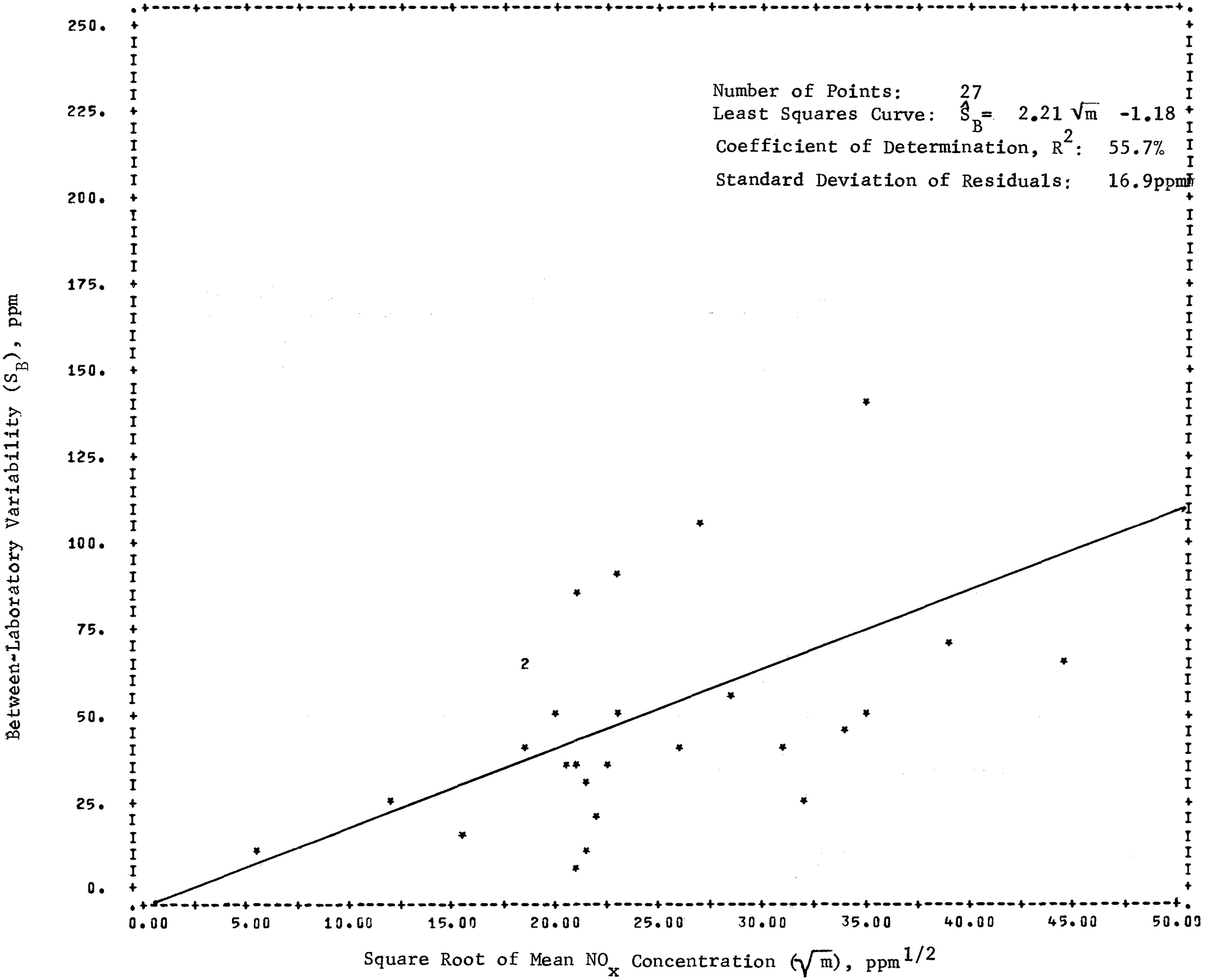


FIGURE 9. SCATTERGRAM AND LEAST SQUARES CURVE RELATING BETWEEN-LABORATORY VARIABILITY (REPRODUCIBILITY) TO THE SQUARE ROOT OF THE MEAN NO_x CONCENTRATION FOR PILOT PLANT DATA

presented in Figure 9.

In Figure 10, a scattergram of the block estimates of within-laboratory variability (repeatability), S_W, versus the square root of the mean NO_x concentration is presented. A curve of the form $S_W = b\sqrt{m} + a$ was fitted to these data points by the method of weighted least squares, using the same weighting procedure used for the reproducibility analysis. The iterative approach which is required, results in the equation, $S_W = 1.52\sqrt{m} - 4.21$, with a standard deviation of residual equal to 7.2 ppm. This regression accounts for approximately 73 percent of the variability in repeatability estimates. The least-square analysis of the data in the concentration ranges of 0 to 600 ppm NO_2 and >600 ppm NO_2 yields curves which did not vary significantly from those shown in Figure 10. The curve in Figure 10 summarizes the estimate of within-laboratory variability (repeatability) over the concentration range of about 20 to 2000ppm NO_2 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 and III are presented in Table 21. The table presents the number of measurements per test, n; the mean value of the NO_x 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 was calculated as the standard deviation of measurements from each test, using the equation

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

where m is the test mean, X_i is the NO_x value determined by the $i^{\underline{th}}$ laboratory and n is the number of NO_x 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,

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

Site II data were not analyzed statistically due to the large variations in concurrent determinations which do not appear related to the test method. An analyses of the determinations by port shows that the lowest

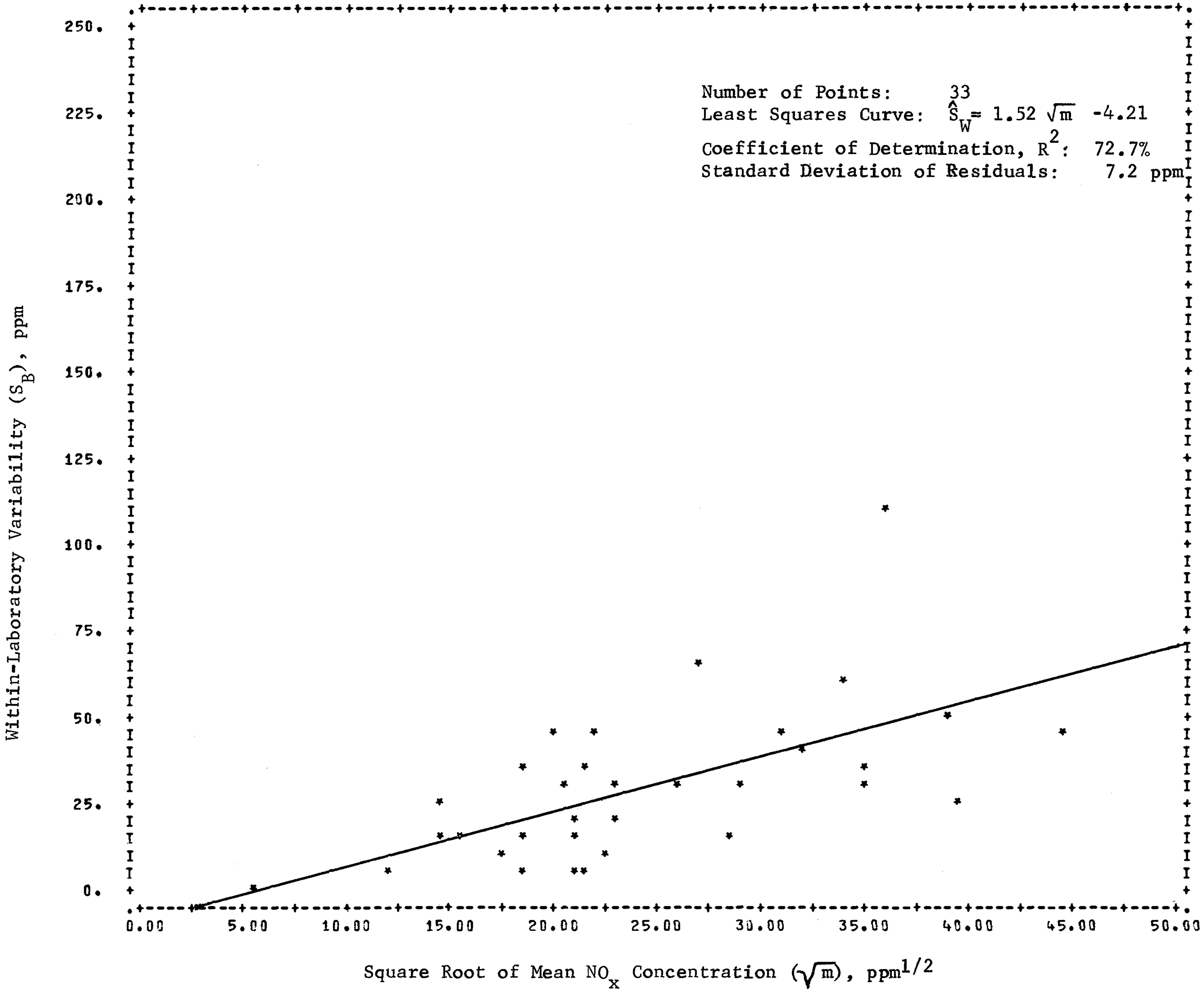


FIGURE 10. SCATTERGRAM AND LEAST SQUARES CURVE REALTING WITHIN-LABORATORY VARIABILITY (REPEATABILITY) TO THE SQUARE ROOT OF THE MEAN NO_x CONCENTRATION FOR PILOT PLANT DATA

TABLE 21. STATISTICAL ANALYSIS OF NO_x MEASUREMENTS PERFORMED AT FIELD TEST SITES

Site	Test Number	Number of Measurements, n	Mean NO_x Conc, ppm NO_2	Standard Deviation (S_T), ppm NO_2	Coefficient of Variation, %
I	1	4	178	19.8	11.1
	2	3	185	0.6	0.3
	3	4	182	5.4	3.0
	4	4	183	5.0	2.7
	5	3	184	3.1	1.7
	6	4	189	4.5	2.4
	7	4	185	7.2	3.9
	8	4	185	11.1	6.0
III	1	4	243	19.4	8.0
	2	4	236	17.6	7.5
	3	4	250	5.8	2.3
	4	4	256	11.0	4.3
	5	4	236	10.9	4.6
	6	4	237	16.7	7.0
	7	4	229	24.8	10.8
	8	4	210	27.3	13.0
	9	3	174	6.7	3.9
	10	4	125	4.4	3.5
	11	4	118	20.7	17.5
	12	4	124	8.8	7.1
	13	3	159	11.0	6.9
	14	4	139	29.5	21.2
	15	4	108	17.4	16.1
	16	4	118	11.4	9.7

NO_x value in nearly all tests (14 of 16) was obtained at Port 1. This could have resulted from a defective probe (probes remained stationary), in-leakage of air around the sampling port (stack pressure was about -6 inches H_2O), or actual concentration differences in the large stack (30-ft diameter).

The Site I and III data exhibit a more random distribution in determinations when examined by laboratory and by sampling location.

A least-squares analysis of the field test data indicated no linear relationship between the between-laboratory standard error and the concentration level over the limited concentration range which was studied. Therefore, the mean of the standard error from all tests can be used to provide an estimate of the between-laboratory standard error from the field data. For the NO_x determinations which spanned the range of about 90 to 260 ppm NO_2 the mean between-laboratory standard error is 14.5 ppm and the standard deviation of the distribution of observed standard errors is 7.3 ppm.

The field test results are compared with the pilot plant data in Figure 11. The pilot plant data result from determinations with mean concentrations in the range of about 20 to 2000 ppm to NO_2, while the field tests data cover a more limited range, about 90 to 260 ppm NO_2. The field test data yield an estimate of the standard error between laboratories; consequently for comparison the pilot plant data have been combined to provide the same measure, using the equation

$$S_T(\text{between laboratory}) = \sqrt{S_B^{\,2} + S_W^{\,2}}$$

where S_B and S_W are the between-laboratory and within laboratory components of variance. The straight line shown in the figure represents the estimated relationship between the square root of the mean concentration and the standard error, S_T (between-laboratory) computed from the reproducibility and repeatability relationships obtained from the pilot plant data, Figures 9, and 10, respectively. The results in Figure 11, show that the observed standard errors between laboratories for the field test data fall below the estimated between-laboratory standard error from the pilot plant data. This suggests that the reproducibility and repeatability measures from the pilot plant experiments may yield conservative estimates of the standard error within this range of concentrations.

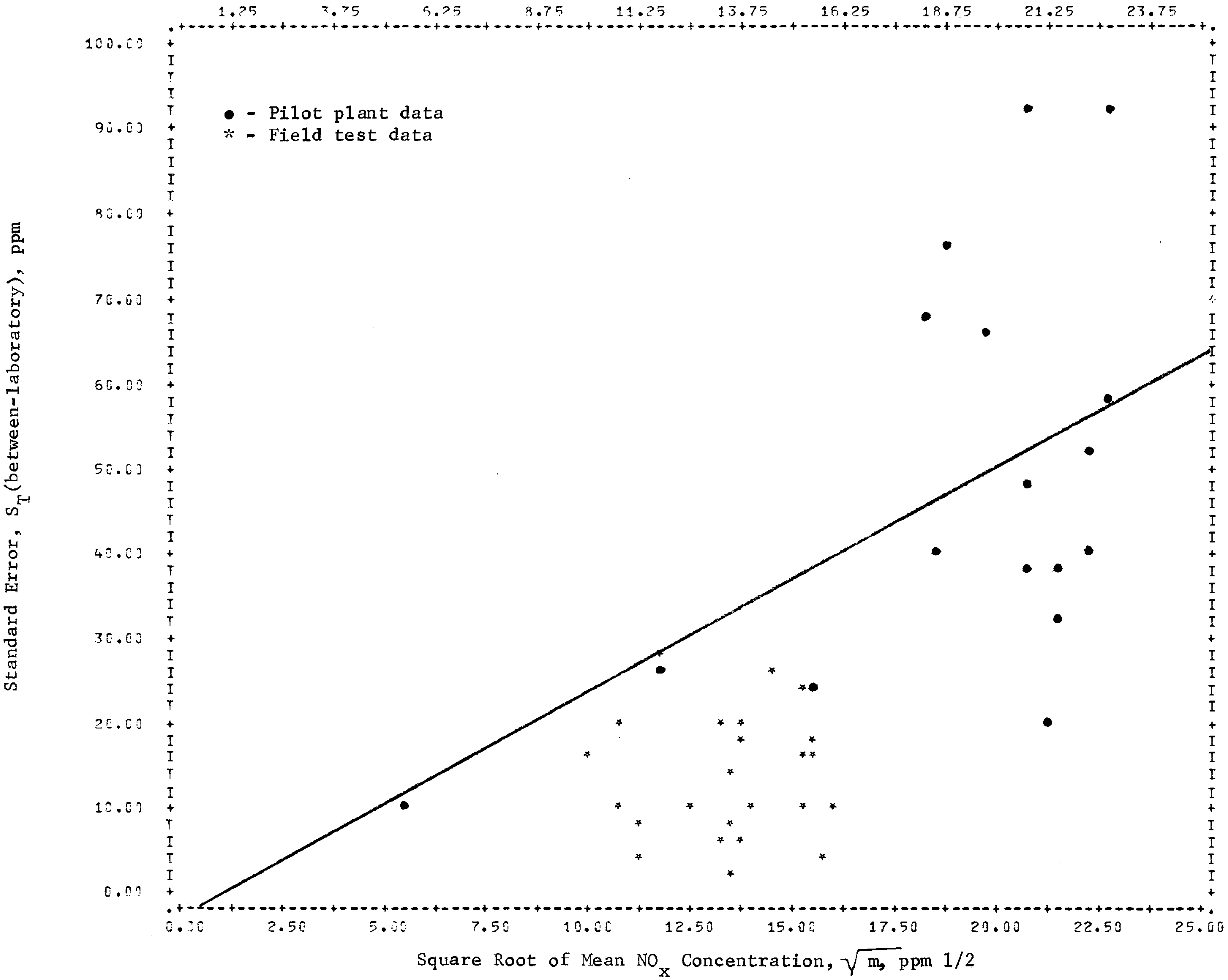


FIGURE 11. COMPARISON OF FIELD AND PILOT PLANT TEST DATA

Analysis of Accuracy

Data from the Blocks in which both spiked and unspiked sample determinations were performed were used to estimate the accuracy of D 1608-60. 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 nitrogen oxides added to the test samples. These differences, obtained by each laboratory are the basis for the analysis of accuracy.

The accuracy is measured as a percentage difference from the true value as calculated by the equation

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

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

Figure 12 presents a histogam of percentage differences for data at all spike concentrations. The distribution appears normal (i.e., Gaussian) with a mean of -3.25 percent and a standard deviation of 25.93, based upon 145 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:

$$t = x\sqrt{n}/s = -3.25\sqrt{145}/25.93 = -1.51$$

For n-1 = 144 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 22. These data permit an investigation of bias in the Test Method at two concentration ranges. The results indicate that there is no statistically significant bias present in either of the concentration ranges examined.

An analysis of the accuracy data based on duration of the sample absorption period is presented in Table 23. The mean percent difference from the true spike value, the standard deviation of the percent differences, and the

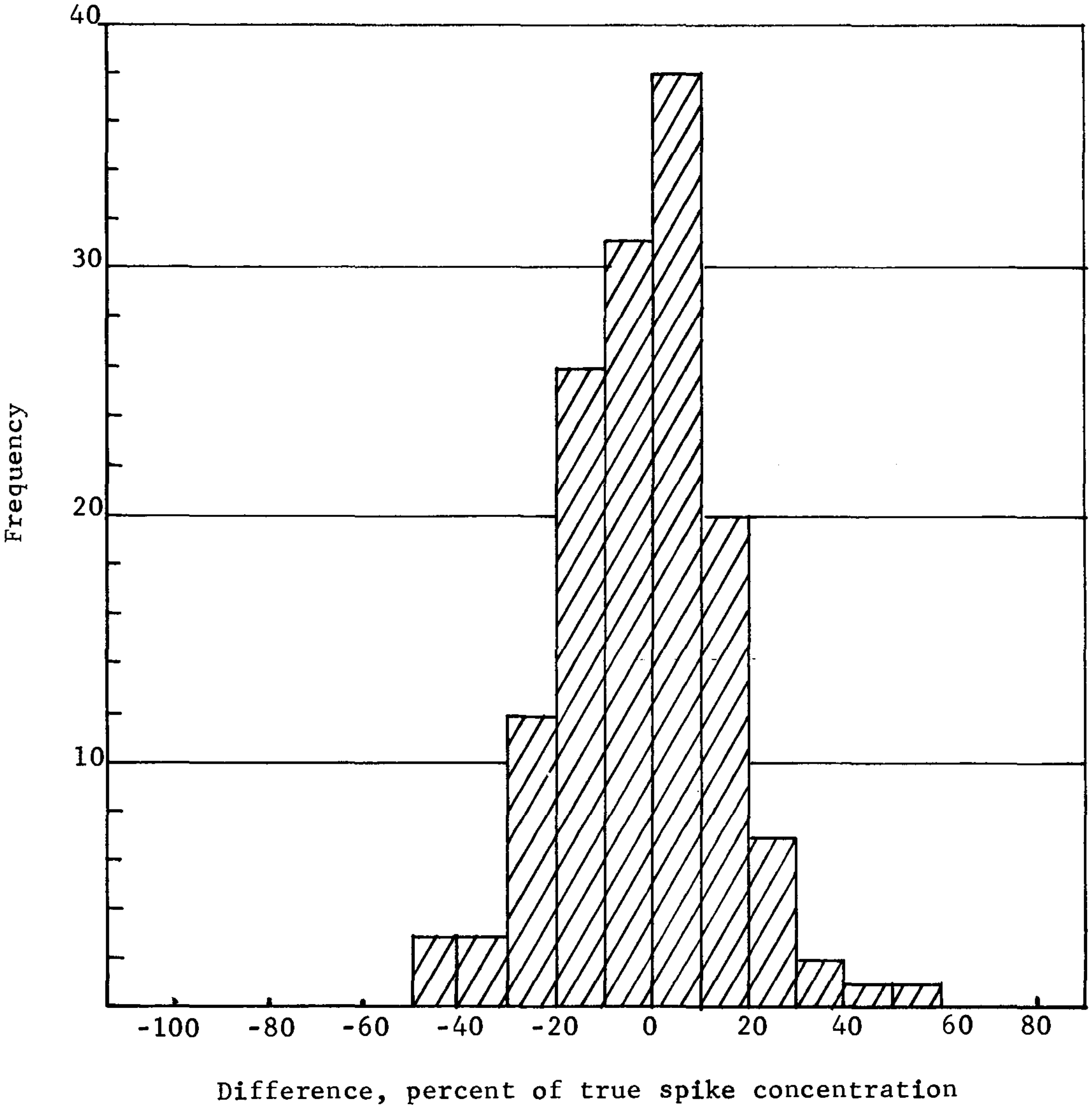


FIGURE 12. DISTRIBUTION OF PERCENTAGE DIFFERENCES BETWEEN ESTIMATED AND TRUE SPIKE CONCENTRATIONS

TABLE 22. SUMMARY OF ACCURACY OF NO_x DETERMINATIONS AS A FUNCTION OF SPIKE CONCENTRATION

Spike Concentration, ppm NO_2	Number of Observations	Mean Percent Difference	Standard Deviation	Student's t	Conclusion[a]
$X \leq 700$	77	-4.55	32.85	-1.22	NS
$700 < X$	68	-1.77	14.71	-0.98	NS
Total	145	-3.25	25.93	-1.51	NS

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

TABLE 23. SUMMARY OF ACCURACY OF NO_x DETERMINATIONS AS A FUNCTION OF ABSORPTION PERIOD DURATION

Absorption Period	Spike Concentrates ppm NO_2	Number of Observations	Mean Percent Difference	Standard Deviation	Student's t Statistic	Conclusion[a]
Overnight	X≤700	41	-9.60	40.16	-1.53	NS
	X>700	34	-2.53	13.55	-1.09	NS
	All	75	-6.40	31.09	-1.78	NS
Two-Hours	X≤700	36	1.21	20.87	0.35	NS
	X>700	34	-1.01	15.96	-0.37	NS
	All	70	0.13	18.55	0.06	NS

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

Students't statistic and conclusions are given for high and low spike concentration ranges. The overnight samples were allowed to stand without shaking for a period of at least 16 hours. The two-hour samples were shaken after sampling and at 20 minute intervals for the two-hour period. The absorbent solution was transfered to a sample bottle at the end of the two-hour period.

The results show that the shorter absorption period does not introduce a statistically significant bias in the determination of NO_x over the concentration range studied. However, the rather wide overall variation in the data would overshadow any slight bias introduced by the shorter absorption period on the order of the -3 percent stated in the method.

A summary of the accuracy of the NO_x determinations by laboratory is given in Table 24. 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 two exceptions, we can conclude that the average bias of each laboratory is probably zero.

TABLE 24. SUMMARY OF ACCURACY OF NO_x DETERMINATIONS BY LABORATORY

Laboratory	No. of Observations	Mean Percent Difference	Standard Deviation	Student's t	Conclusion[a]
A	14	-17.20	16.872	-3.81	S
B	17	-13.17	61.636	-0.88	NS
C	12	-3.52	19.438	-0.63	NS
D	18	-2.95	14.911	-0.84	NS
E	7	-4.83	21.134	-0.60	NS
F	17	14.68	9.378	6.45	S
G	22	-1.70	13.219	-0.60	NS
H	19	-2.62	13.222	-0.86	NS
I	0	---	---	---	--
J	21	-3.51	14.963	-1.07	NS
Total	145	-3.25	25.926	-1.51	NS

(a) NS=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.

Analysis of Standard Nitrate Solutions

Series of standard potassium nitrate 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 2.33, 4.66, and 7.75mg NO_2 were provided following the pilot plant tests. The results of the analysis of these samples by the various laboratories are given in Table 25. The laboratory code designations for the standard data are the same as those used for the test results.

The means and standard deviations of the quantity found by the various laboratories and the differences in milligrams and in percent between the actual value and quantity found (based on the actual value) are listed 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 nitrate using the D 1608-60 analytical procedure.

A more detailed statistical analysis of the pilot plant standards data are presented in Table 26. In this table, the variability observed in the standards data are compared with estimates which are derived from the reproducibility and repeatability relationships presented earlier in this report. Reproducibility and repeatability estimates were calculated, using the values of the concentration levels of the standards in ppm and were used to estimate the standard error between-laboratories shown in line 3c of the table. The standard error was squared to yield the estimated total variance of a single measurement, S^2, which includes sources of variation due to both sampling and to analysis.

The estimate of variance calculated directly from the standards data by the equation

$$S^2 = \frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n-1}$$

is shown as line 2b of the Table. In the equation $\bar{X}$ is the mean of the n laboratories determination, X_i. Since laboratories were provided standard solutions and sampling was not involved, this variance is assumed to result from analytical errors. The ratio of these two variances is an indication of the percent of total variance which is due to analysis. Thus, if the variations in the standards are representive of the test sample analyses, line 4a

TABLE 25. RESULTS OBTAINED FOR STANDARD NITRATE SOLUTIONS ANALYZED FOLLOWING PILOT PLANT TESTS

Laboratory	Standard 1			Standard 2			Standard 3		
	mg Found	Difference (a)		mg Found	Difference (a)		mg Found	Difference (a)	
		mg	%		mg	%		mg	%
A	2.13	-0.20	-8.58	4.53	-0.13	-2.79	7.28	-0.47	-6.06
B	2.24	-0.09	-3.86	4.44	-0.22	-4.72	7.14	-0.61	-7.87
C	1.79	-0.54	-23.18	3.67	-0.99	-21.24	6.61	-1.14	-14.71
D	2.18	-0.15	-6.44	4.25	-0.41	-8.80	7.15	-0.60	-7.74
E	2.43	0.10	4.29	4.73	0.07	1.50	7.84	0.09	1.16
F	2.28	-0.05	-2.15	4.48	-0.18	-3.86	7.48	-0.27	-3.48
G	2.38	0.05	2.15	4.25	-0.41	-8.80	7.18	-0.57	-7.35
H	2.38	0.05	2.15	4.50	-0.16	-3.43	7.35	-0.40	-5.16
I (b)									
J	2.22	-0.11	-4.72	4.36	-0.30	-6.44	7.26	-0.49	-6.32
Means ± Std. Dev.	2.23 ±0.19	-0.10 ±0.19	-4.48 ±8.22	4.36 ±0.30	-0.30 ±0.30	-6.51 ±6.37	7.25 ±0.33	-0.50 ±0.33	-6.39 ±4.20
Actual Value, mg NO_2	2.33			4.66			7.75		
Equivalent ppm NO_2	642.6			1285.2			2137.4		

(a) Difference based on actual value of standard.
(b) Invalid calibration curve.
(c) Assuming a sample volume of 1900 ml.

TABLE 26. STATISTICAL ANALYSIS OF STANDARDS DATA OBTAINED FOLLOWING PILOT PLANT TESTS

Statistical Measure	Standard 1	Standard 2	Standard 3
1. Standards-True Values			
(a) Actual Value, mg NO_2	2.33	4.66	7.75
(b) Equivalent ppm NO_2 (a)	642.6	1285.2	2137.4
2. Analytical Variation Based on Standards, ppm NO_2			
(a) Mean, $\bar{x}$	615.0	1203.4	2001.0
(b) Variance, S^2	2780.4	6701.3	8135.5
(c) Standard error, S	52.7	81.9	90.2
(d) Coefficient of variation, %	8.7	6.8	4.5
3. Estimated Total Variation Based on Pilot Plant Data, ppm NO_2			
(a) Reproducibility, $\hat{S}_B = 2.21\sqrt{m} - 1.18$	55.0	78.1	101.0
(b) Repeatability, $\hat{S}_W = 1.52\sqrt{m} - 4.21$	34.4	50.3	66.0
(c) Standard error, $\hat{S} = \sqrt{\hat{S}_B^2 + \hat{S}_W^2}$	64.9	92.9	120.7
(d) Variance, $\hat{S}^2$	4212.0	8630.4	14568.5
4. Comparison of Analytical and Total Variance			
b (a) Percent of total variance attributable to analytical variation	66.1	77.6	55.8
(b) Percent variance due to other sources	33.9	22.4	44.2
5. Bias Analysis			
(a) Mean difference (x), %	-4.5	-6.5	-6.4
(b) Standard deviation of differences (s), %	8.2	6.4	4.2
(c) Number of observations (n)	9	9	9
(d) Student's t-statistic $t = X\sqrt{n}/s$	-1.64	-3.07	-4.56
(e) Critical value for n-1 = 8 degrees of freedom, 95% confidence level	2.31	2.31	2.31
(f) Conclusion of test for bias NS - not significant S - significant	NS	S	S

(a) Based on sample volume of 1900 ml

of the table indicates that 56 to 78 percent of the estimated total variance in measurements obtained in the pilot plant test may be attributed to the analytical portion of the method. The remaining 22 to 44 percent of variance may be attributed to sampling errors and other sources.

Section 5 of Table 26 presents an analysis of bias in the standards data based on Student's test. The conclusions drawn from the tests are that bias is not statistically significant for the lowest concentration (2.33mg) but the negative biases of about 6.5 percent are significant for the two higher concentration standards (4.66 and 7.75 mg).

A set of nine standard potassium nitrate solutions were sent to the cooperating laboratories after both the Site II and Site III tests. These series included triplicate samples of three different NO_2 concentrations; 0.455, 1.82 and 7.28 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 27. 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 28. 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.

An analysis of the variation in the Site II and III analytical data relative to the estimated total variation is summarized in Table 29. As before, separate estimates of the between- and within-laboratory components of variance are made using the relationship developed from the pilot plant test data, substituting the standard value in ppm NO_2. From the components, an estimate of the total variance of a single measurement is calculated which includes variations due to the both the sampling and analytical processes.

Line 4a shows the percentage of the total variation in the Site II and III test data which may be attributed to the analytical procedure if it is assumed that variation in the standards and test sample analyses are comparable.

Based on Site II standards data, 30 to 71 percent of the total variance may be attributed to the nitrate analyses procedure. This measure

TABLE 27. RESULTS OBTAINED FOR STANDARD NITRATE SOLUTIONS ANALYZED FOLLOWING TESTS AT SITES II AND III

		Milligrams of NO_2 Found in Standards		
Site	Lab	N-1, 4 and 7	N-2, 5 and 8	N-3, 6, and 9
II	A	0.575	2.07	6.80
		0.625	2.12	6.70
		0.550	2.10	6.70
	B	0.425	1.88	7.00
		0.510	1.85	7.00
		0.460	1.88	7.50
	C	0.432	1.73	6.96
		0.432	1.77	6.96
		0.451	1.77	6.81
	D	0.407	1.72	6.92
		0.465	1.79	6.77
		0.413	1.65	6.74
		N-13, 15, and 18	N-11, 14, and 19	N-12, 16, and 17
III	A	0.452	1.74	7.15
		0.450	1.78	7.15
		0.452	1.69	7.09
	B	0.413	1.79	7.58
		0.420	1.76	7.51
		0.407	1.75	7.66
	C	0.455	1.77	6.78
		0.452	1.78	6.76
		0.460	1.77	6.70
	F	0.429	1.59	5.41
		0.441	1.62	5.43
		0.434	1.59	5.42
Actual Value, mgNO		0.455	1.82	7.28
Equivalent ppm NO_2 (a)		125.6	502.3	2009.3

(a) Based on sample volume of 1900 ml

TABLE 28. BETWEEN-AND WITHIN-LABORATORY VARIATION IN THE RESULTS OBTAINED FROM ANALYSIS OF STANDARD NITRATE SOLUTIONS

Site	Conc. of Standard, mg NO_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	0.455	3	12	0.479	0.069	14.4	0.033	6.9
III	0.455	3	12	0.439	0.019	4.3	0.004	0.9
II	1.82	3	12	1.86	0.17	9.1	0.04	2.2
III	1.82	3	12	1.72	0.08	4.7	0.03	1.7
II	7.28	3	12	6.91	0.16	2.3	0.16	2.3
III	7.28	3	12	6.72	0.93	13.8	0.05	0.7

TABLE 29. STATISTICAL ANALYSIS OF STANDARDS DATA OBTAINED WITH SITE II AND III TEST SAMPLES

Statistical Measures	Site II			Site III		
1. Standards-True Values						
(a) Actual value, mg NO_2,	0.455	1.82	7.28	0.455	1.82	7.28
(b) Equivalent, ppm NO_2,(a)	125.6	502.3	2009.3	125.6	502.3	2009.3
2. Analytical Variation Based on Standards, ppm NO_2						
(a) Mean, $\bar{X}$	132.2	513.6	1905.8	121.2	474.4	1854.7
(b) Reproducibility, S_B	19.0	46.4	45.4	5.2	22.0	257.0
(c) Repeatability, S_W	9.2	11.0	44.4	1.2	7.3	12.9
(d) Variance, $S^2 = S_W^2 + S_B^2$	445.6	2274.0	4032.5	28.5	537.3	66215.4
(e) Standard error, S	21.1	47.7	63.5	5.3	23.2	257.3
(f) Coefficient of Variation, %	16.0	9.3	3.3	4.4	4.9	13.9
3. Estimated Total Variation Based on Pilot Plant Data, ppm NO_2						
(a) Reproducibility, $S_B = 2.21\sqrt{m} - 1.18$	23.6	48.3	97.8	23.6	48.3	97.8
(b) Repeatability, $S_W = 1.52\sqrt{m} - 4.21$	12.8	29.8	63.8	12.8	29.8	63.8
(c) Variance, $S^2 = S^2_B + S^2_W$	720.8	3220.9	13635.3	720.8	3220.9	13635.3
(d) Standard error, S	26.8	56.8	116.8	26.8	56.3	
4. Comparison of Analytical and Total Variance						
(a) Percent of total variance attributable to analytical variation	61.8	70.6	29.6	4.0	16.7	485.6
(b) Percent of total variance due to other sources	38.2	29.4	70.4	96.0	83.3	
5. Bias Analysis						
(a) Mean difference (x), %	5.2	2.2	-5.2	-3.6	-5.5	-7.7
(b) Standard deviation of differences (s), %	15.5	8.6	3.0	3.9	4.2	11.6
(c) Number of observations (n)	12	12	12	12	12	12
(d) Student's t-statistic $t = x\sqrt{n}/s$	1.16	0.93	-6.00	-3.20	-4.54	-2.30
(e) Critical value for n-1 = 11 degrees of freedom, 95% Confidence Level	2.20	2.20	2.20	2.20	2.20	2.20
(f) Conclusion of Test for bias NS - not significant S - significant	NS	NS	S	S	S	S

(a) Based on sample volume of 1900 ml

of variation attributable to the analysis steps is comparable in magnitude to the pilot plant results. Site III standards and test data indicates a lower percentage of the variance is assignable to the nitrate analysis for the two lower concentration standards. Variation in the highest level standard is clearly out of proportion to the total estimated variance. This large disparity in the analytical and total variance results primarily from the low determinations (about - 26 percent) by Laboratory F and indicates, at least in this case, that the analytical variance as determined from the standards is not representive of the test samples.

The bias in the analysis of Site II and III nitrate standards is summarized in Section 5 of Table 29. Student's test is used to estimate the statistical significance of the observed bias. In rigorous application, Student's Test is only 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 to be warranted. The mean difference between the true and experimentally determined values are positive for the two lower concentration Site II standards and do not result in a statistically significant bias. The mean differences for all other standards analyses result in statistically significant negative biases in the range of about 4 to 8 percent.

Comparison of Sample Volume Measurement Method

The NO_x concentration data from the eight tests at Site I were calculated using both the ASTM sample volume measurement method and the procedure described in Federal Register, Method 7. The results reported in ppm NO_2 are compared in Table 30. In the ASTM procedure, it is assumed that an initial flask pressure equal to the vapor pressure of water is obtained by evacuation prior to sampling. The sample volume is computed from the flask pressure and temperature measured at the end of the absorption period and the vapor pressure of water. The sample volume calculation as described in Method 7 is made from the sample flask pressure and temperature measurements taken prior to sampling and at the end of the absorption period.

The comparison of the results presented in Table 30 shows that in all samples the ASTM procedure gave slightly higher sample volumes which resulted in proportionately lower NO_x concentrations. The differences based on the ASTM values range from 0.5 to 5 percent. The average difference of the 30 typical determinations is 2.5 percent and the standard deviation of the differences is 1.5 percent.

TABLE 20. COMPARISON OF SITE I RESULTS OBTAINED FROM ASTM D 1608-60 AND METHOD 7 SAMPLE VOLUME MEASUREMENTS

Test Number	Laboratory A				Laboratory B				Laboratory C				Laboratory D			
	ASTM	Method 7	Difference(a) ppm	%	ASTM	Method 7	Difference(a) ppm	%	ASTM	Method 7	Difference(a) ppm	%	ASTM	Method 7	Difference(a) ppm	%
1	183	183	0	0	174	180	+6	+3.4	148	150	+2	+1.4	195	197	+2	+1.0
2	184	186	+2	+1.1	179	185	+6	+3.4	---	(b)	----	----	183	185	+2	+1.1
3	180	187	+7	+3.9	170	176	+6	+3.5	189	195	+6	+3.2	179	182	+3	+1.7
4	187	192	+5	+2.7	176	183	+7	+4.0	179	186	+7	+3.9	174	176	+2	+1.1
5	181	185	+4	+2.2	181	187	+6	+3.3	---	(b)	----	----	181	185	+4	+2.2
6	186	187	+1	+0.5	182	188	+6	+3.3	177	185	+8	+4.5	190	195	+5	+2.6
7	191	192	+1	+0.5	177	183	+6	+3.4	167	176	+9	+5.4	188	191	+3	+1.6
8	182	183	+1	+0.5	166	172	+6	+3.6	181	190	+9	+5.0	195	198	+3	+1.5
Average Difference	---	---	+2.6	+1.4	---	---	+6.1	+3.5	---	---	+6.8	+3.9	---	---	+3.0	+1.6
Overall Average Difference = 2.5 ± 1.5 % (30 determinations)																

(a) Differences based on ASTM calculation.

(b) Outlier.

DISCUSSION AND CONCLUSIONS

The Project Threshold Study provides thefollowing measures of precision and accuracy of ASTM D 1608-60 for determination of NO_x in gaseous combustion products. A discussion of practical applications of these measures is presented in Appendix C.

Between-Laboratory Component of Variance (Reproducibility)

The relationship of the between-laboratory component of variance, S_B, and the mean NO_x concentration, m, over the range 20 to 2000 ppm NO_2 may be estimated by the equation

$$S_B = 2.21 \sqrt{m} - 1.18$$

where S_B and m are expressed in ppm NO_2.

Within-Laboratory Component of Variance (Repeatability)

The relationship of the within-laboratory component of variance, S_W, and the mean NO_x concentration, m, over the range 20 to 2000 ppm NO_2 may be estimated by the equation

$$S_W = 1.52 \sqrt{m} - 4.21$$

where S_W and m are expressed in ppm NO_2.

Between-Laboratory Standard Error

The field tests at NO_x concentrations in the range of about 90 to 260 ppm NO_2 yield a between-laboratory standard error estimate of 14.5 ppm.

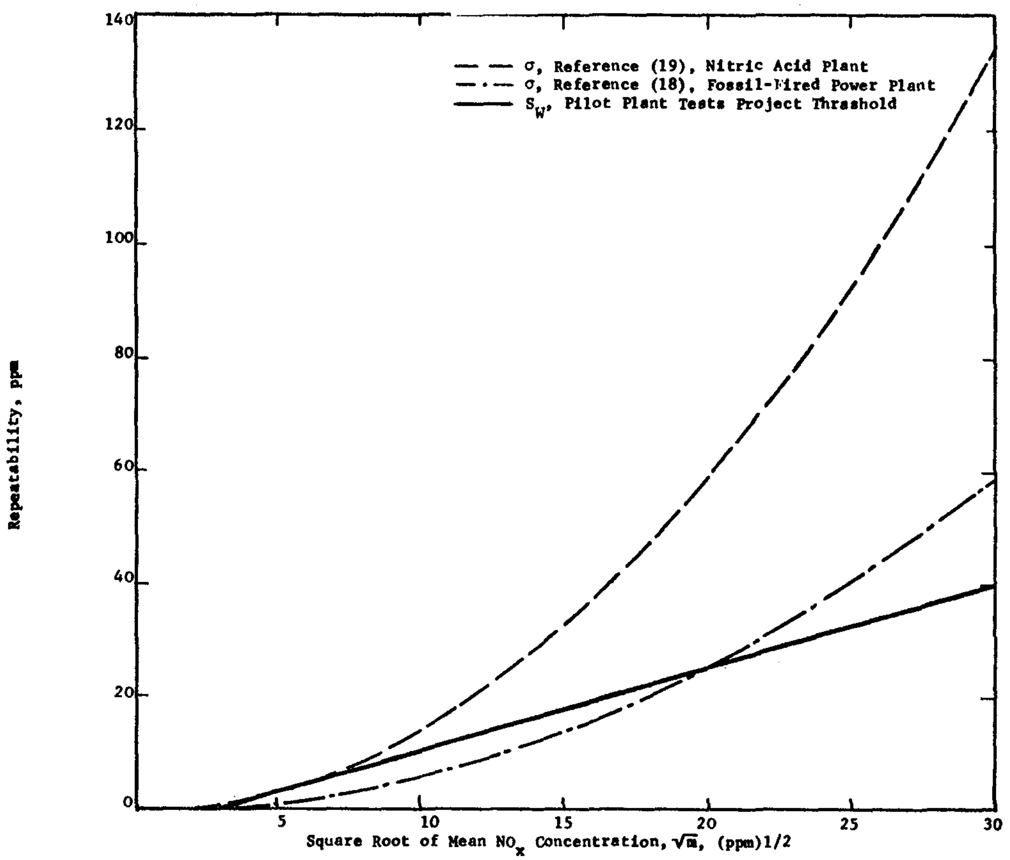
Accuracy

The average of NO_x determinations with known nitric oxide spikes differed from the true values by -4.6 and -1.8 percent (based on true value) in the respective concentration ranges $X \leq 700$ and $X > 700$ ppm NO_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 -3.25 percent based on the true value. Statistically, this difference can not be distinguished from zero.

The precision estimates derived in the study appear reasonable and in the range of limited data reported by Berger, Driscoll, and Morgenstern for the PDS method.(17) Berger, et al. report a 13.0 percent coefficient of variation for a series of measurements with a mean NO_x concentration of 236 ppm. Based on relationships derived from the pilot plant tests, a slightly higher, 16.1 percent coefficient of variation (calculated from the between-laboratory standard error) is predicted for the same mean concentration. The coefficient of variation for a mean NO_x concentration of 236 ppm estimated from the field data relationship is much lower, 6.1 percent. In general, estimates of the coefficient of variation from the pilot plant data for higher NO_x concentrations result in higher values than those reported by Berger, et. al.

Collaborative testing of Method 7, the EPA version of the PDS Method, has been conducted on fossil-fired power plants by Hamil and Camann(18) and on nitric acid plants by Hamil and Thomas(19). Estimates of repeatability and reproducibility obtained from these studies and from the Project Threshold study are presented in Figures 13 and 14. Agreement in the estimates of repeatability for determination of NO_x from a combustion source is very good with the major difference being the models used to fit the test data. Comparison of reproducibility obtained in the three collaborative studies indicates that estimates obtained in this study from the pilot plant tests exhibit a higher component of between-laboratory variation. However, the reproducibility estimates derived from field tests conducted in this study are in good agreement with the combustion source data of Hamil and Camann.

Based on comparison with other data, it appears that the measures of between-laboratory precision resulting from the pilot plant tests probably provides a conservative estimate of the variability inherent in the test method. Sources which might tend to increase the observed variability in the pilot plant data include variations in source emissions and inexperience of some of the laboratories in performance of the test method. Since the laboratories obtained samples at consecutive 10-second intervals to eliminate flow perturbation, short-term changes in the NO_x emission level would be confounded in the measure of between-laboratory variability. The estimate of within-laboratory variation should not have been affected by this procedure since the two samples taken by each laboratory in each test block were obtained concurrently. The significant number of outlying observations and data points lost due to experimental error, which decreased markedly as the tests weeks progressed, suggests the presence of a "learning curve situation" with improvement of performance with increased testing. Variations resulting from cooperator inexperience with the application of the test method or in adapting to the test routine would also be confounded with and increase the measured variability. The relationship of experience and variability has practical implications since increased variation would also be expected in



FIRUGE 13. REPEATABILITY ESTIMATES FROM COLLABORATIVE TESTS OF THE PDS METHOD FOR DETERMINATION OF OXIDES OF NITROGEN

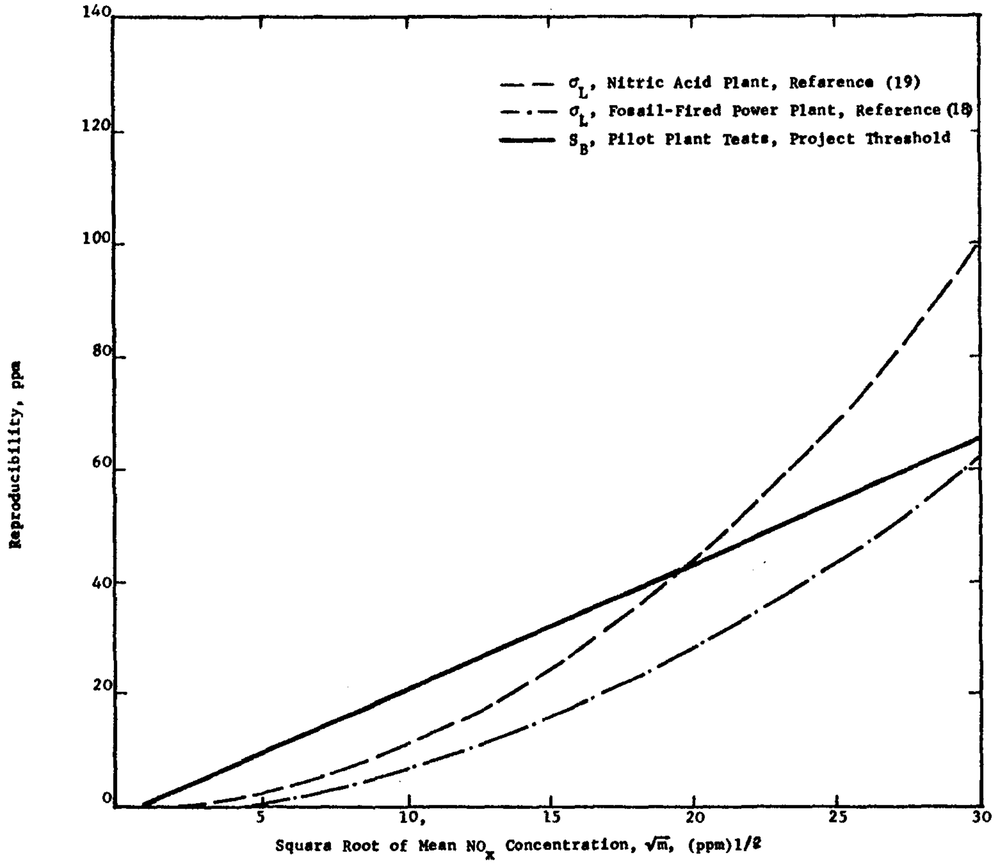


FIGURE 14. REPRODUCIBILITY ESTIMATES FROM COLLABORATIVE TESTS OF THE PDS METHOD FOR DETERMINATION OF OXIDES OF NITROGEN

"real world" determinations by less experienced operators. However, in this study, the cooperating laboratories were not specifically selected in order to assemble a typical cross section of potential users of the method. Consequently, the results are not presented as necessarily representative of the entire user population.

The field test data would include variation in the NO_x concentration in the stack, i. e. as a function of sampling location, confounded with the between-laboratory standard error measures. Examination of the Site II test conditions and results indicates that concentration differences in the stack probably account for much of the observed variation.

The large stack size necessitated concurrent sampling at points which were about 25 feet apart in the flue. In addition, the normal four foot sampling probe required withdrawing the gas sample relatively close to the stack wall. Another complicating factor at Site II was the relatively high negative stack pressure, ~ 6 inches of water, which accentuated the problems of sampling system leakage, in-leakage of air between the glass probe and metal sheath and through the sampling port, and incomplete purging of the probe and lines prior to sampling, particularly with suction bulbs. The difficulties indicate that special attention must be given to obtaining a representive measure of NO_x concentration under the conditions encountered at Site II. Data at the other test sites do not show a sampling location-concentration relationship which would increase the observed variability.

The analyses of standard nitrate solutions by the D 1608-60 analytical procedure show greater than expected variation in the determination of nitrate concentration. The coefficient of variation (between-laboratory standard error) of standards analyzed with the pilot plant samples was 8.7, 6.8, and 4.5 percent for solutions containing the equivalent of 2.33, 4.66, and 7.75 mg NO_2, respectively. The analysis of solutions containing 0.455, 1.82, and 7.28 mg NO_2 following two site tests showed coefficients of variation (between-laboratory standard error) in the range of 3.3 to 16 percent with no consistent relationship between variability and concentration.

If the variability observed in the standards is representative of test sample analysis, a significant fraction of the total variation in the NO_x determinations is associated with the analytical steps of the method. In the pilot plant study, analytical variations could account for about 60 to 80 percent of the overall variation in NO_x determinations. Similarly, the source of a significant fraction of the variation (30 to 70 percent) in the Site II

NO_x determinations could be attributed to the nitrate analysis. Site III standards data show less variability except for the inordinate variation in the highest level standard.

The standards data show predominately negative biases associated with the analysis of nitrate solutions containing 0.455 to 7.75 mg NO_2. In cases in which bias was statistically significant, the mean difference between experimentally determined and true NO_2 values ranged from -3.6 to -7.7 percent based on the true values.

The pilot plant spiking experiments produced NO_x determinations with a slight negative bias (-3.25 percent for all measurements) which may result from the nitrate determination procedure. However, it is concluded from the spiking experiments that the difference between the observed and true value is not statistically significant and, therefore, the method is unbiased. Similar conclusions were drawn by Hamil and Camann(18) and Hamil and Thomas(19) with regard to the accuracy of the PDS method.

Statistical comparison of test data using the optional two-hour absorption period with shaking detected no bias in relation to the usual overnight absorption.

Sample volume determinations using the D 1608-60 procedure yield results which were consistently higher than the FR, Method 7 technique. The mean difference of 30 comparisons is 2.5 percent (based on the ASTM method) which is a statistically significant bias based on Student's t test.

The Method 7 volume determination procedure has some advantages. For example, leaks in the evacuation system and sampling flask joints can be detected by observing the manometer after evacuation and poor pump performance does not adversely affect results.

In conclusion, this study shows that NO_x determinations in combustion source emissions using ASTM D 1608-60 can be performed with acceptable accuracy and precision. Significant variations can occur if care is not exercised to use proper procedure and equipment to obtain a representative flue gas sample. However, while sampling technique is usually suspected as the major source of error, the results of this study suggest that the analysis procedure may account for a significant fraction of the variation in most determinations. Additional study of the D 1608-60 analytical procedure should be performed to determine its contribution to the overall variation. The study could be performed by round-robin measurements of nitrate solutions.

RECOMMENDATIONS

It is recommended that the accuracy and precision estimates developed in this study be incorporated into the description of the method and that the following additions, modifications, and corrections be made in the test procedure.

(1) The Scope, Section 1 should include a discussions of some of the features of the method which might result in limitations in its application e.g. the method provides an instantaneous measure of NO_x and sample size is small and unless sample stream is well mixed, results may not be representative of emissions.

(2) The following additions and changes should be made to Section 4, Apparatus.

   (a) Beckman, Model B spectrophotometer mentioned in Reference 2 is obsolete.

   (b) Paragraph 4.1. Two-liter flasks are recommended in place of one-liter size. The suggestion should be included that flasks be encased in polyurethane to protect against breakage.

   (c) Paragraph 4.1. Include option to use pipettes for dispensing standard solutions.

   (d) Paragraph 4.7. A 36-inch rollup-type manometer is commonly used.

   (e) Include the following apparatus

      - Heated, borosilicate glass probe similar to that described in D 3226. Probe should be designed to prevent leakage of ambient air between the glass probe and the metal sheath into the region of the sample inlet when used in a stack with a negative static pressure. Probe length should be considered in relation to stack size.
      - Vacuum pump to purge system prior to sampling
      - Barometer

   (f) A diagram of the sampling system should be included in the method.

(3) Paragraph 7.1. Purging the system with a vacuum pump is recommended prior to sampling. This procedure is particularly important on stacks with a high, negative static pressure.

(4) Paragraph 7.1. It is recommended that the sampling procedure be modified to include flask pressure and temperature measurements after evacuation to incipient boiling and just prior to sampling. Initial pressure and temperature should used to calculate sample volume in Paragraph 10.1.1.

(5) Note 3. Instructions are accurate only when male part of joint is attached to flask. Modify to state that 1/4-inch (6mm) of the joint in contact with the gas sample should not be greased.

(6) Paragraph 8.1. Range of lower concentration calibration curve is about 20 to 100 ppm. Temperature should be 70F.

(7) Paragraph 8.1.1. 20 to 100 ppm NO_2.

(8) Paragraph 9.2. In field work, it is frequently desirable to transfer a known volume of the absorbent to a bottle for later analysis. This option should be mentioned.

(9) Paragraph 9.2., Note 7. It would be helpful to include dilution schemes for various NO_x concentration ranges.

(10) Paragraph 9.4. Centrifugation is suggested as an alternate to filtration.

(11) Paragraph 10.1. 70F and 20.1C are not equivalent. 70F= 21.1C.

(12) Paragraph 10.1.1. Use the following equation to calculate sample sample volume based on presampling pressure and temperature measurements (See Recommendation 4).

$$V_c = (V_f - V_a)(P_f/T_f - P_i/T_i) \quad 294.3/760$$

where V_c, V_f, and V_a have the same significance and

P_i = absolute pressure in flask prior to sampling, mm Hg,

P_f = absolute pressure in flask after absorption period, mm Hg,

T_i = absolute temperature of flask prior to sampling, K (centigrade + 273.2),

T_f = absolute temperature of flask after absorption period, K (centrigrade + 273.2)

(13) Paragraph 10.2. Standard molar volume (760mm Hg and 70F) should be 24.1 X 10^3 instead of 23.7 X 10^3.

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APPENDIX A

REPRINT OF ASTM

STANDARD METHOD OF TEST FOR OXIDES OF NITROGEN IN GASEOUS COMBUSTION PRODUCTS (PHENOL DISULFONIC ACID PROCEDURE)

ASTM Designation: D 1608-60

Designation: D 1608 – 60 (Reapproved 1967)

American National Standard Z116.4-1966
American National Standards Institute

Standard Method of Test for
OXIDES OF NITROGEN IN GASEOUS COMBUSTION PRODUCTS (PHENOL - DISULFONIC ACID PROCEDURE)[1]

This Standard is issued under the fixed designation D 1608; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 This method covers the phenol-disulfonic acid colorimetric procedure for the determination of total oxides of nitrogen (nitrous oxide (N_2O) excepted) in gaseous effluents from combustion and other nitrogen oxidation processes. It is applicable to a concentration range of oxides of nitrogen as nitrogen dioxide (NO_2) of five to several thousand parts per million.

2. Summary of Method

2.1 The gas sample is admitted into an evacuated flask containing an oxidizing absorbent consisting of hydrogen peroxide in dilute sulfuric acid. The oxides of nitrogen are converted to nitric acid by the absorbent solution and the resulting nitrate ion is reacted with phenol disulfonic acid to produce a yellow compound which is measured colorimetrically. Calibration curves, prepared from samples of known nitrate content, are used to determine the amount of nitrate in the sample.

3. Interferences

3.1 Inorganic nitrates, nitrites, or organic nitrogen compounds that are easily oxidized to nitrates interfere with the method and give erroneously high results. The presence of certain reducing agents, for example, sulfur dioxide (SO_2), may interfere by consuming part of the hydrogen peroxide in the absorbing solution to leave an inadequate amount for reaction with the oxides of nitrogen. Halides tend to lower the results but interference from halide ion (and lead) are negligible in the concentration usually encountered in automotive engine exhaust gases.

3.2 The role of some of the constituents of combustion effluents as possible interfering substances has not been thoroughly investigated.

4. Apparatus

4.1 *Photometer*—Any commercial photoelectric filter photometer or spectrophotometer[2] suitable for measurements at 400 nm.

4.2 *Gas Sampling Flask, Calibrated*—Standard 1000-ml round-bottom glass flask with a male standard taper 24/40 neck and a female adapter with a sealed-on three-way stopcock.

4.3 *Microburet*, 10-ml capacity.

4.4 *Pipets*, 25-ml capacity.

4.5 *Evaporating Dishes or Casseroles*, heat-resistant glass,[3] 200-ml capacity.

4.6 *Volumetric Flasks*, 50-ml capacity.

4.7 *Mercury Manometer*, open end.

4.8 *Water Bath*.

5. Purity of Reagents

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,

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

Current edition effective Sept. 19, 1960. Originally issued 1958. Replaces D 1608 - 58 T.

[2] The Beckman spectrophotometer, Model B, with 0.5 and 1.0-cm thick Corex cells has been found satisfactory for this purpose.

[3] Borosilicate glass has been found satisfactory for this purpose.

where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to ASTM Specification D 1193, for Reagent Water.[5]

6. Reagents

6.1 *Absorbent Solution*—Add 1.0 ml of hydrogen peroxide (H_2O_2, 3 percent) to 100 ml of sulfuric acid (H_2SO_4, 3+997).

NOTE 1—Where high concentrations of oxides of nitrogen are anticipated, as in automotive engine exhaust gases, 3 ml of H_2O_2 (3 percent) in 100 ml of H_2SO_4 (3+997) is preferred.

6.2 *Ammonium Hydroxide* (*sp gr 0.90*)—Concentrated ammonium hydroxide (NH_4OH). A fresh solution must be used.

6.3 *Hydrogen Peroxide* (*3 percent*)—Dilute 10 ml of concentrated H_2O_2 (30 percent) to 100 ml.

NOTE 2—If the strength of the H_2O_2 (30 percent) is in doubt, test as follows:

Weigh accurately about 5 ml of the H_2O_2 solution and dilute to exactly 500 ml. To 20 ml of the dilute solution add 20 ml of H_2SO_4 (1+9) and titrate with 0.1 *N* potassium permanganate ($KMnO_4$) solution to a permanent pink color. One milliliter of 0.1 *N* $KMnO_4$ solution = 0.001701 g of H_2O_2.

6.4 *Phenol Disulfonic Acid Solution*—Dissolve 25 g of phenol in 150 ml of concentrated H_2SO_4 (sp gr 1.84) by heating on a steam bath (100 C). Cool, add 75 ml of fuming H_2SO_4 (15 percent SO_3) and heat on the water bath for 2 h. Cool and store in a brown glass bottle. The solution should be colorless; it deteriorates on long standing.

6.5 *Potassium Nitrate, Standard Solution* (*1 ml = 0.1941 mg NO_2*)—Dry potassium nitrate (KNO_3) in an oven at 105 ± 1 C for 2 h. Dissolve 0.4266 g of the salt in water and dilute to 1 liter in a volumetric flask.

6.6 *Potassium Nitrate, Standard Solution* (*1 ml = 0.0194 mg NO_2*)—Dilute 10 ml of KNO_3 solution (1 ml = 0.1941 mg NO_2) to 100 ml with water in a volumetric flask and mix well.

6.7 *Sodium Hydroxide Solution* (*42 g/liter*)—Dissolve 42 g of sodium hydroxide (NaOH) in water and dilute to 1 liter. Prepare a fresh solution before using.

6.8 *Sulfuric Acid* (*sp gr 1.84*)—Concentrated H_2SO_4.

6.9 *Sulfuric Acid* (*3+997*)—Mix 3 ml of H_2SO_4 (sp gr 1.84) with water and dilute to 1 liter.

7. Sampling

7.1 Pipet 25.0 ml of absorbent solution into the calibrated sampling flask and evacuate the flask to the incipient boiling point of the solution. Attach the flask (Note 3) to the sampling line and by means of the three-way stopcock bypass the gas until the line and stopcock are warmed to the gas temperature and free from condensate. Turn the stopcock so that the gas enters the flask and the pressures in the flask and the sample line are equalized (usually about 15 s are sufficient). Turn the stopcock to seal the flask and allow the gas to remain in contact with the absorbent overnight (Note 4). For further information on sampling, refer to ASTM Recommended Practice D 1357, Planning the Sampling of the Atmosphere[5] and ASTM Recommended Practices D 1605, Sampling Atmospheres for Analysis of Gases and Vapors.[5]

NOTE 3—The upper ¼ in. (6 mm) of the male standard taper joint of the sampling flask is not lubricated, to minimize contact of the gas sample with stopcock grease during absorption. An inert hydrogen-free chlorofluorocarbon lubricant[6] may be used.

NOTE 4—If an overnight absorption period is not feasible, the sample can be shaken initially and every 20 min for a 2-h period. The result will be about 3 percent low.

8. Preparation of Calibration Curves

8.1 Prepare two calibration curves (milligrams of NO_2 plotted against absorbance), one to cover a range of 2 to 100 ppm and the other to cover a range of 100 to 500 ppm NO_2, based on 1000 ml samples of dry gas (60 F and 760 mm Hg).

8.1.1 *2 to 100 ppm NO_2*—Using a microburet, transfer 0.0, 2.0, 4.0, 6.0, and 10.0 ml

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

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

[6] "Halocarbon Chemically Inert Stopcock Grease" made by the Halocarbon Products Corp., 82 Burlews Court, Hackensack, N. J., has been found satisfactory for this purpose.

of KNO_3 solution (1 ml = 0.0194 mg NO_2) into 200-ml evaporating dishes and add 25.0 ml of absorbent solution to each. Proceed in accordance with 9.3 to 9.5.

NOTE 5—If the Beckman spectrophotometer, Model B, is used, the absorbancies should be read using the 1.0-cm cell.

8.1.2 *100 to 500 ppm NO_2*—Proceed as in 8.1.1 except transfer 0.0, 1.0, 1.5, 2.0, 3.0, 4.0, and 5.0 ml of KNO_3 solution (1 ml = 0.1941 mg NO_2) into the 200-ml evaporating dishes.

NOTE 6—If the Beckman spectrophotometer, Model B, is used the absorbancies should be read using the 0.5-cm cell.

8.2 Construct calibration curves for each of the two concentration ranges by plotting the absorbancies of the solutions at 400 nm against the milligrams of NO_2.

9. Procedure

9.1 After the absorption period is completed, record the barometric pressure and the room temperature where the sample has stood. Connect one arm of the sample flask stopcock to the open-end manometer, turn the stopcock to open the flask to the manometer, and read the difference between the mercury levels in the manometer. The absolute internal pressure in the flask is then the barometric pressure less this difference. Correct the gas volume in the flask as directed in 10.1.

9.2 Transfer the absorbent solution quantitatively from the flask into a 200-ml evaporating dish (Note 7). Pipet 25.0 ml of unused absorbent solution into another evaporating dish for a blank and add the same amount of water to this dish as was used in transferring the sample. Proceed with the blank in the same manner as directed for the sample.

NOTE 7—If the sample is expected to have a high concentration of oxides of nitrogen, transfer it to a 250-ml volumetric flask instead of the evaporating dish, and dilute to the mark with water. Select a suitable aliquot and pipet it into a 200-ml evaporating dish. Likewise dilute 25.0 ml of unused absorbent solution to 250 ml and pipet an aliquot equal to that of the sample into a 200-ml evaporating dish for a blank.

NOTE 8—To save time a 15-ml aliquot of the used absorbent solution may be pipetted into the evaporating dish, rather than quantitatively transferring the whole solution. This is permissible if the concentration of nitrogen dioxide (NO_2) is high enough, and if the evacuation of the flask prior to admitting the sample was to the incipient or flash boiling point of the unused absorbent solution. Evacuation up to 1 min after flash boiling appears to result in about 1 percent decrease in the volume of the solution.

9.3 Add NaOH solution to the sample solution in the evaporating dish and to the blank until each is just basic to litmus paper. Evaporate each to dryness on the water bath and allow to cool. Very carefully add 2 ml of phenol disulfonic acid solution to each residue and triturate thoroughly with a glass rod to ensure complete contact of the residue with the solution. Add 1 ml of water and 4 drops of H_2SO_4 (sp gr 1.84) to each and heat on the water bath for 3 min with occasional stirring. Allow the mixture to cool, add 10 ml of water to each and mix well by stirring. Add 15 ml of fresh, cool NH_4OH dropwise to each, with constant stirring. Test with litmus paper to make sure an excess of the NH_4OH is present.

9.4 Filter the solutions through 7-cm, rapid, medium-texture filter papers (Note 9) into 50-ml volumetric flasks. Wash the evaporating dishes three times with 4 to 5 ml of water and pass the washings through the filters. Make up the volumes of the solutions to 50 ml with water and mix thoroughly.

NOTE 9—The use of the same grade of filter paper should be adhered to in preparing the calibration curves and running the samples. It has been found that some yellow color is retained on the paper when filtering more concentrated samples and this factor must be taken into account by use of the same type of filter paper throughout, or by continued washing until no color is retained in any case.

9.5 Read the absorbance of the sample solution against the blank in suitable equipment for measurement at 400 nm (Note 10). If the absorbance falls beyond the range of calibration, thinner cells may be used or a suitable aliquot selected. Dilute the aliquot and the blank to the same volume and read the absorbance of the sample aliquot against that of the blank aliquot.

NOTE 10—With the Beckman instrument, use a slit width of 0.55 mm.

9.6 Convert the photometric readings to milligrams of NO_2 by means of the calibration curves.

NOTE 11—The calibration curves must not be assumed to be usable over any protracted length of time. It is suggested that standards be run along with the samples every day if a series is being run.

10. Calculations

10.1 *Gas Sample Volume Correction*—Correct the volume of the dry gas sample (after removal of absorbed constituents) to 760 mm Hg and 20.1 C (70 F).

10.1.1 Calculate the volume of gas sample as follows:

$$V_c = (V_f - V_a)(P_{ab} - P_w)293.3/760T_r$$
$$= 0.39(V_f - V_a)(P_{ab} - P_w)/T_r$$

where:

V_c = collected volume of gas, ml,
V_f = volume of sampling flask, ml,
V_a = volume of absorbent solution used, ml,
P_{ab} = absolute pressure in flask after absorption (equal to barometric pressure at this time less the difference in pressure as measured by the manometer, mm Hg,
P_w = vapor pressure of water at room temperature after absorption, mm Hg, and
T_r = room temperature after absorption, K (deg C + 273.2).

10.2 Calculate the concentration of NO_2 in parts per million by volume as follows:

$$NO_2\text{, ppm} = (24.1W \times 10^6)/46V_c$$
$$= [524W \times (10^3)]/V_c$$

where:

V_c = corrected volume of sample, ml,
W = NO_2 found, mg,
23.7×10^3 = standard molar volume (760 mm Hg at 70 F), ml, and
46 = formula weight of NO_2.

11. Precision

11.1 The method gives a repeatability of 1 percent of the mean when applied to synthetic samples of inorganic nitrates.

11.2 Application of the method to exhaust gases from automotive engines gives a repeatability of 5 percent.

APPENDIX B

REPORT ON PROJECT THRESHOLD STUDY OF THE PHENOL DISULFONIC ACID METHOD

by

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PROJECT THRESHOLD

STUDIES OF THE PHENOLDISULFONIC ACID METHOD FOR NITROGEN OXIDES ASTM D 1608

Introduction

Several studies were undertaken to determine various characteristics of the phenoldisulfonic acid (PDS) method for NO_x. The original intent was to compare the response of the method to typical stack levels of nitric oxide, nitrogen dioxide, and mixtures of the two. Because of experimental difficulties in the preparation of samples containing NO_2, and the inherent storage instability of NO_x samples in general, this study was redirected. Work with the PDS method was continued as a comparative study of the response of the method to stack concentrations of nitric oxide when diluted, respectively, with air and with nitrogen. This study arose out of a suspicion that reference samples of NO, prepared on on-stream dilution of the gas with nitrogen, were not fully representative of NO samples from stacks, insofar as PDS response was concerned. It was speculated that complete oxidation of NO in the PDS procedure required that a minumum concentration of oxygen be present in the original stack sample.

A final study was undertaken to examine the conversion of nitric oxide to nitrate in the absorption step of the PDS procedure. In order to circumvent some of the variables of the PDS analysis itself, a specific ion electrode was employed for the measurement of nitrate following absorption of the gas sample.

Experimental Procedure

The phenoldisulfonic acid method was set up and run according to the procedure specified in ASTM D 1608. The absorbent solution was prepared according to the high-peroxide option because the concentration of the test samples was in the range of 1,000 parts per million. The PDS color reagent was prepared according to instructions, but it was necessary to try several different batches of ACS-grade phenol before a reagent of satisfactory color was obtained. The commercial reagent supplied by Harleco was also used, and is probably to be preferred. Spectrophotometric measurements were made with a Shimadzu QV-50 quartz spectrophotometer. Sampling was done with 1-liter round-botton flasks which were calibrated according to D 1608. These were equipped with the usual 3-way stopcocks. Since samples were drawn from a generator manifold designed for the experiment, no heated probe was needed; an arm of the 3-way stopcock served this purpose. Calculations were done according to the ASTM procedure.

A sample generator was designed and fabricated which was substantially similar to the spiking system used in the Battelle Pilot Plant tests of Project Threshold. The same calibrated orifices and precision pressure gage were used with the same cylinder of C.P. nitric oxide (99.23 volume percent) which had been previously analyzed at Battelle. A glass mixing manifold was fabricated which allowed the orifice-controlled contaminant stream to be mixed with a diluent whose rate was measured by a rotameter previously calibrated at NBS. Under typical operating conditions, 70 ml/min of NO was mixed with 70 l/min of diluent to produce a sample stream containing 1,000 ppm of the contaminant. An auxilliary take-off manifold provided three sampling stations compatible with the fittings on the collection flasks. The three diluents used were nitrogen, line air (which gave no response to PDS), and a mixture prepared at NBS which contained 5.023 volume percent oxygen in nitrogen.

Results and Discussion

The phenoldisulfonic acid method is sensitive to many variables, some of which remain poorly defined. The synthesis of the color reagent itself leads to varying products, and nowhere in the literature is the desired isomer of phenoldisulfonic acid defined. Certain batches of reagent-grade phenol yield the desired, colorless, product whereas others yield one which is colored a deep orange. As a practical matter it is probably desirable to standardize on the commercial reagent available from Harleco, Philadelphia, Pennsylvania.

Batches of replicate samples run by the PDS method show good reproducibility within each batch and poorer day-to-day reproducibility. Table I shows the results from six replicate samples of nitric oxide in air which were prepared, sampled and analyzed as described in the previous section.

Table I

Nitric Oxide in Air

Sample	Generated, ppm	Found, ppm*
1	1035	1023
2	1035	1021
3	1035	1036
4	1035	1025
5	1035	965
6	1035	1013

*Expressed as NO_2, throughout, according to D 1608.

The problem of day-to-day reproducibility is illustrated by the following: A group of five independent PDS calibration curves, run over a period of several weeks, showed a range in slope from 0.34 to 0.38 mg NO_2/Absorbance unit (a range of 10 percent). Each curve consisted of five points, was fitted by a least-squares procedure, and contained no scatter of data which could account for the range of slopes observed.

The PDS method is probably adequate for its intended purpose, despite the foregoing observations. It is, however, a difficult procedure to study in the usual sense of analytical methods development. Herein, one ordinarily makes a stepchange in some sampling, instrumental or other factor and seeks a resultant change in response. If the resultant change in response is in or near the noise level of the system, or sensitive in addition to a time factor, interpretation of the results is risky and frustrating. The time constant of the PDS method is painful--analysis of a batch of ten samples requires a full day, and experience has shown that half of these must be recalibration standards. In consideration of the foregoing, much of the data from the comparative study of diluents should probably be interpreted from a semi-quantitative standpoint.

A group of nitric oxide samples, five diluted with air and five diluted with nitrogen were compared. All ten samples were analyzed as a batch, but the calibration curve was run at another time. This is to say that the data are reliable relative to one another but that they may not be accurate. The results are shown in Table II.

Table II

Nitric Oxide in Air and Nitrogen

Sample	Generated, ppm	Found, ppm
1	1084 in Air	1137
2	1084 in Air	1137
3	1084 in Air	1137
4	1084 in Air	1144
5	1084 in Air	1043
6	1076 in Nitrogen	976
7	1076 in Nitrogen	878
8	1076 in Nitrogen	861
9	1076 in Nitrogen	1048
10	1076 in Nitrogen	618

These results show that the PDS response to NO samples diluted with nitrogen is both lower and more scattered than to the same contaminant diluted with air. This apparently results from incomplete oxidation of nitric oxide during the absorption step of the procedure. In order to test the time dependency of this absorption step, a group of comparative samples was run in which the nitrogen-diluted samples were allowed to stand for an extended absorption period of 64 hours (the procedure specifies an overnight period). The results of this experiment are shown in Table III. (Because of a malfunction, the generated concentration was unknown, but constant).

Table III

NO in Air		NO in Nitrogen	
Sample	Found, ppm	Sample	Found, ppm
1	376	5	277
2	374	6	285
3	378	7	291
4	374	8	282

The data for nitrogen-diluted samples show much less scatter than those of Table II, yet the response of the method to these samples remains about 75 percent of that obtained with air-diluted samples. The two sets of data (Tables II and III) are not fully comparable because of the difference in NO concentrations; the amount of excess oxidant in the absorption flask is greater in the second case because of the lower level of nitric oxide sampled.

Another group of comparative sampling tests was run to obtain confirmatory data on dilutent effects in the concentration range of 1,000 ppm nitric oxide. Three air-diluted samples and three nitrogen-diluted sample were compared with great care that the be handled indentically and in the same batch. The results of this study are given in Table IV.

Table IV

Sample	Generated, ppm	Found, ppm
1	1057 In Air	969
2	1057 in Air	963
3	1057 in Air	984
4	1048 in Nitrogen	890
5	1048 in Nitrogen	846
6	1048 in Nitrogen	834

The accuracy discrepancy between "generated" and "found" probably results from the use of a "stale" calibration curve in interpreting the colorimetric results. Relative response of the two sets of samples should nonetheless be fully comparable. It is observed that nitrogen-diluted samples of NO produced about 88 percent of the response of air-diluted samples when analyzed by the PDS procedure. The data in Table IV probably provide the most reliable estimate of diluent effects for nitric oxide samples at the 1,000 ppm level.

Because the diluent effects under study produce changes in response which are near the noise level experienced with the PDS analysis itself, a new approach to the diluent study was undertaken. The sampling and absorption procedures were carried out exactly according to D 1608, but a specific ion electrode was used to measure the final nitrate concentration in the absorbate. In addition, a third diluent condition was imposed--a diluent containing 5 percent oxygen in nitrogen, and fairly representing the oxygen concentration in stacks.

The specific ion electrode was of the liquid-ion-exchanger design and was read against a calomel reference, using an expanded-scale pH meter. This apparatus was calibrated against nitrate reference standards (NBS SRM-756) which had been prepared in a background of PDS absorbent solution. Recalibration was carried out along with each group of samples which was measured. The nitrate concentration of the absorbate was read directly, without aliquoting or diluting the sample. Results were calculated according to a modification of D 1608 which reflects difference in concentration units and dilution factors.

Six replicate samples of nitric oxide were collected on successive days under each of three diluent conditions. The concentration of NO was in the range of 1,000 ppm, and the diluents were Air, 5 percent oxygen in nitrogen, and nitrogen. The results of this study are summarized in Table V.

Table V

Nitric Oxide in Various Diluents
(Specific Ion Electrode Measurements)

Generated	1049 ppm in Air	1048 ppm 5% O_2 in N_2	1046 ppm in Nitrogen
Found	863	903	910
	864	902	878
	839	880	860
	837	862	891
	816	754	886
	---	783	909
Average	844	847	889

It is disappointing that the results of the specific ion electrode study tend to further cloud the issue which they were intended to clarify. Since the results under all three diluent conditions were appreciably low, the generation system became subject to suspicion and generator recalibration was undertaken. The generator was assembled at a test site where a chemiluminescent NO_x analyzer and 950 ppm nitric oxide standard were available. The generator was found to produce samples which were accurate to the uncertainty of the calibration standard, thus proving that the original calibration of its jeweled orifice had remained stable.

In summary, it is qualitatively evident that the response of the PDS method to nitric oxide in the 1,000 ppm range is dependent on the composition of the diluent in which the sample is found. Samples of nitric oxide diluted with nitrogen show 75-90 percent of the response of similar samples diluted with air. As a consequence, it is likely that the method yields low results for NO_x in stacks operated under conditions of very low excess oxygen. More important, it is evident that reference samples of nitric oxide in nitrogen are not truly representative of the contaminant as is exists under normal stack conditions.

APPENDIX G

PRACTICAL APPLICATIONS OF THE STATISTICAL MEASURES GENERATED FROM THE STUDY OF ASTM METHOD D 1608-60

PRACTICAL APPLICATIONS OF THE STATISTICAL MEASURES GENERATED FROM THE STUDY OF ASTM METHOD D 1608-60

The measures of reproducibility, repeatability and between-laboratory standard error generated in this study are useful as a means of quantifying the uncertainty associated with a single measurement of NO_x concentration using the test method. With these measures, it is possible to place confidence limits about several types of estimates, for example:

(1) A confidence limit for any single observation by a particular laboratory,

(2) A confidence limit for any single observation by any laboratory, and

(3) A confidence limit for an average of several observations by any laboratory.

In general, if the measurement of NO_x concentration by this method is assumed to be unbiased, and further that the distribution of measurements follows a normal distribution, then a 95 percent confidence interval for the measurement can be determined as $m \pm 1.96s$, where m is the observed measurement and s is the appropriate estimated standard deviation (e.g. S_W, S_B, or S_T).

If a particular laboratory were to make repeated simultaneous measurements at the same NO_x concentration, approximately 95 percent of these simultaneous measurements should be included in the confidence interval calculated as $m \pm 1.96\ S_W$, where m is the estimated concentration from a determination, and S_W is the within-laboratory component of variance (repeatability) estimated from the study. Alternatively, this confidence interval represents the best estimate of the range in which any randomly selected measurement by a particular laboratory of the NO_x concentration will fall.

The confidence interval for any single estimate by any laboratory would be calculated as $m \pm 1.96\ S_T$, where S_T is a standard deviation which includes variability between laboratories as well as variability within a laboratory. Thus for this situation, the appropriate standard deviation is calculated as $S_T = \sqrt{S_B^2 + S_W^2}$, where S_B and S_W are the reproducibility and repeatability estimates as determined by this study. If a large number of laboratories were to make repeated simultaneous determinations, 95 percent of such determinations would be expected to lie within the calculated interval. Alternatively, this interval represents the best estimate of the range in which any single measurement by any single laboratory will fall.

As an example, assume that a randomly selected laboratory determined that the NO_x concentration was 550 ppm. The repeatability estimate for this concentration is $\hat{S}_W = 1.52\sqrt{550} - 4.21 = 31.44$ ppm, and the reproducibility estimate is $\hat{S}_B = 2.21\sqrt{550} - 1.18 = 50.70$ ppm. The between-laboratory standard error associated with a single observation is $\hat{S}_T = \sqrt{S_B^2 + S_W^2} = 59.66$ ppm.

The two confidence intervals discussed above would be calculated as:

(1) Confidence interval for any observation by a particular laboratory:

$m \pm 1.96\ \hat{S}_W = 550 \pm 1.96\ (31.44) = (488.38,\ 611.62)$.

(2) Confidence interval for any single observation by any single laboratory:

$m \pm 1.96\ \hat{S}_T = 550 \pm 1.96\ (59.66) = (433.07,\ 666.93)$.

If each of several laboratories calculated an average NO_x concentration based upon several simultaneous determinations obtained concurrently by all laboratories, a 95 percent confidence interval for any one of these averages would be estimated as

$$\bar{m} \pm 1.96\sqrt{S_B^2 + S_W^2/n} \quad ,$$

where n is the number of determinations used in calculating the average. Thus, for example, if a randomly selected laboratory made four simultaneous determinations of NO_x concentration which were 540 ppm, 519 ppm, 575 ppm and 592 ppm, resulting in an average concentration of $\bar{m} = 556.50$ ppm, with $\hat{S}_W = 1.52\sqrt{556.50} - 4.21 = 31.65$ ppm, and $\hat{S}_B = 2.21\sqrt{556.50} - 1.18 = 51.01$ ppm, the 95 percent confidence interval for any average of four determinations by any laboratory would be: $\bar{m} \pm 1.96\sqrt{S_B^2 + S_W^2/4} = 556.50 \pm 1.96\ (53.41) = (451.82,\ 661.18)$.

The repeatability measure, S_W, allows for the direct calculation of confidence intervals concerning a particular laboratory's measurements, as illustrated above. It also bears a relationship to the repeatability measure suggested by Mandel (10). Mandel defined repeatability as the quantity that will be exceeded only about 5 percent of the time by the difference, taken in absolut value, of two randomly selected test results obtained in the same laboratory on a given material. This value is calculated as $2.77\ \sigma/\sqrt{n}$ where σ is the within-laboratory standard deviation, and n is the number of replicates which were averaged to yield a test result. The within-laboratory component of variance S_W, is an estimate of the σ used by Mandel; thus in terms of Mandel's definition, the repeatability of ASTM D 1608-60 is estimated by

$$\frac{2.77\ S_W}{\sqrt{n}} = \frac{4.21\sqrt{m} - 11.66}{\sqrt{n}}$$

If a test result is based upon a single determination, then Mandel's measure of repeatability becomes $4.21\sqrt{m} - 11.66$, where m is the estimated concentration level.

The statistical measures of precision developed in this study can also be related to Mandel's definition of reproducibility. Mandel states that if specimens of the materials are sent to a random selection of laboratories, and each laboratory provides a single test result, which is an average based upon n replicates, 95 percent of the time differences between any two such results, taken in absolute value, should not exceed $2.77\sqrt{\sigma_L^2 + \sigma^2/_n}$, where σ_L^2 is a measure of the between-laboratory variability and σ^2 is a measure of the within-laboratory variability. This value is defined by Mandel to be the reproducibility measure. Thus in terms of Mandel's definition, the reproducibility of this test method is estimated by $2.77\sqrt{S_B^2 + S_W^2/n}$, where S_B^2 and S_W^2 can be obtained from the expressions determined for this study. Because these expressions are functions of the concentration level, the expression for Mandel's reproducibility in this case, is not easily expressible in general terms. However it can readily be evaluated for any specified concentration level.

This study's estimates of within-laboratory and between-laboratory components of variance (repeatability and reproducibility) can be directly used in statements on precision as outlined in ASTM Method D 2906. The within-laboratory component of variance, S_W^2, is equal to the square of the repeatability measure, S_W; likewise the between-laboratory component of variance, S_B^2, is equal to the square of the reproducibility measure, S_B. The single-operator component of variance, S_S^2, was not isolated from the within-laboratory variance in this study, and can be assumed to be a part of the within-laboratory variance.