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THE COLLABORATIVE STUDY OF EPA METHODS 5, 6, AND 7 IN FOSSIL FUEL-FIRED STEAM GENERATORS FINAL REPORT

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THE COLLABORATIVE STUDY OF EPA METHODS 5, 6, AND 7 IN FOSSIL FUEL-FIRED STEAM GENERATORS FINAL REPORT

by

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SUMMARY AND CONCLUSIONS

This report summarizes the results of collaborative studies of EPA test methods promulgated for use in the determination of emission levels of specified pollutants from stationary sources. The methods tested were Method 7 (Oxides of Nitrogen), Method 6 (Sulfur Dioxide), and Method 5 (Particulates). The tests were conducted using four collaborative teams sampling simultaneously.

In conjunction with the collaborative tests of Methods 6 and 7, auxiliary tests were incorporated into the test plan to allow the partitioning of the methods into field and analytical phases for analysis. The collaborators were required to sample standard gas mixtures at three concentration levels in addition to the stack samples. The collaborators were also provided with standard liquid samples of either potassium nitrate or sulfuric acid, the concentrations of which were unknown to them. These samples were submitted to replicate analysis during the same period in which the stack and standard gas samples were being analyzed. These determinations allowed the accuracy of the method to be ascertained and the precision of the method to be partitioned into its component parts. In this way, areas in which improvements in the methods would have the greatest overall effect could be determined. No auxiliary tests were available for use with Method 5.

The concentrations determined by the collaborators from all sources were submitted to statistical analysis. The results presented below summarize the findings presented in detail in the individual reports on each study. The terminology used varies from the reports on Methods 7 and 6 due to a change in policy with respect to statistical treatment subsequent to their release. In all three studies, the precision estimates obtained are shown to be proportional to the true mean of the determinations, δ.

The principal conclusions derived from the statistical analysis of the data are presented below for each method.

Method 7—The test of Method 7 was conducted at two sites, an oil-fired pilot plant and a coal-burning power plant. A total of 32 runs were made, 16 at each test site. The source test data plus the data from the standards were submitted to statistical analysis and provide the basis for the following conclusions:

Accuracy—Because of chemically significant distortions in the gas cylinder accuracy test, the accuracy of Method 7 could not be adequately demonstrated.

Precision—The estimated within-laboratory standard deviation is 6.56% of δ, with 96 degrees of freedom. The estimated between-laboratory standard deviation is 9.49% of δ with 3 degrees of freedom. From these, a laboratory bias standard deviation of 6.58% of δ is estimated.

Minimum Detectable Limit—The estimated minimum detectable limit of Method 7 is 5.33×10^{-7} lb/scf.

Method 6—The test plan for Method 6 was essentially identical to that of the Method 7 test. The data were submitted to statistical analysis and provide the basis for the following conclusions:

Accuracy—Method 6 is shown to be accurate below 300×10^{-7} lb/scf, but it acquires a significant negative bias in the range from 300-500 $\times 10^{-7}$ lb/scf.

Precision—The estimated within-laboratory standard deviation is 4.00% of δ with 96 degrees of freedom. The estimated between-laboratory standard deviation is 5.80% of δ with 3 degrees of freedom. From these, a laboratory bias standard deviation may be estimated as 4.19% of δ.

Minimum Detectable Limit—The estimated minimum detectable limit is 3.16×10^{-7} lb/scf.

Method 5—The test of Method 5 was conducted at a coal-fired power plant. A total of 16 runs were made by the four teams, with no ancillary tests available. The data from one of these laboratories were eliminated from the statistical analysis since there was sufficient cause to believe that the results obtained by that collaborator were not representative of actual Method 5 determinations. The statistical analysis of the remaining data yields the following conclusions:

Precision—The estimated within-laboratory standard deviation is 31.07% of δ, and has 34 degrees of freedom associated with it. The estimated between-laboratory standard deviation is 36.68% of δ with 2 degrees of freedom. From these, a laboratory bias standard deviation of 19.50% of δ is estimated.

Recommendations are made concerning each method based upon the conclusions presented above, and upon input from the collaborators and test personnel. The recommendations are intended to improve the precision of the various methods as well as to provide considerations for the use of the method in field testing.

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I. INTRODUCTION

This report describes the work performed and results obtained on Southwest Research Institute Project 01-3487-001, EPA Contract No. 68-02-0623, which includes the collaborative testing in fossil fuel-fired steam generators of Method 5 for particulate emissions, Method 6 for sulfur dioxide emissions, and Method 7 for nitrogen oxides emissions as given in "Standards of Performance of New Stationary Sources".[1]

The objective of the preliminary evaluation of the methods specified in the above source reference was to determine if the methods were suitable for collaborative testing. Once judged suitable, the methods were collaboratively tested to determine, to the extent possible, the accuracy and precision of each method. Attempts were made to design the collaborative test plans and ancillary tests to allow determination of the sources of variabiltiy by suitable statistical analytic techniques. By obtaining the above information on the accuracy and precision for a given method, assessment of the reliability and acceptability of the method for field testing could be made. In addition, the relative weak and strong points of the methods could be ascertained, and recommendations for method modifications to enhance the precision of the methods could be made.

This report presents in summary form the results and conclusions derived from the collaborative studies.[2,3,4]

II. COLLABORATIVE TESTING OF METHODS

A. Philosophy of Collaborative Testing

The concept of collaborative testing followed in the tests discussed in this report involves conducting the test in such a manner as to simulate "real world" testing as closely as possible. " Real world" testing implies that the results obtained during the test by each collaborator would be the same results obtainable if he were sampling alone, without outside supervision, and without any additional information from outside sources, i.e test supervisor or other collaborators.

The function of the test supervisor in such a testing scheme is primarily to see that the method is adhered to as written and that no individual innovations are incorporated into the method by any collaborator. During the test program, the test supervisor observed the collaborators during sampling and sample recovery. If random experimental errors were observed, such as mismeasurement of volume of absorbing solution, improper rinsing of flasks, etc., no interference was made by the test supervisor. Since such random errors will occur in the every day use of this method in the field, unduly restrictive supervision of the collaborative test would bias the method with respect to the field test results which will be obtained when the method is put into general usage. However, if gross deviations were observed, of such magnitude as to make it clear that the collaborator was not following the method as written, these would be pointed out to the collaborator and corrected by the test supervisor.

While most of the instructions in the *Federal Register* are quite explicit, some areas are subject to interpretation. Where this was the case, the individual collaborators were allowed to exercise their professional judgment as to the interpretation of the instructions.

The overall basis for this so-called "real-world" concept of collaborative testing is to evaluate the subject method in such a manner as to reflect the reliability of the method that would be expected in performance testing in the field.

B. Collaborative Test Sites

Three collaborative test sites were utilized in this study. Two sites were coal-fired steam generating power plants, and the third site was a combination gas/oil-fired combustion pilot plant.

Collaborative testing of Methods 6 and 7 was conducted both at Dayton Power and Light's Tait Station, Dayton, Ohio, and at Walden Research Corporation's combustion pilot plant, Cambridge, Massachusetts.

At the Dayton Power and Light Tait Station, tests were conducted on the No. 5 unit. This unit is a tangentially-fired steam generator burning pulverized coal. The unit is equipped with both conventional and mirror-grid electrostatic precipitators. Rated output is 140 megawatts.

A sample line was installed after the electrostatic precipitators and ahead of the induced draft (I.D.) fans. The sample delivery line ran to a 10 X 14 ft. utility shed installed on the roof of the Tait Station.

Inside the shed was a manifold for distribution of the flue gas. The manifold was 10 ft long, with an upper 2-in.-square duct fitted with 12 outlets and a lower 8-in.-square return duct. The sample delivery line was connected directly to the manifold for use on this test. The 2-in. black iron

connecting pipe was wrapped with heating tape and insulated. The entire system could be heated, and the temperature controlled by sections. Additional sample preparation capabilities included a Rotron Simplex spiral blower for supplying dilution air.

The installation of the Rotron Simplex blower allowed the addition of ambient air to dilute the stack gas to give different levels of sulfur dioxide or nitrogen oxides.

Sulfur dioxide or nitrogen oxides concentrations in the stack gas and diluted stack gas were monitored with a calibrated Dynasciences instrument.

At Walden Research Corporation, tests were conducted on a combustion pilot plant. The unit consists of a 400,000 BTU/hr (Jackson and Church) furnace with a combination gas/oil burner. The waste heat from the unit is discharged through the roof, and the flue gas is passed through an eight-inch diameter exhaust line to an air-cooled heat exchanger, where it is cooled to about 300°F. The flue gas then passes into a nine-foot test section of eight inch diameter line which contains the sample ports. The gas is pulled out of the test section by a Westinghouse I.D. fan and exhausted through the roof. Precise control of furnace firing conditions plus accurate addition of sulfur dioxide or nitrogen oxides to the furnace exhaust gas would allow evaluation of the methods under carefully controlled emission levels. The gas doping system consists of a 1A gas cylinder of either pure sulfur dioxide or pure nitric oxide, a glass rotometer (Fisher and Porter 448-209) and a simple toggle valve. The dopant gas is introduced into the flue gas immediately after the fire box to provide time to come to equilibrium temperature and concentration before reaching the sample test section. The sample probes were mounted to be at the centroid of the duct.

Collaborative testing of Method 5 was conducted at the Allen King Power Plant of Northern States Power Company near St. Paul, Minnesota. The combustion chamber in this plant consists of twelve cyclone units exhausting into a common heat exchanger system. The emission gas splits into two identical streams shortly upstream of twin electrostatic precipitators which normally collect 98 to 99 percent of the fly ash (by weight). The twin emission streams meet at the base of the vertical stack, entering the base of the stack through two horizontal ducts (north and south). Interior dimensions of the horizontal ducts are 27 feet high and 12 feet wide. Sample ports for the collaborative test were in the south duct just upstream of the vertical stack. Two sampling ports, one on each side of the duct, are located 6 ft above the center line of the duct; and two sampling ports, one on each side of the duct, are located 6 ft below the center line of the duct. The opposing ports are offset slightly to prevent probe interference.

C. Collaborators

The collaborators for both the Dayton and Cambridge tests of Method 7 were Mr. Rudy Marek (Dayton) and Mr. David Tarazi (Cambridge) of Southwest Research Institute, Houston Laboratory, Houston, Texas; Mr. John Millar of Southwest Research Institute, San Antonio Laboratory, San Antonio, Texas; Mr. James Becker of Walden Research Corporation, Cambridge, Massachusetts; and Mr. Paul Sherman of Monsanto Research Corporation, Dayton, Ohio.

The collaborators for both the Cambridge and Dayton tests of Method 6 were Mr. Charles Cody of Southwest Research Institute, Houston Laboratory, Houston, Texas; Mr. John Millar of Southwest Research Institute, San Antonio, Texas; Mr. James Becker of Walden Research Corporation, Cambridge, Massachusetts; and Mr. Paul Sherman of Monsanto Research Corporation, Dayton, Ohio. The latter two collaborators were under subcontract to Southwest Research Institute and, in addition to serving as collaborators, had the responsibility for site preparation and test facility maintenance at their respective test sites for both the Method 7 and Method 6 collaborative tests.

The collaborators for the Allen King Power Plant test of Method 5 were Mr. Mike Taylor and Mr. Hubert Thompson of Southwest Research Institute, Houston Laboratory, Houston, Texas; Mr. Charles Rodriguez and Mr. Ron Hawkins of Southwest Research Institute, San Antonio Laboratory, San Antonio, Texas; Mr. Gilmore Sem, Mr. Vern Goetsch, and Mr. Jerry Brazelli of Thermo-Systems, Inc, St. Paul, Minn.; and Mr. Roger Johnson and Mr. Harry Patel of Environmental Research Corporation, St. Paul, Minn.* Thermosystems, Inc, under a subcontract with Southwest Research Institute, had the responsibility for site preparation and test facility maintenance at the Allen King Power Plant.

Collaborative tests of Methods 7 and 6 were conducted under the supervision of Dr. Henry Hamil; the collaborative test of Method 5 was conducted under the supervision of Mr. Nollie Swynnerton, both of Southwest Research Institute. The test supervisor had the overall responsibility for assuring that the collaborators were competent to perform the test, that the test was conducted in accordance with the collaborative test plan, and that all collaborators adhered to the methods as written in the *Federal Register*, December 23, 1971.[1]

D. Field Evaluation of Methods

After a review of the methods as written,[1] a field evaluation of the methods was made at the site selected for the collaborative test. From the information obtained in the field evaluation, decisions on the suitability of the method for collaborative testing could be made. Also, suitability of the site for collaborative testing with regard both to emission levels and the mechanical aspects of sampling could be made.

Field evaluations were conducted on Method 7 for determination of nitrogen oxide emissions at the Tait Station of Dayton Power and Light Company by personnel from Monsanto Research Corporation and Southwest Research Institute. Samples were taken over a four-day period at four different concentration levels. Nitrogen oxide concentrations were monitored with a Dynasciences analyzer.

One laboratory was high, relative to the other, on the block mean concentration on all four runs, with the discrepancy ranging from about 5 to 21 percent of the NO_X concentration. This same laboratory indicated NO_X concentrations of from 4 % to 12 % higher than the monitor, while the other laboratory indicated NO_X concentrations lower than the monitor in three cases (−6 to −12 %) and higher in one case (+3 %). Reasons for the discrepancies between laboratories and the monitor could not be ascertained at the time of the evaluation. Based on the available information, the method and site were judged suitable for collaborative testing.

Field evaluations of Method 6 for determination of sulfur dioxide were conducted at the Walden Research Corporation combustion pilot plant by personnel from Walden Research Corporation and Southwest Research Institute. Samples were taken over a three-day period at two different concentration levels. Sulfur dioxide levels were monitored with a Dynasciences analyzer. There was no pattern to the results obtained between the two laboratories; for the eight samples taken, each laboratory was high on four samples, relative to the other laboratory, and low on four samples. There was considerable variation between the two laboratories when comparing the block means; up to 35 % variation in the block means was observed. Also, variation of the block means for both laboratories varied from +5 % to −43 % of the block mean value of the monitor concentration. Investigation led to determination of sampling problems in the duct as the cause of the variations.

*Throughout the remainder of this report, the collaborative laboratories are referenced by randomly assigned code numbers as Lab 101, Lab 102, Lab 103, and Lab 104. These code numbers do not correspond to the above ordered listing of collaborators.

Correction of these problems gave lab to lab agreement for the block mean of 1.5%, with both labs about 14% low compared with the monitor. Based upon these findings, the method and the site were judged suitable for collaborative testing.

Field evaluations of Method 5 for determination of particulate emissions were conducted at the Allen King Power Plant. Initial evaluations were carried out by Thermosystems, Incorporated (TSI) personnel in connection with site preparation. This work was done during the period prior to the annual plant shutdown for repairs, and considerable variation in the particulate concentrations determined was observed due to unstable combustion conditions caused by leaks in the air preheaters to the furnace. Particulate loadings observed were in the range of 80×10^{-7} to about 800×10^{-7} lb/scf.* After the plant shut down to repair the leaks, particulate loadings in the lower range of the reported values were expected.

Southwest Research Institute personnel visited the Allen King Power Plant to participate in a final evaluation, along with TSI personnel. A three-day test was planned. After setting up the first day, it was discovered that SwRI's glass probe liner had been broken during shipment. After locating a glassblower and having the probe repaired, attempts to run were thwarted by leaks in the SwRI sample train due to warpage of the filter holder clamping rings upon heating the filter oven. As a result, no particulate loading data were obtained by SwRI for comparison with TSI data. Plant shutdown for repairs precluded further site evaluation. Based upon the preliminary data from TSI, and the information gained by the SwRI visit with regards to site preparation, the method and site were judged suitable for collaborative testing.

E. The Experimental Test Design

A randomized block design was employed to collaboratively test Method 6[2] at both the Dayton site (Dayton Power & Light Company's Tait Station) and the Cambridge site (Walden Research Corporation's combustion pilot plant). Table 1 provides a schematic representation of the randomized block design utilized in the Dayton test. As this table illustrates, the Dayton test was conducted at four different blocks of emission concentration levels; these blocks had SO_2 concentration levels of about 840×10^{-7}, 580×10^{-7}, 175×10^{-7}, and 1090×10^{-7} lb/scf.* These blocks, each of which consisted of four runs sampled at 60-min. intervals, were obtained on consecutive days. The intent was to maintain a constant true SO_2 emission concentration level in the stack on the four runs within each block to permit an accurate determination of the within-lab precision on Method 6. Each run involved the simultaneous collection of an exhaust sample from the stack over a 20- to 23-min. interval by each of the four collaborative laboratory teams through their assigned port (A, B, C, or D). During the course of conducting each block's four runs, as Table 1 shows, the laboratory teams rotated systematically from port to port so that each team sampled once from each port. The systematic rotation was made in such a manner to facilitate the transfer of sampling apparatus between runs.

In terms of experimental design, the Cambridge test of Method 6 was similar in nearly all aspects to the Dayton test. Only a few of the details were different. The four Cambridge blocks had SO_2 concentration levels around 145×10^{-7}, 550×10^{-7}, 830×10^{-7}, and 1010×10^{-7} lb/scf. The time interval between runs within a block was reduced from 60 min on the Dayton test to 45 min on the Cambridge test, in order to minimize the effect of drift in the stack gas SO_2 concentration during a block.

*EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice will result in undue cost or difficulty in clarity, NERC/RTP is providing conversion factors for the particular nonmetric units used in the document. For this report, the factor is:

$$10^{-7} \text{ lb/scf} = 1.6018 \times 10^{3} \ \mu g/M^3$$

TABLE 1. RANDOMIZED BLOCK DESIGN OF THE DAYTON COLLABORATIVE TEST OF METHOD 6

Block (concentration level), lb/scf	Sample	Laboratory Team			
		Lab 101	Lab 102	Lab 103	Lab 104
~840 x 10^{-7}	1	B	C	A	D
	2	C	D	B	A
(2/5/73)	3	D	A	C	B
	4	A	B	D	C
~580 x 10^{-7}	11	C	D	B	A
	12	D	A	C	B
(2/6/73)	13	A	B	D	C
	14	B	C	A	D
~175 x 10^{-7}	15	D	A	C	B
	16	A	B	D	C
(2/7/73)	17	B	C	A	D
	18	C	D	B	A
~1090 x 10^{-7}	25	A	B	D	C
	26	B	C	A	D
(2/8/73)	27	C	D	B	A
	28	D	A	C	B

Notes: The letters A, B, C, and D denote the sampling ports to which each collaborative laboratory team was assigned on each run. The twelve sample numbers not listed here (5-10, 19-24) were obtained from standard gas cylinders in the gas cylinder test to assess the accuracy of Method 6.

In addition to the Method 6 collaborative test itself, two auxiliary tests were also conducted at both the Dayton and Cambridge sites to complement the information obtained from the collaborative test. A gas cylinder accuracy test was conducted to provide an independent assessment of the accuracy of Method 6. This test involved three different standard gas cylinders furnished by Scott Research Laboratories at each test site that contained mixtures of sulfur dioxide and nitrogen. Scott Research determined the sulfur dioxide concentration of each cylinder with an accuracy of ±1 percent. The three gas cylinders were labeled X, Y, and Z. On each of the four collaborative test days, each collaborative team obtained one sample from each cylinder according to the Method 6 procedure. These samples were later analyzed in the laboratory along with the day's collaborative test samples. Thus, the Method 6 values could be compared against the Scott Research measurements which were unknown to the collaborative teams, to determine the accuracy and any possible bias in Method 6.

The second test involved the repeated analytical determination of the SO_2 concentration implicit in four unknown sulfate solutions to isolate the accuracy and precision of the sample analysis phase of Method 6. Four accurately determined sulfuric acid solutions were prepared by Southwest Research Institute and furnished to each collaborative team for sample analysis, together with the collaborative test and gas cylinder samples. A complete factorial design was specified for this unknown sulfate solution test in which each laboratory was to analyze a 10-mℓ aliquot of each solution in triplicate on each of three days during which each site's test samples were being analyzed. An example of the unknown sulfate solution instruction and reporting form is presented as Figure 1.

A virtually identical test design was used for the Method 7[3] collaborative tests. The Cambridge test was conducted at four different blocks of NO_X levels: at approximately 1450 X 10^{-7}; 1000 X 10^{-7}; 675 X 10^{-7}; and 385 X 10^{-7} lb/scf NO_X concentration. The Dayton test used the same test design, the only important difference being that the four concentration blocks were approximately 465 X 10^{-7}, 355 X 10^{-7}, 225 X 10^{-7}, and 120 X 10^{-7} lb/scf. On both tests of Method 7, the four runs in a block were conducted at 15- to 20-minute intervals, just as rapidly as the sampling apparatus could be disconnected, transferred from port to port, and reassembled. This minimized the random ambient variation in the true NO_X emission level during the collection of a block of data.

Also, two auxiliary tests were conducted at both Cambridge and Dayton to complement the information available from the collaborative test. These two tests were the gas cylinder accuracy tests, as described above except for using standard mixtures of nitric oxide in nitrogen as the test gas,

Each unknown solution is to be analyzed in triplicate on each of three separate days. Use a 10 ml aliquot and follow the procedure in Section 4.3 of Method 6 and report results as lb/ft^3 assuming a sample volume of 1 cubic foot at standard conditions.

Submit the results on this sheet along with your other collaborative test data.

Analyst _____ Lab 104 _____

		Concentration, lb/ft^3			
Day	Replicate	Solution A	Solution B	Solution C	Solution D
Day 1 Date 3-13-73	1	3.61×10^{-5}	0	5.35×10^{-5}	1.81×10^{-5}
	2	3.63 "	0	5.35 "	1.80 "
	3	3.59 "	0	5.35 "	1.78 "
Day 2 Date 3-14-73	1	3.56 "	0	5.34 "	1.80 "
	2	3.54 "	0	5.36 "	1.81 "
	3	3.56 "	0	5.36 "	1.80 "
Day 3 Date 3-15-73	1	3.59 "	0	5.44 "	1.83 "
	2	3.61 "	0	5.41 "	1.81 "
	3	3.58 "	0	5.32 "	1.83 "

FIGURE 1. COLLABORATIVE TEST OF METHOD 6, INSTRUCTIONS FOR ANALYSIS OF UNKNOWN SULFATE SOLUTIONS

and the analytical determination test using four unknown potassium nitrate solutions provided to the collaborators by Southwest Research Institute. An example of the unknown nitrate solution instruction and reporting form is presented in Figure 2.

Various potential complications result from the real-world conduct of a mathematically idealized experimental design because the ideal assumptions on which a straight forward statistical analysis of the experimental design is based may prove to be wholly or partially invalid in the actual practical application. In the randomized block designs for the Method 6 tests conducted at Dayton and Cambridge, there are two readily apparent possible complications. The first is that the true SO_2 emission concentration in the stack, instead of remaining constant throughout the four runs comprising a block as the randomized block design implies, does in fact vary significantly during the block's runs. Should such "true drift" actually occur within a four-run block, it would invalidate the usual precision determination technique. It should be noted that because the time intervals between the runs within a block were necessarily larger on the Method 6 tests (45 to 60 min) than on the Method 7 tests (15 to 25 min), the existence of the true drift situation is more likely in the Method 6 collaborative test data. The second potential complication is the existence of a port effect. Although the four ports through which the collaborative teams simultaneously sample were designed so as to be geometrically equivalent, they do not, of course, provide all four teams with access to the same sampling location at the same time. Thus, there is a possibility that there are consistent differences between the true SO_2 or NO_X concentrations at the sampling ports, some having consistently higher SO_2 or NO_X concentrations than others. If this phenomenon exists, it is termed a port effect. If either of these potential complications exist to the extent that they are detectable in the collaborative test data, then suitable statistical techniques must be applied to counteract such effects by appropriately adjusting the reported test data prior to statistical analysis.

The test plan for Method 5[4] was somewhat different than those for Methods 6 and 7. First, no independent method of obtaining an estimate of the true value of particulate concentration in the stack gas during a run is available. Second, no manner of introducing diluent air to give controlled concentration changes is feasible. Therefore, a test design based on blocking by concentration of particulates is not possible.

The collaborative test plan called for 16 samples to be taken by each of the four collaborators over a 2-week period. The sampling was done through four ports in the horizontal duct, two on the east side (EU and EL), and two on the west side (WU and WL). The experiment was designed so that on each day, each collaborator took one sample from the east side ports and one from the west. At the middle of each run, the collaborators using the upper ports shifted to the lower ones, and those on the lower ports began to use the upper ones. In this manner, any potential port effect was intended to be nullified.

After receiving and making preliminary calculation checks on the data, an attempt was made to group the samples into blocks. Considerations in setting up blocks included time—whether each week constituted a block, load—whether megawatt hour load was a basis for a block, and coal burned—whether the particulate concentration was a function of the amount of coal burned. There is no accurate procedure for the determination of true particulate concentrations, and thus it was impossible to establish blocks based on true or theoretical concentration levels.

The plant provided its daily logs of the hourly operating characteristics of the plant during the collaborative test period, and the pertinent information was extracted from these logs. It was assumed that the amount of particulate matter which was emitted should depend upon how much fuel was burned. Thus, the average amount of coal burned during the course of each run was determined, and this was selected as the blocking criterion. These amounts are listed in Table 2.

Each unknown solution is to be analyzed in triplicate on each of three separate days. Use a 10 ml aliquot and follow the procedure in Section 5.2 (and 4.3) of Method 7 and report results as micrograms of NO_2 per ml of unknown solution.

Submit the results on this sheet along with your other collaborative test data.

Analyst Lab 104

Day	Replicate	Concentration, μg NO_2 per ml			
		Solution A	Solution B	Solution C	Solution D
Day 1 Date 1-16-73	1	24.8	13.7	39.9	1.0
	2	26.7	12.7	37.0	0.6
	3	26.6	14.1	40.0	0.5
Day 2 Date 1-18-73	1	26.0	12.7	38.6	0.4
	2	24.4	12.9	37.0	0.4
	3	25.8	13.0	38.3	0.4
Day 3 Date 1-22-73	1	25.1	13.0	34.0	0.6
	2	24.4	13.3	34.7	0.6
	3	25.8	12.8	36.2	0.8

FIGURE 2. COLLABORATIVE TEST OF METHOD 7, INSTRUCTIONS FOR ANALYSIS OF UNKNOWN NITRATE SOLUTIONS

TABLE 2. HOURLY AVERAGE COAL BURNED

Day	Run	Coal Burned ton	Block
8-14	1	351.0	1
	2	247.2	2
8-15	3	304.1	1
	4	322.0	1
8-16	5	231.4	3
	6	300.9	1
8-17	7	232.6	3
	8	228.8	4
8-20	9	232.1	3
	10	241.3	2
8-21	11	246.0	2
	12	214.4	4
8-22	13	225.5	4
	14	244.5	2
8-23	15	229.2	4
	16	238.3	3

Natural blocking of the sample runs appeared to be in groups of four, from the highest fuel burn average to the lowest. The result was four blocks each of size four, in a randomized block design.

F. Statistical Treatment

1. Terminology

To facilitate the understanding of this report and the utilization of its findings, this section explains the statistical terms used in this report. Let $x_1, x_2, \ldots, x_n$ be a sample of n replicate method determinations at a true stack concentration, μ. Then we define:

$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i$, as the sample mean, estimating δ the true mean determination. For an accurate method, δ is equal to μ, the true concentration.

$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2}$, as the sample standard deviation, estimating σ, the true standard deviation.

The ratio of the sample mean and standard deviation

$$b = \frac{s}{\bar{x}}$$

is referred to as the sample coefficient of variation. If we apply a correction factor, α_n, based on the sample size to remove a bias in this estimator, we have an alternate to the coefficient of variation,

$$\hat{\beta} = \frac{\alpha_n s}{\bar{x}} = \alpha_n b.$$

In the test data tables, the term coefficient of variation refers to the value b, while beta refers to $\alpha_n b$. Both values estimate β, the true coefficient of variation.

The coefficient of variation estimates the percentage scatter in the observations about the mean. The analysis of the collaborative test results was performed using a coefficient of variation approach to obtain precision estimates. The fundamental assumption is that for both the run data and the collaborator block data, the true coefficients of variation remain constant over all levels of emission concentration and in all collaborator block combinations. In this report, a run result is one taken from the values obtained by all collaborators during a given run. A collaborator block result is taken from the values reported by an individual collaborator in a given block.

The precision estimates for a concentration determination can be partitioned into its variance components, consisting of within-laboratory, between-laboratory, and laboratory bias terms. Coefficients of variation are developed for each variance component of interest.

For the within-laboratory standard deviation, the sample beta values are obtained from each collaborator block combination. These are then averaged over all combinations, and this, then, is the best estimate of the true value, β. The within-laboratory standard deviation, σ, is estimated by

$$\hat{\sigma} = \hat{\beta}\delta.$$

for a true determination mean, δ. This measures the variability in a single determination due to replicate determination by the same laboratory using the same field operators, laboratory analyst, and equipment at a given level of true concentration, μ.

For the between-laboratory variance, $\sigma_b^2 = \sigma_L^2 + \sigma^2$, a coefficient of variation, β_b, is estimated as the average of the sample beta values for the runs, across collaborators. The between-laboratory standard deviation, σ_b, is estimated as

$$\hat{\sigma}_b = \hat{\beta}_b \delta.$$

This measures the total variation in simultaneous emission level determinations by different laboratories at the same concentration, μ.

The laboratory bias standard deviation, σ_L, can be estimated from the above components. Solving, we have $\sigma_L = \sqrt{\sigma_b^2 - \sigma^2}$. Substituting the estimates obtained, we have

$$\hat{\sigma}_L = \sqrt{\hat{\beta}_b^2 - \hat{\beta}^2}\,\delta$$

$$= \hat{\beta}_L \delta.$$

This measures the amount of variability in a single determination due to differences in the field operators, analysts, and instrumentation, and due to different manners of performance of procedural details left unspecified in the appropriate method. These differences result from the use of the method by separate laboratories as well as from use by a single laboratory at separate times.

Since there are missing values in the Method 5 concentration determinations, the estimated coefficients of variation are obtained using a weighted average of the individual betas rather than a simple average. The weights used vary according to the number of observations used to obtain the estimate, giving more weight to those values obtained from larger samples. This procedure would have no effect on the Method 6 or Method 7 data, since missing data points were substituted for, and all sample sizes were equal.

In the collaborative test reports on Methods 6 and 7,[2,3] the terms repeatability and reproducibility were used to express the precision of the methods in terms of a performance test result. However, subsequent discussion with EPA personnel revealed two problems with this approach.

(a) The values shown in this report are not performance test replicates, but merely concentration determinations. Test replicates for fossil fuel-fired steam generators are expressed in terms of emission rates per 10^6 BTU heat input.

(b) Confusion exists in the use of the 95 percent confidence factor in the Mandel definitions of repeatability and reproducibility.[5] The terms repeatability and reproducibility do not as yet have any standardized usages, and questions arise as to whether the Mandel approach is valid for small numbers of degrees of freedom.

Because of these factors, the precision estimates are now expressed only in terms of within-laboratory and between-laboratory standard deviations for a single method determination, and the extension to a compliance test result is not considered.

III. DISCUSSION OF RESULTS, CONCLUSIONS, AND RECOMMENDATIONS FROM COLLABORATIVE TESTS

This section of the report presents the collaborative test data, the results and conclusions obtained from statistical analysis of the data, and recommendations concerning the methods obtained both from the data analysis and from collaborator observations.

Due to numerous calculation errors in the test data from all three method tests detected in the initial outlier analysis, all collaborative test data were corrected or verified prior to statistical analysis. In this report, the corrected collaborative test data are presented. The original test data and justification for data correction can be found in the reports of the individual collaborative studies.[2, 3, 4]

Since calculation errors appear to be so prevalent in obtaining the emission concentrations for all three methods, it is recommended that standard computer programs be written to alleviate this problem. If the Quality Assurance and Environmental Monitoring Laboratory were to design and implement a program to compute each method's emission concentration from a laboratory's raw data, then the calculation error problem could be minimized. If the program were run by EPA, then the additional problem of bias in performance test reporting (e.g., reporting of only the best of many field test samples in determining compliance) could also be reduced.

A. Method 7

Method 7 specifies the collection of a grab sample in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution and the colorimetric measurement of the nitrogen oxides, except nitrous oxide, using the phenoldisulfonic acid procedure.

The corrected collaborative test data from the Cambridge and Dayton collaborative tests are presented in Tables 3 and 4, respectively. Also included in Tables 3 and 4 are some run summary and collaborator summary statistics.

1. The Accuracy of Method 7

The gas cylinder accuracy test proved to be inadequate, inasmuch as the lack of molecular oxygen in the cylinder gases leads to a difference in the total chemistry of the method, as compared to the chemical reactions occurring in oxygen-containing samples.[6]

Since the Cambridge site was a pilot plant, Walden Research was able to calculate a theoretical concentration of NO_X in the duct at the sample test section based upon the NO doping level, the NO_X due to fuel combustion, and the volumetric flow calculated stoichiometrically. The Walden calculation of theoretical concentration is given in Appendix A. At both the Cambridge and Dayton sites, a Dynasciences Analyzer, Model SS 330, equipped with a Total Oxides of Nitrogen Cell, Model NX-130, was available to measure the stack NO_X concentrations. This type of analyzer utilizes the oxides of nitrogen as one reactant in a fuel cell. The output of the fuel cell, displayed on a meter or recorder, is proportional to the NO_X concentration, and can be calibrated to read NO_X concentration directly. However, the Cambridge Dynasciences monitor was malfunctioning throughout the course of the Cambridge test due to a defective fuel cell. Thus, the Cambridge Dynasciences NO_X readings were not usable. The Cambridge theoretical NO_X concentrations obtained by Walden Research and the Dayton Dynasciences monitor readings obtained by Monsanto are summarized in Table 5 as "true" values for comparison with the corresponding average Method 7 NO_X concentration of the four collaborators in each block. The Table 5 data are plotted in Figure 3. Figure 3 also contains the 95% confidence limits for the

TABLE 3. THE CORRECTED CAMBRIDGE COLLABORATIVE TEST DATA

METHOD: EPA METHOD 7 --- NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

TEST VARIABLE: X = CONCENTRATION OF NOX AS NO2 (DRY BASIS), 10**(-7) LB/SCF

TRANSFORMATION: X LINEAR

TEST SITE: CAMBRIDGE

COLLABORATORS: LAB 101 , LAB 102 , LAB 103 , LAB 104 ,

INTER-LABORATORY RUN SUMMARY

		LAB 101		LAB 102		LAB 103		LAB 104		RUN SUMMARY		
BLOCK	RUN	DATA	PORT	DATA	PORT	DATA	PORT	DATA	PORT	MEAN	STD DEV	BETA
1	8	1440.0	(D)	1337.0	(B)	1450.0	(A)	1350.0	(C)	1394.25	58.98	.0459
	9	1480.0	(A)	1472.0	(C)	1810.0	(B)	1350.0	(D)	1520.50	200.17	.1429
	10	1500.0	(B)	1447.0	(D)	1500.0	(C)	1410.0	(A)	1464.25	43.96	.0326
	11	1446.0	(C)	1531.0	(A)	1370.0	(D)	1420.0	(B)	1441.75	67.34	.0507
2	12	1000.0	(A)	1322.0	(C)	1040.0	(B)	1080.0	(D)	1110.50	144.73	.1415
	13	789.0	(B)	1027.0	(D)	1000.0	(C)	1030.0	(A)	961.50	115.79	.1307
	14	968.0	(C)	1120.0	(A)	941.0	(D)	1040.0	(B)	1016.00	81.29	.0868
	15	669.0	(D)	1081.0	(B)	996.0	(A)	960.0	(C)	926.50	179.01	.2097
3	20	436.0	(B)	736.0	(D)	763.0	(C)	670.0	(A)	651.25	148.72	.2479
	21	630.0	(C)	663.0	(A)	750.0	(D)	660.0	(B)	650.75	90.68	.1512
	22	664.0	(D)	675.0	(B)	806.0	(A)	670.0	(C)	703.75	68.31	.1054
	23	700.0	(A)	740.0	(C)	697.0	(B)	700.0	(D)	709.25	20.55	.0314
4	30	347.0	(C)	411.0	(A)	412.0	(D)	360.0	(B)	382.50	33.91	.0962
	31	377.0	(D)	391.0	(B)	447.0	(A)	360.0	(C)	393.75	37.70	.1039
	32	359.0	(A)	374.0	(C)	385.0	(B)	380.0	(D)	374.50	11.27	.0327
	33	360.0	(B)	392.0	(D)	423.0	(C)	380.0	(A)	388.75	26.37	.0736

COLLABORATOR SUMMARY

COLLABORATOR	LAB 101	LAB 102	LAB 103	LAB 104
MEAN	814.37	919.94	924.37	863.75
STD. DEVIATION	434.06	422.43	429.72	392.80

PORT SUMMARY

PORT	A	B	C	D
MEAN	901.44	873.81	888.75	858.44
STD. DEVIATION	409.31	461.52	425.61	389.48

TABLE 4. THE CORRECTED DAYTON COLLABORATIVE TEST DATA

METHOD: EPA METHOD 7 --- NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

TEST VARIABLE: X = CONCENTRATION OF NOX AS NO2 (DRY BASIS), 10**(-7) LB/SCF

TRANSFORMATION: X LINEAR

TEST SITE: DAYTON

COLLABORATORS: LAB 101 , LAB 102 , LAB 103 , LAB 104 ,

INTER-LABORATORY RUN SUMMARY

		LAB 101		LAB 102		LAB 103		LAB 104		RUN SUMMARY		
BLOCK	RUN	DATA	PORT	DATA	PORT	DATA	PORT	DATA	PORT	MEAN	STD DEV	BETA
1	5	445.0	(A)	413.0	(B)	497.0	(C)	460.0	(D)	453.75	34.87	.0834
	2	466.0	(B)	480.0	(C)	529.0	(D)	500.0	(A)	493.50	27.67	.0609
	3	465.0	(C)	485.0	(D)	496.0	(A)	470.0	(B)	479.00	14.17	.0321
	4	437.0	(D)	399.0	(A)	491.0	(B)	430.0	(C)	439.25	38.25	.0945
2	9	320.0	(B)	321.0	(C)	362.0	(D)	350.0	(A)	338.25	21.08	.0676
	10	323.0	(C)	296.0	(D)	373.0	(A)	360.0	(B)	338.00	35.11	.1127
	11	348.0	(D)	356.0	(A)	421.0	(B)	390.0	(C)	378.75	33.54	.0961
	12	342.0	(A)	348.0	(B)	408.0	(C)	380.0	(D)	369.50	30.61	.0899
3	16	223.0	(C)	231.0	(D)	212.0	(A)	250.0	(B)	229.00	16.02	.0759
	17	217.0	(D)	251.0	(A)	227.0	(B)	240.0	(C)	233.75	14.86	.0690
	18	217.0	(A)	227.0	(B)	215.0	(C)	230.0	(D)	222.25	7.37	.0360
	19	210.0	(B)	223.0	(C)	189.0	(D)	230.0	(A)	213.00	18.02	.0918
4	23	121.0	(D)	141.0	(A)	114.0	(B)	130.0	(C)	126.50	11.68	.1002
	24	117.0	(A)	129.0	(B)	103.0	(C)	130.0	(D)	119.75	12.63	.1145
	25	114.0	(B)	136.0	(C)	116.0	(D)	130.0	(A)	123.75	10.97	.0962
	26	116.0	(C)	130.0	(D)	100.0	(A)	130.0	(B)	119.00	14.28	.1303

COLLABORATOR SUMMARY

COLLABORATOR	LAB 101	LAB 102	LAB 103	LAB 104
MEAN	280.00	285.37	303.25	300.62
STD. DEVIATION	130.29	121.22	159.52	132.54

PORT SUMMARY

PORT	A	B	C	D
MEAN	291.19	293.06	293.75	291.25
STD. DEVIATION	134.25	135.19	138.22	140.31

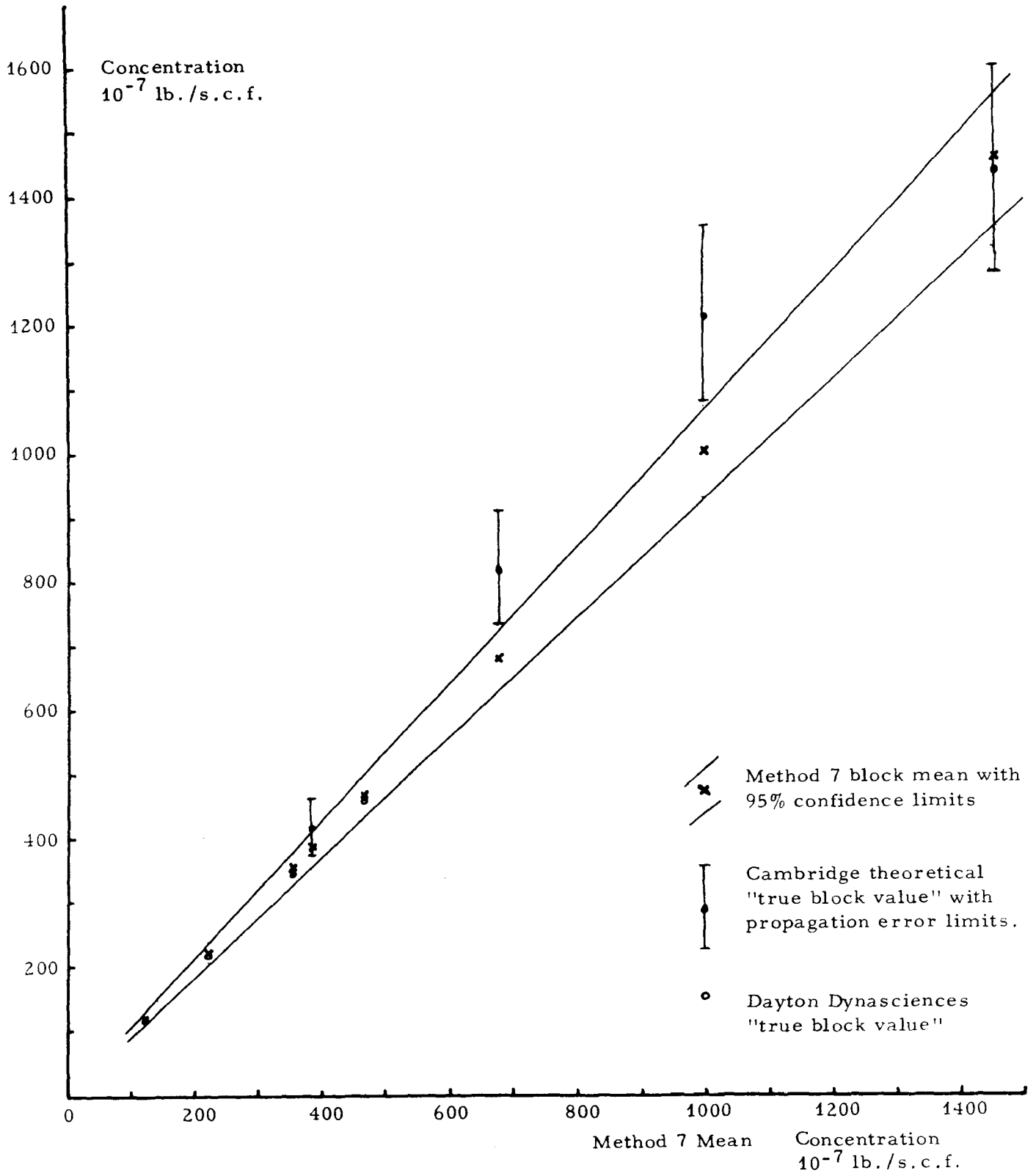

FIGURE 3. THE ACCURACY OF METHOD 7

Method 7 means of each block and Walden's error range of ±11% for the Cambridge theoretical "true block value" obtained by standard propagation of error analysis.[7]

TABLE 5. METHOD 7 ACCURACY DATA

Test Site	Block	NO_x Emission Concentration, 10^{-7} lb/scf			
		"True Value"		Method 7 Mean	Percentage Differences
		Theoretical	Dynasciences		
Cambridge	1	1440		1455	+1.0
	2	1216		1004	−17.4
	3	822		679	−17.4
	4	417		385	−7.7
Dayton	1		460	466	+1.3
	2		344	356	+3.5
	3		219	224	+2.3
	4		118	122	+3.4

It is evident from Figure 3 that Method 7 and the Dayton Dynasciences monitor were in close agreement throughout the Dayton NO_x test. However, there appears to be a discrepancy between Method 7 and Walden's theoretical calculation method in the Cambridge test, particularly in the second and third blocks at the Method 7 concentrations of 1000×10^{-7} and 680×10^{-7} lb/scf. In considering the Cambridge data, one must view the Walden theoretically calculated "true values" with as much suspicion as the Method 7 means, since neither procedure has been verified. In light of the Method 7–Dynasciences agreement in the Dayton test, it is plausible to suppose that Walden's theoretically calculated "true values" are unreliable. However, some doubt does remain as to the accuracy of Method 7. It is strongly recommended that on future collaborative tests involving Method 7 every reasonable effort be made to ascertain its accuracy.

2. The Precision of Method 7

A major purpose of the NO_x collaborative test is to determine the precision of Method 7. The precision estimates are expressed in accordance with the definitions in the previous statistical section.

The 32 collaborator block point estimates of β are averaged to yield the within-laboratory coefficient of variation estimate $\hat{\beta} = 0.06558$.

There are 32 run point estimates of the between-laboratory coefficient of variation $\hat{\beta}_b$ shown in the last column of Tables 3 and 4. These run point estimates are averaged to yield the between-laboratory coefficient of variation estimate $\hat{\beta}_b = 0.09485$.

Using the above estimates of β and β_b, the following table (Table 6) of precision estimates for Method 7 may be completed. Thus, the within-laboratory standard deviation is 6.6% of δ, with 96 degrees of freedom. The between-laboratory standard deviation is 9.5% of δ, with 3 degrees of freedom.

3. Accuracy and Precision of the Analytical Procedure

The accuracy and precision determinations for the analytical procedure were obtained from the analysis of the standard nitrate solution data.

The accuracy assessment was made by comparing the mean reported NO_2 concentrations of each solution against the actual concentration of each standard solution. The mean reported NO_2 concentration of each solution was obtained by averaging the reported concentrations for all replicate analyses by all four collaborators at both test sites. Using variance estimates obtained through an analysis

TABLE 6. PRECISION ESTIMATES FOR METHOD 7

Variability Component	Coeff. of Var.	Estimate	$\hat{\sigma}$
Within-Lab	β	0.06558	$(0.06558)\delta$
Between-Lab	β_b	0.09485	$(0.09485)\delta$
Lab Bias	$\beta_L = \sqrt{\beta_b^2 - \beta^2}$	0.06853	$(0.06853)\delta$

of variance, 95% confidence intervals around the mean reported NO_2 concentrations were established. The method can be said to be accurate at a given concentration if the true concentration lies within the 95% confidence interval around the mean reported concentration.

TABLE 7. ACCURACY OF THE METHOD 7 ANALYTICAL PROCEDURE

Solution	NO_2 Concentration, μg per 10 ml of Absorbance Sample				
	Actual Value	Mean Reported Concentration	95% Confidence Interval for Mean	Difference	Percentage Difference
D	0.00	0.83	(0.05, 1.61)	0.83	
B	12.50	13.01	(11.86, 14.16)	0.51	+4.08
A	25.00	25.46	(23.94, 26.98)	0.46	+1.84
C	37.50	38.03	(36.13, 39.93)	0.53	+1.41

As can be seen in Table 7, this criterion was met by all solutions except the blank Solution D. Therefore, the laboratory analytical part of Method 7 appears to be unbiased in the normal working range of the calibration curve. However, the collaborator mean was always somewhat larger than the prepared true value. The difference was actually significant for the blank Solution D. This suggests that the accuracy of the Method 7 analytical procedure deteriorates considerably at very low nitrate concentrations.

Analysis of variance was performed on the data for each of the four nitrate solutions. These analyses show that, for the analytical portion of Method 7, laboratory-to-laboratory variation is overwhelmingly due to large day-to-day variations in measurements that occur within every laboratory rather than to a significant laboratory-to-laboratory bias.

It is noteworthy that, in contrast to Method 7 itself, the standard deviation components $\hat{\sigma}$ and $\hat{\sigma}_L$ are not proportional to the mean μ. It was found that $\hat{\sigma}_L$, and particularly $\hat{\sigma}$, are linear functions of the mean with a positive intercept at $\mu = 0$. The regression equations are:

$$\hat{\sigma} = 0.03142\mu + 0.2321 \ \mu g \ NO_2/10 \ m\ell.$$

$$\hat{\sigma}_L = 0.0300\mu + 0.7705 \ \mu g \ NO_2/10 \ m\ell.$$

Based upon the analytical data for the blank Solution D, an estimate of the minimum detectable limit can be made. The minimum detectable limit for Method 7 is estimated as 5.33×10^{-7} lb/scf. This represents the smallest Method 7 concentration determination that is significantly larger than a zero nitrogen oxide emission concentration.

4. Recommendations

The results obtained in this study provide a firm basis for the following recommendations concerning Method 7:

(1) Conduct a thorough critical review of Method 7 as currently written to locate ambiguous statements and to modify them so as to be more explicit.

(2) Due to the many handling steps and chance for mishap, it is strongly recommended that an aliquoting section be inserted in the procedure. Aliquoting of samples is a basic procedure in analytical chemistry and would help in the determination of precision in the results. It would also guard against loss of sample and data if a mishap occurs in analysis.

(3) Provide more detail regarding the proper spectrophotometer calibration procedure. These details ought to include a requirement for daily re-calibration and generation of the appropriate calibration line. This calibration line should be forced to pass through the origin, by linear regression. At least three significant digits should be maintained in the calculated slope of the regression line. Mass of NO_2 in the sample could then be calculated with greater consistency by forming the product of sample absorbance, slope, and dilution factor.

(4) Restrict use of the calibration line to only the more accurate portion of the calibration range. If (3) above is enacted, absorbance readings for samples containing from 1.0 to 4.0 μg NO_2 per mℓ. are considered accurate. If calibration data are collected between 4.0 and 5.0 μg NO_2 per mℓ. and the relationship remains linear, then the effective ranges above could be extended from 4.0 to 5.0 μg NO_2 per mℓ. as the upper limit. This argument is based on the use of absorbtion cells with a 1 cm. path length.

Enactment of these four recommendations could greatly enhance the precision, especially the laboratory bias, that is herein reported for the current version of Method 7.

B. Method 6

Method 6 specifies the extraction of a gas sample from the stack, the separation of the sulfur dioxide from the acid mist including sulfur trioxide, and the measurement of the sulfur dioxide fraction by the barium-thorin titration method.

The corrected collaborative test data from the Dayton and Cambridge collaborative tests are presented in Tables 8 and 9, respectively, Also included in these tables are some run summary and collaborator summary statistics.

1. The Accuracy of Method 6

A summary of the pertinent accuracy data on Method 6 from the gas cylinder test is presented in Table 10. For each cylinder at the two test sites, Table 10 displays the "true value" determined by

TABLE 8. THE CORRECTED DAYTON COLLABORATIVE TEST DATA WITH REPLACEMENT VALUES

METHOD: METHOD 6 --- DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

TEST VARIABLE: X = CORRECTED SO2 CONC. AT STD. COND. WITH REPLACEMENTS (DRY BASIS), 10**(-7) LB/SCF

TRANSFORMATION: X LINEAR

TEST SITE: DAYTON

COLLABORATORS: LAB 101 , LAB 102 , LAB 103 , LAB 104 ,

INTER-LABORATORY RUN SUMMARY

		LAB 101		LAB 102		LAB 103		LAB 104		RUN SUMMARY		
BLOCK	RUN	DATA	PORT	DATA	PORT	DATA	PORT	DATA	PORT	MEAN	STD DEV	BETA
1	1	729.0	(B)	948.0	(C)	903.0	(A)	714.0	(D)	823.50	119.36	.1573
	2	912.0	(C)	924.0*	(D)	914.0	(B)	736.0	(A)	871.50	90.49	.1127
	3	789.0	(D)	814.0	(A)	828.0	(C)	763.0	(B)	798.50	28.64	.0389
	4	865.0	(A)	910.0*	(B)	860.0	(D)	786.0	(C)	855.25	51.35	.0652
2	11	595.0	(C)	602.0*	(D)	600.0	(B)	558.0	(A)	588.75	20.71	.0382
	12	612.0	(D)	584.0	(A)	572.0	(C)	526.0	(B)	573.50	35.83	.0678
	13	586.0	(A)	583.0*	(B)	582.0	(D)	528.0	(C)	569.75	27.89	.0531
	14	588.0	(B)	607.0	(C)	599.0	(A)	534.0	(D)	582.00	32.93	.0614
3	15	175.0	(D)	203.0	(A)	183.0	(C)	172.0	(B)	183.25	13.96	.0827
	16	182.0	(A)	180.0	(B)	185.0	(D)	184.0	(C)	182.75	2.22	.0132
	17	170.0	(B)	182.0	(C)	180.0	(A)	169.0	(D)	175.25	6.70	.0415
	18	157.0	(C)	174.0	(D)	168.0	(B)	166.0	(A)	166.25	7.04	.0460
4	25	1040.0	(A)	1070.0	(B)	1037.0	(D)	889.0	(C)	1009.00	81.38	.0875
	26	1060.0	(B)	1202.0	(C)	1142.0	(A)	986.0	(D)	1097.50	94.41	.0934
	27	1170.0	(C)	1209.0	(D)	1176.0	(B)	1089.0	(A)	1161.00	50.97	.0477
	28	1090.0	(D)	1084.0	(A)	1147.0	(C)	1009.0	(B)	1082.50	56.63	.0568

COLLABORATOR SUMMARY

COLLABORATOR	LAB 101	LAB 102	LAB 103	LAB 104
MEAN	670.00	704.75	692.25	613.06
STD. DEVIATION	351.07	371.63	365.13	313.69

PORT SUMMARY

PORT	A	B	C	D
MEAN	670.69	663.62	680.62	665.12
STD. DEVIATION	347.03	350.40	364.69	349.22

*Replaced concentration value.

TABLE 9. THE CORRECTED CAMBRIDGE COLLABORATIVE TEST DATA WITH REPLACEMENT VALUES

METHOD: METHOD 6 --- DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

TEST VARIABLE: X = CORRECTED SO2 CONC. AT STD. COND. WITH REPLACEMENTS (DRY BASIS), 10**(-7) LB/SCF

TRANSFORMATION: X LINEAR

TEST SITE: CAMBRIDGE

COLLABORATORS: LAB 101 , LAB 102 , LAB 103 , LAB 104 ,

INTER-LABORATORY RUN SUMMARY

		LAB 101	LAB 102	LAB 103	LAB 104	RUN SUMMARY		
BLOCK	RUN	DATA PORT	DATA PORT	DATA PORT	DATA PORT	MEAN	STD DEV	BETA
1	4	134.0 (D)	153.0 (B)	155.0 (C)	150.0 (A)	149.25	7.14	.0519
	5	142.0* (A)	146.0 (C)	143.0 (D)	147.0 (B)	144.50	2.38	.0179
	6	152.0 (B)	146.0 (D)	151.0 (A)	143.0 (C)	148.00	4.24	.0311
	7	143.0* (C)	143.0 (A)	150.0 (B)	147.0 (D)	145.75	3.40	.0253
2	8	412.0 (A)	513.0 (C)	489.0 (D)	502.0 (B)	479.00	45.73	.1036
	9	547.0 (B)	568.0 (D)	516.0 (A)	522.0 (C)	550.75	38.60	.0761
	10	565.0 (C)	609.0 (A)	556.0 (B)	560.0 (D)	572.50	24.61	.0467
	11	593.0 (D)	629.0 (B)	549.0 (C)	604.0 (A)	593.75	33.42	.0611
3	18	847.0 (B)	826.0 (D)	844.0 (A)	805.0 (C)	830.50	19.36	.0253
	19	807.0 (C)	838.0 (A)	812.0 (B)	809.0 (D)	816.50	14.48	.0192
	20	837.0 (D)	824.0 (B)	787.0 (C)	834.0 (A)	820.50	23.01	.0304
	21	862.0 (A)	850.0 (C)	838.0 (D)	825.0 (B)	843.75	15.88	.0204
4	29	940.0 (C)	1123.0 (A)	1061.0 (B)	1007.0 (D)	1032.75	77.91	.0819
	26	990.0 (D)	882.0 (B)	1061.0 (C)	961.0 (A)	973.50	74.07	.0826
	27	1020.0* (A)	1086.0 (C)	1053.0 (D)	997.0 (B)	1039.00	38.86	.0406
	28	990.0 (B)	899.0 (D)	1070.0 (A)	999.0 (C)	989.50	70.15	.0769

COLLABORATOR SUMMARY

COLLABORATOR	LAB 101	LAB 102	LAB 103	LAB 104
MEAN	627.25	639.69	639.69	625.75
STD. DEVIATION	334.81	337.07	351.85	329.88

PORT SUMMARY

PORT	A	B	C	D
MEAN	642.44	632.75	629.44	627.75
STD. DEVIATION	353.75	327.82	339.74	332.19

*Replaced concentration value.

TABLE 10. METHOD 6 ACCURACY FROM SO_2 STANDARD GAS CYLINDER TEST

Test Site	Cylinder	Sulfur Dioxide Concentration, 10^{-7} lb/scf				Mean Percentage Difference, %
		True Value -Scott Research*		Method 6		
		Value	±1-Percent Uncertainty Range	Collab. Mean	95-Percent Confidence Interval for Mean	
Dayton	Y Low	137.0	(135.6, 138.4)	130.9	(124.7, 137.1)	-4.5
	Z Medium	676	(669,683)	620.4	(589.7, 651.2)	-8.2
	X High	1300	(1287, 1313)	1229.2	(1170.5, 1287.9)	-5.4
Cambridge	X Low	142.8	(141.4, 144.2)	145.4	(138.5, 152.3)	+1.8
	Z Medium	706	(699,713)	636.6	(606.2, 667.0)	-9.8
	Y High	1370	(1356, 1384)	1248.8	(1189.2, 1308.4)	-8.8

*Scott Research measured the SO_2 concentration of each cylinder by a modification of the West-Gaeke method in which the cylinder sample was diluted in glass to about 3 ppm prior to the West-Gaeke determination.

Scott Research for the cylinder, the mean of the collaborator's Method 6 measurements from the cylinder, uncertainty intervals for both these values, and the percentage difference in their values. The 95-percent confidence interval for the collaborators' Method 6 mean is based on variance estimates for Method 6 presented in Section 2 below. The only Method 6 95-percent confidence intervals that include the Scott Research determinations are for the two low concentration cylinders, cylinder Y at Dayton and cylinder X at Cambridge.

The sulfur dioxide concentrations reported for the gas cylinders were obtained by a modified West-Gaeke procedure, in which the cylinder sample is accurately diluted and analyzed along with a "master standard" for comparison. Use of the "master standard" provides a reference to minimize effects of colorimeter calibration curves, etc. Discussions with Scott Research personnel indicate that this analytical procedure is both accurate and precise.

The obvious inference to be drawn from Table 10 is that Method 6 is unbiased at low concentrations, but that as the concentration increases in the range from 300 to 500 $\times$ 10^{-7} lb/scf, Method 6 progressively acquires a low value bias with a magnitude of about 5 to 10 percent of the reported value.

2. The Precision of Method 6

The following assessments of the precision associated with a Method 6 test result may be made.

The 32 collaborator block point estimates of β are averaged to yield the within-laboratory coefficient of variation estimate $\hat{\beta} = 0.04004$.

There are 32 run point estimates of the between-laboratory coefficient of variation β_b shown in the last column of Tables 8 and 9. These run point estimates are averaged to yield the between laboratory coefficient of variation estimate $\hat{\beta}_b = 0.05795$.

Using the above estimates of β and β_b, the following table (Table 11) of precision estimates for Method 6 can be completed.

Thus, the within-laboratory standard deviation is 4.0% of δ with 96 degrees of freedom. The between-laboratory standard deviation is 5.8% of δ with only 3 degrees of freedom.

TABLE 11. PRECISION ESTIMATES FOR METHOD 6

Variability Component	Coeff. of Var.	Estimate	$\hat{\sigma}$
Within-Lab	β	0.04004	$(0.04004)\delta$
Between-Lab	β_b	0.05795	$(0.05795)\delta$
Lab Bias	$\beta_L = \sqrt{\beta_b^2 - \beta^2}$	0.04190	$(0.04190)\delta$

3. Accuracy and Precision of the Analytical Procedure

The accuracy and precision determinations for the analytical procedure were obtained from the analysis of standard sulfuric acid solution data.

The accuracy assessment was made by comparing the mean reported SO_2 concentration of each solution against the actual concentration of each standard solution. The mean reported SO_2 concentration of each solution was obtained by averaging the reported concentrations for all replicate analyses by all four collaborators at both test sites. Using variance estimates obtained through an analysis of variance, 95% confidence intervals around the mean reported SO_2 concentrations were established. The method can be said to be accurate at a given concentration if the true concentration lies within the 95% confidence interval around the mean reported concentration. As can be seen in Table 12, the prepared true concentrations for all four solutions meet the above criterion, and the analytical phase of Method 6 is unbiased within the precision of the method. The previously reported low value bias of Method 6 at higher SO_2 concentrations is not due to the analytical phase of the method.

TABLE 12. ACCURACY OF THE ANALYTICAL PHASE OF METHOD 6

Solution	Sulfur Dioxide Concentration, 10^{-7} lb/scf				Percentage Difference, %
	Prepared "True" Value	Collab. Mean	95-Percent Confidence Interval for Mean	Difference	
B	0.00	0.10	(−0.39, 0.59)	+0.10	
D	176.25	174.40	(170.60, 178.20)	−1.85	−1.05
A	352.50	348.97	(341.37, 356.57)	−3.53	−1.00
C	528.75	522.03	(510.63, 533.43)	−6.72	−1.27

Separate precision estimates for the analytical phase of Method 6 can be derived from the standard sulfuric acid solution data by an analysis of variance. These precision estimates are presented in Table 13.

The within-laboratory standard deviation for the Method 6 analytical phase is 1.1% of δ, while the between-laboratory standard deviation is 2.4% of δ.

Based upon the analytical data for the blank solution, an estimate of the minimum detectable limit can be made.

TABLE 13. ANALYTICAL PHASE PRECISION ESTIMATES FOR METHOD 6.

Variability Component	Determination Result		
	Coeff. of Var.	Estimate	$\hat{\sigma}$
Within-Lab	β	0.01103	$(0.01103)\delta$
Between-Lab	β_b	0.02448	$(0.02448)\delta$
Lab Bias	$\beta_L = \sqrt{\beta_b^2 - \beta^2}$	0.02185	$(0.02185)\delta$

The minimum detectable limit for a Method 6 test result is estimated as 3.16×10^{-7} lb/scf. This value is a conservative estimate; it may well be too large. It represents the smallest Method 6 test result that is significantly larger than a zero sulfur dioxide emission concentration.

4. Recommendations

Based upon the results obtained and upon comments from the collaborators, the following recommendations can be made concerning Method 6:

(1) The preliminary data analysis uncovered a potentially serious weakness of Method 6: the repeated collection of extraordinarily low SO_2 samples without any field indication that the sampling had been deficient. Efforts must be made to determine if this sporadic under-sampling problem which apparently afflicts Method 6 is due to leakage or to some other malfunction in the sampling apparatus. Then a means of detecting the problem condition in the field before or during Method 6 sample collection must be devised and suitable acceptance criteria established.

(2) The analytical phase of the method does not specify replicate analysis of the sample. Due to the somewhat indistinct endpoint in the barium ion-Thorin titration, duplicate or triplicate analysis of sample aliquots should be specified, with limits set on the acceptable spread of the titrant volumes for identical aliquots.

(3) Conduct a thorough critical review of Method 6 as currently written to locate ambiguous statements and to modify them to be more explicit.

Method 6 appears to be a reliable SO_2 determination technique. If the current version of Method 6[1] is rewritten to specify more procedural details, and to incorporate as many of the recommendations as prove feasible, then it should become a more reliable test method.

C. Method 5

Method 5 specifies that particulate matter be withdrawn isokinetically from the source and its weight be determined gravimetrically after removal of uncombined water.

The corrected collaborative test data from the Allen King Power Plant collaborative test are presented in Table 14. Also included in the table are some run summary statistics. Table 14 presents the data from three laboratories only; after the test was completed, it was ascertained that data from Laboratory 101 were unacceptable due to problems in the sampling train.

TABLE 14. PARTICULATE COLLABORATIVE TEST DATA ARRANGED BY BLOCK

Method: EPA Method 5--Determination of Particulate Emissions From Stationary Sources
Test Variable: X = Concentration of Particulates, (lb/scf) × 10^7
Transformation: X Linear
Test Site: Allen King Power Plant
Collaborators: Lab 102, Lab 103, Lab 104.

Inter-Laboratory Run Summary

Block	Run	Lab 102		Lab 103		Lab 104		Run Summary		
		Data	Port*	Data	Port	Data	Port	Mean	Std Dev	Coef of Var
1	1	137.3	(B)	58.4	(C)	334.4E†	(D)	97.8	55.8	0.5702
	3	176.8	(C)	225.7	(A)	375.1	(B)	259.2	103.3	0.3986
	4	185.3	(A)	154.9	(C)	103.5	(D)	147.9	41.3	0.2796
	6	173.6	(C)	146.9	(A)	163.8	(B)	161.4	13.5	0.0837
2	2	191.2	(D)	146.2	(B)	151.5	(A)	163.0	24.6	0.1509
	10	217.5	(D)	130.9	(B)	151.3	(A)	166.6	45.3	0.2718
	11	188.5	(C)	124.5	(A)	351.2	(B)	221.4	116.9	0.5279
	14	205.2	(D)	107.0	(B)	0.0M‡	(A)	156.1	69.4	0.4448
3	5	194.9	(B)	102.2	(D)	102.8	(C)	133.3	53.3	0.4002
	7	335.7	(C)	313.9	(B)	132.3	(A)	260.6	111.7	0.4285
	9	405.3	(B)	197.0	(D)	161.8	(C)	254.7	131.6	0.5167
	16	167.3	(A)	103.8	(C)	99.9	(D)	123.7	37.8	0.3060
4	8	190.4	(B)	122.0	(D)	125.9	(C)	146.1	38.4	0.2629
	12	198.5	(B)	161.8	(C)	111.5	(D)	157.3	43.7	0.2777
	13	210.9	(A)	157.4	(D)	119.4	(C)	162.6	46.0	0.2828
	15	138.8	(C)	112.3	(A)	123.8	(B)	125.0	13.3	0.1063

*Port designation is the sequence of ports from which the sample was taken.
†E indicates an erroneous value due to isokinetic variation being out of acceptable range.
‡M indicates no value was reported for that collaborator in that run.

In a particulate matter determination, no measurement of the accuracy of the method can be obtained. There are no on-stream techniques for analysis and no indicators of true concentration levels. Also, no type of standard sample for laboratory analysis can be prepared either, which would give an estimate of lab bias and of the analysis component of the total variation. Thus, the only technique available for evaluating Method 5 is that of estimating the precision of the concentration estimates obtained and the degree to which the results may be duplicated by a separate independent laboratory.

1. The Precision of Method 5

The 12 collaborator block point estimates of β are multiplied by the appropriate bias correction factor and by weights dependent upon the number of valid determinations. The estimated within-laboratory coefficient of variation is $\hat{\beta} = (0.3107)$.

The 16 run point estimates of β_b are multiplied by the appropriate bias correction factor and a weighted average yields the between-laboratory coefficient of variation estimate, $\hat{\beta}_b = (0.3668)$.

Using the above estimates of β and β_b, the following table (Table 15) of precision estimates for Method 5 can be completed.

TABLE 15. PRECISION ESTIMATES FOR METHOD 5

Variability Component	Coeff. of Var.	Estimate	$\hat{\sigma}$
Within-Lab	β	0.3107	$(0.3107)\delta$
Between-Lab	β_b	0.3668	$(0.3668)\delta$
Lab Bias	$\beta_L = \sqrt{\beta_b^2 - \beta^2}$	0.1950	$(0.1950)\delta$

Thus, we have a within-laboratory standard deviation of 31.1% of δ, with 34 degrees of freedom. The between-laboratory standard deviation is 36.7% of δ with 2 degrees of freedom.

2. Comments

Assessments of Method 5 have been made by the collaborative test supervisor and by the collaborators themselves as a result of their observations and experience in conducting the field testing. These assessments have included the following:

(1) In previous field experience as well as in conversations with many other persons using the method, it has become obvious that this method is more elaborate and time-consuming than most stack sampling methods. This results from mechanical design of the equipment plus the necessity to move heavy equipment items to the sampling point, especially if the sampling point is elevated on a high stack. The necessity for mounting the sampling probe and sample box assembly on a railing for traversing across the stack also complicates the mechanical arrangement of equipment. These difficulties are inherent in the method as published, however, and cannot be avoided.

(2) The extensive use of large amounts of glassware and ground glass connecting joints in the sampling train may result in leaks arising during the course of the run, which will influence the test result.

(3) The movement of equipment required in obtaining a test result often leads to breakage of the glassware used in the sampling equipment. In addition, mechanical shock placed on the equipment by raising it to platforms high on the stacks, from which sampling often must be done, can affect the calibration of the equipment as well as cause further glassware damage.

(4) The collection of matter from the probe is a probable cause of high and low reported concentration levels. During the extraction of the probe, the tip may scrape against the inside of the port, resulting in a large amount of particulate matter becoming lodged in the probe tip. This matter is then weighed and analyzed as if it were part of the sample. A loss of particulate matter may occur during the probe wash, if care is not taken. It was noted that, from run to run and collaborator to collaborator, there was considerable variation in the relative amount of particulate collected in the probe wash as compared to the filter collection.

3. Recommendations

The conclusions and comments presented above provide a firm basis for the following recommendations.

(1) Further testing at power plants is warranted in order to assess the precision of Method 5. The relatively high values for the precision estimates may be representative of the true values. However, with usable data from only three of the collaborators, and with only one site being tested, these results are inconclusive, and additional testing should be arranged.

(2) It is recommended that a standard technique for cleaning the filter apparatus be specified in the method. As it stands now, the cleaning technique used varies somewhat from lab to lab, depends greatly on the carefulness of the laboratory team, and is highly susceptible to major sampling errors.

(3) It is recommended that the technique for cleaning the probe be specified in greater detail in the method. Much of the variation in the method results from the probe cleaning, and details should be included in the method concerning the handling of the probe during recovery and the manner of recovering particulate matter from the probe.

(4) During sampling, many problems arise from the equipment used to obtain the samples. The design and reliability of some of the equipment now available for use with Method 5 does not seem adequate. As previously noted, the amount of glassware used in the equipment leads to unreliability, both in the equipment itself, from the high breakage levels, and in the performance, due to the probability of leaks arising during the course of the run. It is recommended that improvements be made in the equipment design and that efforts be made to eliminate the use of glassware and ground glass joints wherever possible. Improvements in this area should be made at an early date, if at all feasible.

By implementing these recommendations, the variation associated with Method 5 test results should be able to be better separated from analytical and mechanical components. This will allow a more thorough investigation of possible alternative procedures for the improvement of Method 5 as written.

APPENDIX A

WALDEN THEORETICAL NO_x CONCENTRATION CALCULATION

APPENDIX A. WALDEN THEORETICAL NO_x CONCENTRATION CALCULATION

The theoretical concentration of NO_x in the duct at the sample test section for the Cambridge test is given by

$$[C] = \frac{0.1183q}{Q_T + q} + K$$

where

$[C]$ = concentration of NO_x in the duct in lb/scf

q = NO flow from the gas doping system (acfm)

Q_T = theoretical volumetric flow in the duct (acfm)

K = 60×10^{-7} lb/scf NO_x due to combustion processes

The calculation of the flow due to the stoichiometric combustion of the No. 2 fuel oil is shown below.

$$Q_s = \left(\frac{0.871 \text{ moles of fuel}}{\text{min}}\right) \times \left(\frac{52.23 \text{ moles of combustion products generated}}{1 \text{ mole of fuel}}\right) \times$$

$$\left(\frac{22.4\ell}{\text{mole}}\right) \times \left(\frac{1 \text{ ft}^3}{28.3\ell}\right) = 36.0 \text{ acfm from combustion only}$$

TABLE A.1. OXYGEN CONSUMPTION FOR OIL COMBUSTION

Element	Wt. %*	Moles†	Moles† O_2 Needed
C	87.7	87.7/12	7.31
H	12.0	12.0/2	12.0/4 = 3.00
S	0.33	0.33/32	0.01
			TOTAL 10.32

*Typical residual oil analysis.
†Pounds moles/100 lb fuel.

TABLE A.2. COMPONENT OF FLOW DUE TO STOICHIOMETRIC COMBUSTION

Species	Moles*
CO_2	7.31
H_2O	2.00 × 3.00 = 6.00
SO_2	0.01
O_2 (No excess air)	0
N_2†	10.32 × 3.77† = 38.91
	TOTAL 52.23

*Pound moles/100 lb fuel.
†(Nitrogen + argon)/oxygen ratio for dry air.

Calculation of the 52.23 moles of combustion products generated per mole of fuel is given in Tables A.1 and A.2.

Q_s is then corrected for the excess air present in the duct as follows:

$$Q_T = \frac{Q_s(100 - \%O_2 - \%CO_2)}{(100 - \%O_2 - \%CO_2) - (3.76)(\%O_2)}$$

where

Q_T = theoretical flow (acfm)

Q_s = flow from stoichiometric combustion (acfm)

$\%O_2$ = Fyrite reading

$\%CO_2$ = Fyrite reading

The values for $\%O_2$ and $\%CO_2$ over the course of the Cambridge test are shown in Table A.3. The averaged Q_T result over a block of runs was used in computing the theoretical concentration.

The theoretical flows and calculated NO_x concentrations for each block of runs is shown in Table A.4. A value of $K = 60 \times 10^{-7}$ lb/scf was used throughout as the background NO_x present due to the furnace combustion. A propagation of error analysis gave an error range of ±11% in the theoretical NO_x concentrations calculated by this procedure.

TABLE A.3. WALDEN PILOT PLANT
FIRING CONDITIONS

Date	Time	% O_2	% CO_2	Duct Temp (°F)		NO Doping Flow (ℓ/min)
				High	Low	
12/11/72	12:20	8.5	9.0	480	275	2.25
	12:30	8.5	8.5	480	275	2.25
	1:40	8.5	8.5	475	290	2.25
12/12/72	11:30	9.5	9.5	480	275	2.1
	11:55	9.5	9.0	480	285	2.1
	12:15	9.0	9.5	480	285	2.1
	1:50	9.5	9.0	480	285	2.1
	2:10	9.5	9.0	480	285	1.75
	2:30	9.5	9.0	480	285	1.75
	3:15	9.0	9.0	475	290	1.75
12/13/72	11:30	9.0	8.5	475	275	1.11
	11:45	8.5	9.0	475	280	1.11
	11:50	9.0	9.0	475	285	1.11
	12:20	9.0	9.0	475	285	1.11
	1:00	9.0	9.0	475	285	1.11
12/14/72	12:30	9.0	8.5	480	–	0.52
	12:55	9.0	9.0	480	230	0.52
	1:00	9.0	9.0	480	240	0.52
	1:05	8.5	9.0	470	250	0.52
	1:20	9.5	9.0	470	260	0.52
	1:30	9.0	–	470	265	0.52
	1:45	8.5	8.0	470	275	0.52

TABLE A.4. THEORETICAL CALCULATED NO_X
CONCENTRATION RESULTS

Date	Theoretical Flow (acfm)	NO Doping Flow (acfm)	Calculated* Level of NO_X 10^{-7} lb/scf
12/11/72	58.70	0.0795	1660
12/12/72 a.m.	63.53	0.0742	1440
12/12/72 p.m.	63.16	0.0618	1216
12/13/72	60.74	0.0392	822
12/14/72	60.90	0.0184	417

*This value includes 60 × 10^{-7} lb/scf due to furnace combustion.

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16. ABSTRACT

This report describes the work performed and results obtained on Southwest Research Institute Project 01-3487-001, EPA Contract No. 68-02-0623, which includes the collaboarative testing in fossil fuel-fired steam generators of Method 5 for particulate emissions, Method 6 for sulfur dioxide emissions, and Method 7 for nitrogen oxides emissions as given in "Standards of Performance of New Stationary Sources." (1)

The objective of the preliminary evaluation of the methods specified in the above source reference was to determine if the methods were suitable for collaborative testing. Once judged suitable, the methods were collaboratively tested to determine, to the extent possible, the accuracy and precision of each method. Attempts were made to design the collaborative test plans and ancillary tests to allow determination of the sources of variability by suitable statistical analytic techniques. By obtaining the above information on the accuracy and precision for a given method, assessment of the reliability and acceptability of the method for field testing could be made. In addition, the relative weak and strong points of the methods could be ascertained, and recommendations for method modifications to enhance the precision of the methods could be made.

This report presents in summary form the results and conclusions derived from the collaborative studies. (2,3,4)

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