COLLABORATIVE STUDY

of

REFERENCE METHOD FOR DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE (PARAROSANILINE METHOD)

(24-Hour Sampling)

Richard A. McCoy
David E. Camann
Herbert C. McKee

Contract CPA 70-40
SwRI Project 01-2811

Prepared for
Methods Standardization Branch: QAEML
National Environmental Research Center
Environmental Protection Agency
Research Triangle Park, N. C. 27711

December 1973

SOUTHWEST RESEARCH INSTITUTE
SAN ANTONIO CORPUS CHRISTI HOUSTON

SOUTHWEST RESEARCH INSTITUTE
Post Office Drawer 28510, 8500 Culebra Road
San Antonio, Texas 78284

COLLABORATIVE STUDY

of

REFERENCE METHOD FOR DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE (PARAROSANILINE METHOD)

(24-Hour Sampling)

Richard A. McCoy
David E. Camann
Herbert C. McKee

Contract CPA 70-40
SwRI Project 01-2811

Prepared for
Methods Standardization Branch: QAEML
National Environmental Research Center
Environmental Protection Agency
Research Triangle Park, N. C. 27711

December 1973

Approved:

John T. Goodwin, Jr.
Technical Vice President and Director,
Department of Chemistry
and Chemical Engineering

ACKNOWLEDGEMENTS

Our sincere appreciation is extended to the following organizations for their participation in the collaborative test of the pararosaniline method of sulfur dioxide determination in the atmosphere using sampling periods of 24 hours.

Bay Area Air Pollution Control District
939 Ellis Street
San Francisco, California 94109
Mr. Milton Feldstein
Mr. Dario Levaggi

Environmental Protection Agency
National Environmental Research Center
Research Triangle Park, North Carolina 27711
Dr. Kenneth T. Knapp

State of California Health and Welfare Agency
Department of Public Health
2151 Berkeley Way
Berkeley, California 94704
Dr. Peter K. Mueller
Mr. Emil R. deVera

Southwest Research Institute, Houston
2600 South Yoakum Boulevard
Houston, Texas 77006
Mr. R. E. Childers
Mr. C. A. Boldt
Mr. Rudy Marek

The participation of Dr. John B. Clements and Mr. John H. Margeson of the Methods Standardization Branch, Environmental Protection Agency, in the planning and reporting of the results was also of great assistance.

SUMMARY AND CONCLUSIONS

This report presents the results of a collaborative study of the pararosaniline reference method which was published by the Environmental Protection Agency in the Federal Register, April 30, 1971, as the reference method to be used in connection with Federal ambient air quality standards for sulfur dioxide. That publication is reproduced as Appendix A of this report. The present study involved four collaborating laboratories sampling synthetic SO_2 atmospheres over a 24-hour period in their own laboratories. The atmospheres were generated from calibrated permeation tubes supplied by the National Bureau of Standards.

The highlights of the statistical analysis which was performed on the data provided by the four collaborating laboratories are as follows:

- The replication error varies linearly with concentration from 2.5 $\mu g/m^3$ at concentration levels of 100 $\mu g/m^3$ to 7.0 $\mu g/m^3$ at concentration levels of 400 $\mu g/m^3$.
- The repeatability (day-to-day variations within an individual laboratory) varies linearly with concentration from 18.1 $\mu g/m^3$ at 100 $\mu g/m^3$ concentration levels to 50.9 $\mu g/m^3$ at 400 $\mu g/m^3$ concentration levels.
- The reproducibility (day-to-day variability between two or more laboratories) varies linearly with concentration from a low of 36.9 $\mu g/m^3$ at 100 $\mu g/m^3$ to a high of 103.5 $\mu g/m^3$ at 400 $\mu g/m^3$.

- A laboratory selection bias was inadvertently introduced in the choice of the four collaborating laboratories for this test, but the effect of this bias on the reproducibility of the method was eliminated through a suitable comparison with the 30-minute test results.
- The 24-hour sampling method does have a concentration dependent bias which becomes significant at the 95% confidence level at the high concentration level. Observed values tend to be lower than the expected SO_2 concentration level.

Whereas this study used sampling periods of 24 hours, an earlier study had examined the method for sampling periods of 30 minutes. A comparison of the results for the two studies at a concentration level of 200$\mu g/m^3$ is summarized in the following table:

	24-hour	30-minute
Repeatability	29 (0.011 ppm)	52 (0.020 ppm)
Reproducibility	59 (0.023 ppm)	102 (0.039 ppm)

This comparison indicates that the 24-hour procedure is capable of better within- and between-laboratory precision than the 30-minute procedure. However, it should be pointed out that these differences are based on collaborative tests that differed in experimental design. Although accepted statistical techniques were used to process the data, these techniques involve assumptions which preclude rigorous comparisons between the test results.

Therefore, it is concluded that the exact degree of improved precision of the 24-hour test method over the 30-minute test method is uncertain.

TABLE OF CONTENTS

		Page
SUMMARY AND CONCLUSIONS		ii
LIST OF ILLUSTRATIONS		v
I.	INTRODUCTION	1
II.	COLLABORATIVE TESTING OF THE METHOD	3
	A. Generation of Test Atmospheres	3
	B. Selection of Collaborators	6
	C. Preliminary Tests by the Controlling Laboratory	7
	D. Additional Collaborative Testing	7
III.	STATISTICAL DESIGN AND ANALYSIS	9
	A. Outlying Observations	9
	B. Analysis of Variance and Variance Components	10
	C. Various Sources of Error Within the Analytical Method	18
	1. Calibration Curves	18
	2. Control Samples	19
	3. Reagent Blanks	19
	D. Application of the Results	20
LIST OF REFERENCES		24

Appendix A - Reference Method for the Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method)
Appendix B - Statistical Design and Analysis
Appendix C - Tabulation of Original Data
Appendix D - Instructions to Collaborators for Collaborative Test of Reference Method for the Determination of Sulfur Dioxide in the Atmosphere

LIST OF ILLUSTRATIONS

Figure		Page
1	Specifications for Permeation Tube System Used in Collaborative Tests	5
2	The Reproducibility, Repeatability, and Replication Error Standard Deviations Obtained by Three Distinct Analyses	11
3	Replication Error, Repeatability, and Reproducibility Versus Concentration for 30-Minute Sampling and 24-Hour Sampling	13
4	Between Laboratory Variability Component (Standard Deviation) Versus Concentration for 30-Minute Sampling and 24-Hour Sampling	16

I. INTRODUCTION

In order to determine the relative merits of the pararosaniline reference method for the determination of sulfur dioxide in the atmosphere as described in the Federal Register, Vol. 36, No. 84 (see Appendix A), a collaborative study was conducted and the results analyzed and reported in September, 1971 [1]. This first study was conducted using a sampling period of 30 minutes. In the interests of thoroughness, since the reference method is recommended for the measurement of sulfur dioxide in ambient air using a sampling period of 24 hours, it was decided that a subsequent study using sampling periods of 24 hours would be conducted.

This document reports the results of this collaborative study as conducted by Southwest Research Institute and the Methods Standardization Branch. The procedures used in conducting the collaborative testing borrow heavily from the experience gained in conducting the 30-minute study. In addition, the results gained from the 24-hour sampling were so similar to those reported for the 30-minute study that the included statistical analysis is practically a carbon copy of that used in the earlier study. Therefore, this reports acts as a complement to that original document; many of the assumptions, analytical arguments, and results from that study apply in the present case. For this reason, it is recommended that the report of the 30-minute SO_2 sampling study be available and referred to in conjunction with this document.

This report of the pararosaniline reference method study was written in two parts. Part one is a general description of the design, organization, operation and analysis which form the 24-hour sampling study. This first section presents the basic assumptions and logic which served to guide the statistical analysis, together with a brief summary of the answers which resulted. Part two of the report consists of a number of appendices in which the many details of the study are documented. A two-page summary appears immediately after the title page in which only the highlights of the study are presented.

II. COLLABORATIVE TESTING OF THE METHOD

Cooperative planning between Southwest Research Institute and the Methods Standardization Branch began shortly after completion of the final report of the 30-minute study in September of 1971. A rigid test method (see Appendix D) was developed and instructions for conducting tests were supplied to each of the collaborating laboratories. The clarity and detail of these instructions were an important element contributing to the efficiency with which the tests were conducted.

A. Generation of Test Atmospheres

Of the available methods for supplying SO_2 samples to the collaborating laboratories, the calibrated permeation tube system was chosen as the most suitable for these tests. Such a system had worked well for the 30-minute sampling study using calibrated permeation tubes supplied by the National Bureau of Standards. At the time of that study, the permeation tube was not a standard reference material; therefore the accuracy of this generation system was determined by pre and post test calibration of the permeation tubes by NBS to assure reliable evaluation of the test method. The SO_2 permeation tube was issued as a standard reference material on December 1, 1970, so that recalibration was not necessary for the present study.

The permeation tubes used consist of a small cylindrical tube of Teflon containing liquid sulfur dioxide . The rate of diffusion of sulfur dioxide through the walls of the cylinder depends only on temperature and is reproducible within a reasonable temperature range. The certification available from the National Bureau of Standards covered the range of 20°-30°C and provided sufficient accuracy if temperature control to within 0.1°C was maintained.

If the rate of permeation is controlled accurately through controlling the temperature, the only other variable controlling the concentration of the test atmosphere is flow rate. By passing air through the permeation tube apparatus at a controlled flow rate, and thus diluting the sulfur dioxide which passed through the walls of the tube by diffusion, the concentration of sulfur dioxide in the final air stream could be accurately controlled. A special apparatus was developed for this purpose which is illustrated in Figure 1. Major portions of this system were fabricated from Pyrex glass, and temperature control was achieved by enclosing the permeation tube holder in a water jacket supplied by circulating water controlled to within 0.1°C. Purified air used for dilution was measured accurately with calibrated rotameters.

The apparatus consisted primarily of a condenser capable of accommodating a permeation tube and a 0.1°C thermometer, a large Kjeldahl trap to be used as a mixing bulb, and a manifold with Teflon stopcocks for sampling. The glassware is connected by ground-glass ball joints. Associated parts for the system include a calibrated flowmeter covering the range of 0 to 100ml/min with an accuracy of 5 percent, a flowmeter covering the range of 0 to 15 l/min with an accuracy of 1 to 2 percent, a 0.1°C thermometer, and a constant-temperature bath equipped with a circulating pump to continuously supply water to the condenser. The bath must be capable of maintaining the temperature within $\pm$ 0.1°C. Cylinder air or compressed air, purified by carbon

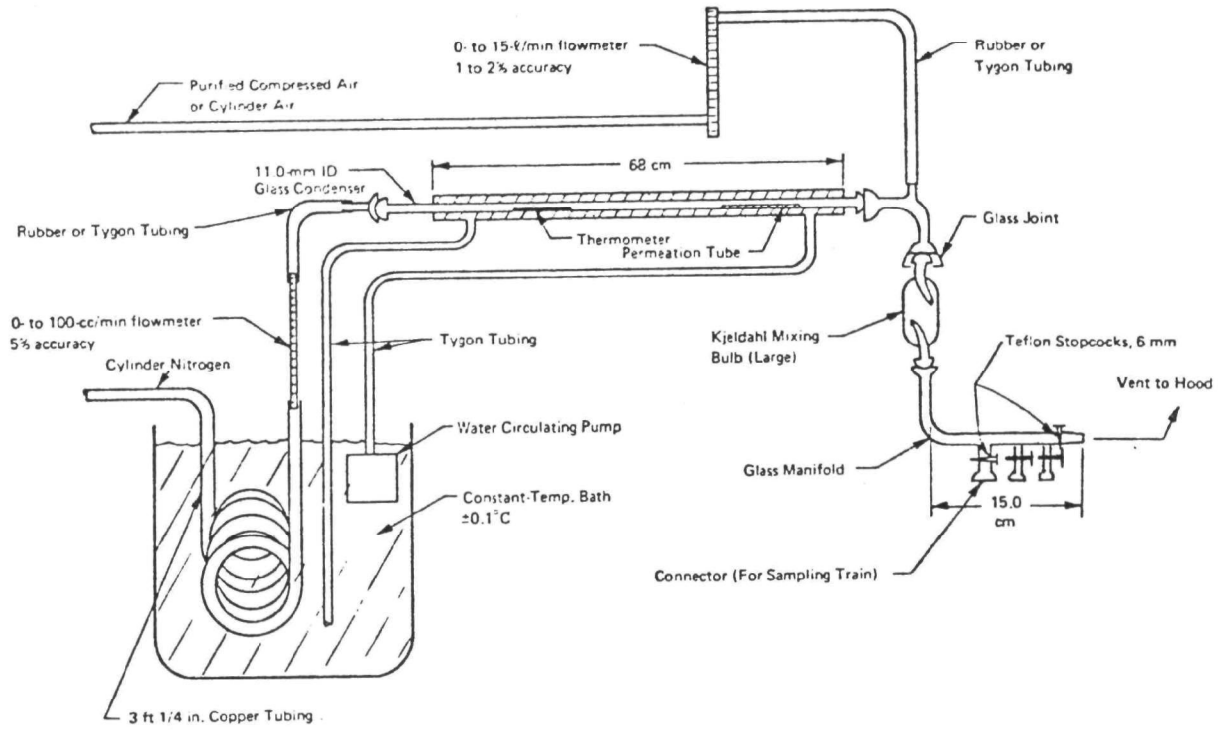


FIGURE 1. SPECIFICATIONS FOR PERMEATION TUBE SYSTEM USED IN COLLABORATIVE TESTS

filters and drier (e.g., silica gel, molecular sieve), and cylinder nitrogen are required to complete the system.

A sulfur dioxide permeation tube obtained from the National Bureau of Standards was inserted into the condenser, and the system assembled as shown in Figure 1. Nitrogen was passed continuously through the condenser, housing the permeation tube and the 0.1°C thermometer, at a rate of 50ml/min. It is advisable to maintain this flow through the system continuously in order to avoid sulfur dioxide accumulation in the condenser tube. The temperature in the system was adjusted to the desired temperature (usually 25.0°C). After the permeation tube had been equilibrated 24 hours, the dilution air was introduced into the system and the flow adjusted to produce the desired test atmosphere. Up to one-half of the total flow of the system may be sampled. The concentration of sulfur dioxide in the standard atmosphere was calculated according to the formula found in Section 9.2.2 of the method (see Appendix A). In order to conserve dilution air, it was shut off at the end of a sampling day; however, the constant-temperature bath and purge nitrogen gas were normally left on.

B. Selection of Collaborators

As is true in all collaborative studies, the selection of collaborators was a compromise between available resources and the quantity of information to be gained from the test. A minimum of six laboratories are desirable for a collaborative test[3]. However, because the test requires 2 to 3 man weeks per collaborator, the cooperation of only four laboratories (see acknowledgements) could be obtained.

In order to minimize familiarization time to the greatest possible extent, it was decided to employ laboratories which had collaborated in the 30-minute sampling study. These conditions were acceptable in view of the fact that a great deal of knowledge regarding the test method had already been generated by the earlier study.

C. Preliminary Tests by the Controlling Laboratory

Southwest Research Institute performed the function of organizing the collaborative test. In order to become familiar with the method as it applies particularly to a 24-hour sampling period, it was decided that SwRI should perform the test sequence that would be required of each collaborating laboratory. Since this test sequence would in every way be equivalent to that of any other collaborating laboratory, it was also decided to include the results as a part of the test method study. The test sequence was performed by SwRI in April, 1972. Difficulty was experienced on the first two days of the test with poor agreement between the control concentrations added and those returned. The implications of this problem are discussed in a subsequent section dealing with outlying observations.

D. Additional Collaborative Testing

Southwest Research Institute and three additional laboratories from the fourteen which participated in the 30-minute sampling study agreed to again participate in the 24-hour study. Each laboratory received a calibrated permeation tube from the National Bureau of Standards as well as instructions, data forms and a copy of the method from SwRI (see

Appendix D) for use in the collaborative study. One of the collaborating laboratories reported equipment malfunctions during particular portions of the test sequence. The ability of this collaborator to identify particular problems with a corresponding set of data was of assistance in dealing with the outlying observations that resulted. Because of their familiarity with the method and the calculations required, the collaborating laboratories experienced a minimum of difficulties, and no calculation errors were discovered.

III. STATISTICAL DESIGN AND ANALYSIS

Each of the collaborating laboratories was able to maintain the necessary physical conditions as specified in the reference method procedure. It was not a requirement to report temperature and pressure at regular intervals, but the spot checks that were reported indicate that none of the laboratories had difficulty in this area. The calibration procedure with sulfite solution was checked for arithmetic errors, and in no case did the check disagree with the reported figures by more than round-off differences.

The four collaborating laboratories were each required to analyze three concentrations of sulfur dioxide. The concentrations were nominally 98, 291 and 475 $\mu g/m^3$. The observed values are recorded in Table B-1, the expected values are recorded in Table C-1, the differences between observed and expected values are shown in Table C-2, the adjusted values are given in Table C-3 and the transformed values are given in Table B-2. The basis for the transformation is discussed in Appendix B.

A. Outlying Observations

The tests that were conducted for outlying observations identified a total of six samples of three replicates each of a total of eighteen observations that proved to be outliers. Appropriate substitutions were

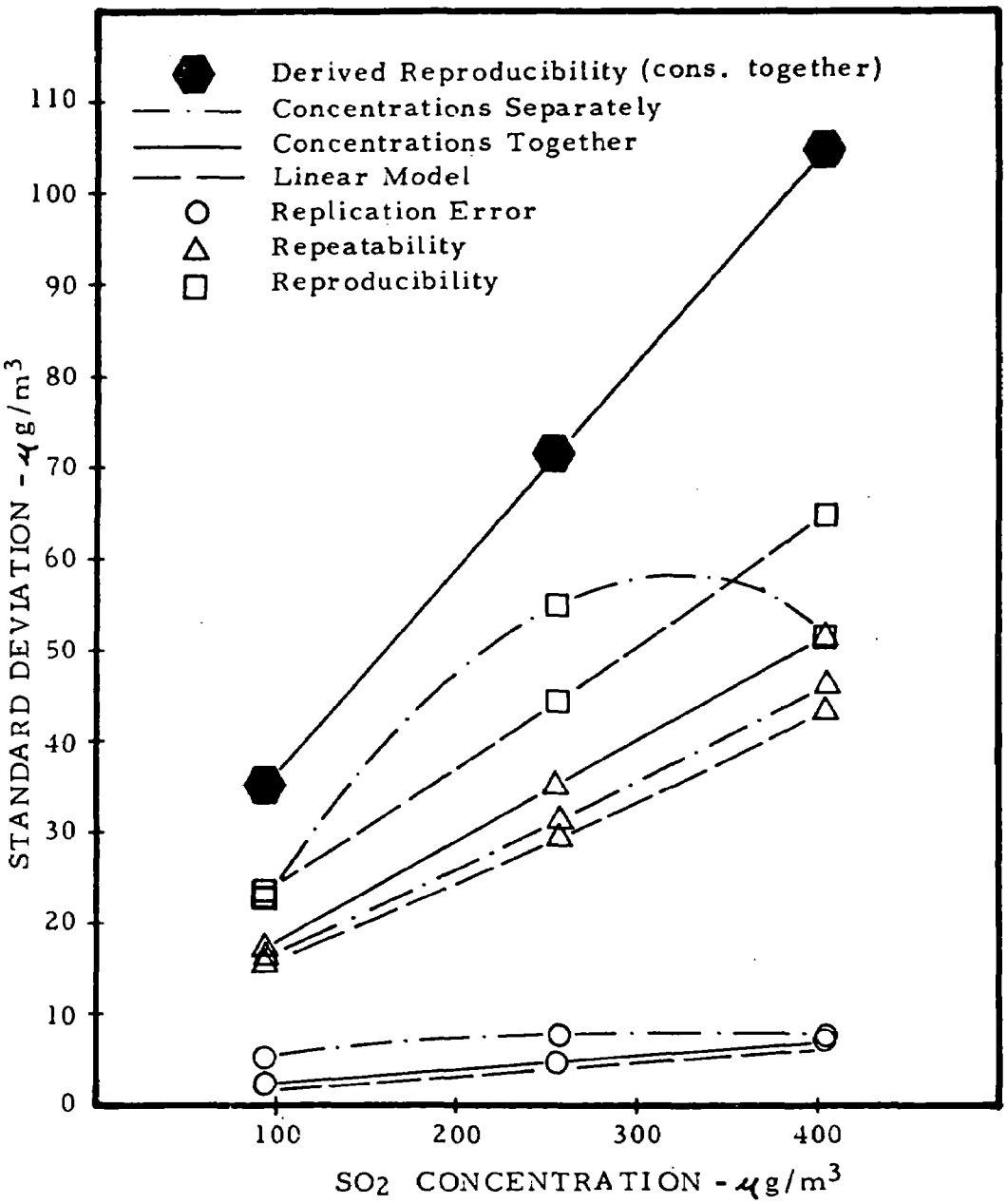
made for these outlying observations in order to keep an equal number of observations for each collaborating laboratory. With only four laboratories participating in the study, the elimination of any data would have seriously affected the statistical analysis.

It was possible in the case of each outlying observation to identify a reasonable cause for the inconsistency. In the case of one laboratory, attention was drawn to sampling difficulties by unusual flowmeter rates which were caused by equipment leaks. This occurred on two separate days and required substitutions for three observations on each of those days. In the case of a second laboratory, a calibration error was evidenced by poor agreement between the added and returned control solution. This necessitated substitutions for all nine observations recorded on that day. Details of the outlier tests and the substitutions that were made are contained in Appendix B.

B. Analysis of Variance and Variance Components

Appendix B is a detailed account of the analysis of the results of the 24-hour SO_2 sampling collaborative study. As in the 30-minute sampling study, three individual analyses were conducted, and the results are compared in Figure 2. The "derived" reproducibility curve is the result of the reproducibility curve for all concentrations analyzed together having been corrected for a laboratory bias. The reasons why this was necessary and the methods by which it was carried out are discussed in Section II B of Appendix B. The data in Figure 2 are in the original scale. The first method was an analysis of variance handling the concentrations

FIGURE 2. THE REPRODUCIBILITY, REPEATABILITY, AND REPLICATION ERROR STANDARD DEVIATIONS OBTAINED BY THREE DISTINCT ANALYSES



individually with the data in the original scale. The second method was again an analysis of variance, but in this case the three concentrations were handled together, and the data were in a transformed scale. The final method, the linear model analysis as described by Mandel[2], again handled the three concentrations together with the data in the transformed scale. The agreement between the three methods as shown in Figure 2 was quite good.

For the purposes of this study, the definitions of replication error, repeatability, and reproducibility are the same as those which apply in the 30-minute sampling study. Basically, replication error describes the variability among observations recorded within an individual laboratory during a single day of sampling. Repeatability is defined as the sum of the replication error and the variability among observations recorded by an individual laboratory on successive days. Reproducibility is then the variability between observations made by different laboratories plus the repeatability for the method. Each of these measures is expressed as a standard deviation of a given concentration in units of micrograms per cubic meter.

The various sources of error within the analytical method will be expressed with reference to the analysis of variance in which the three concentrations were treated together in the transformed scale for the following reasons: (1) the method results in simpler expressions for replication error, repeatability and reproducibility as a function of concentration which are more generally understood, and (2) the results of this method were chosen to express these quantities in the earlier study and, by duplicating this choice, direct comparisons can be made between the 30-minute and the 24-hour sampling studies. The results of this comparison are illustrated in Figure 3.

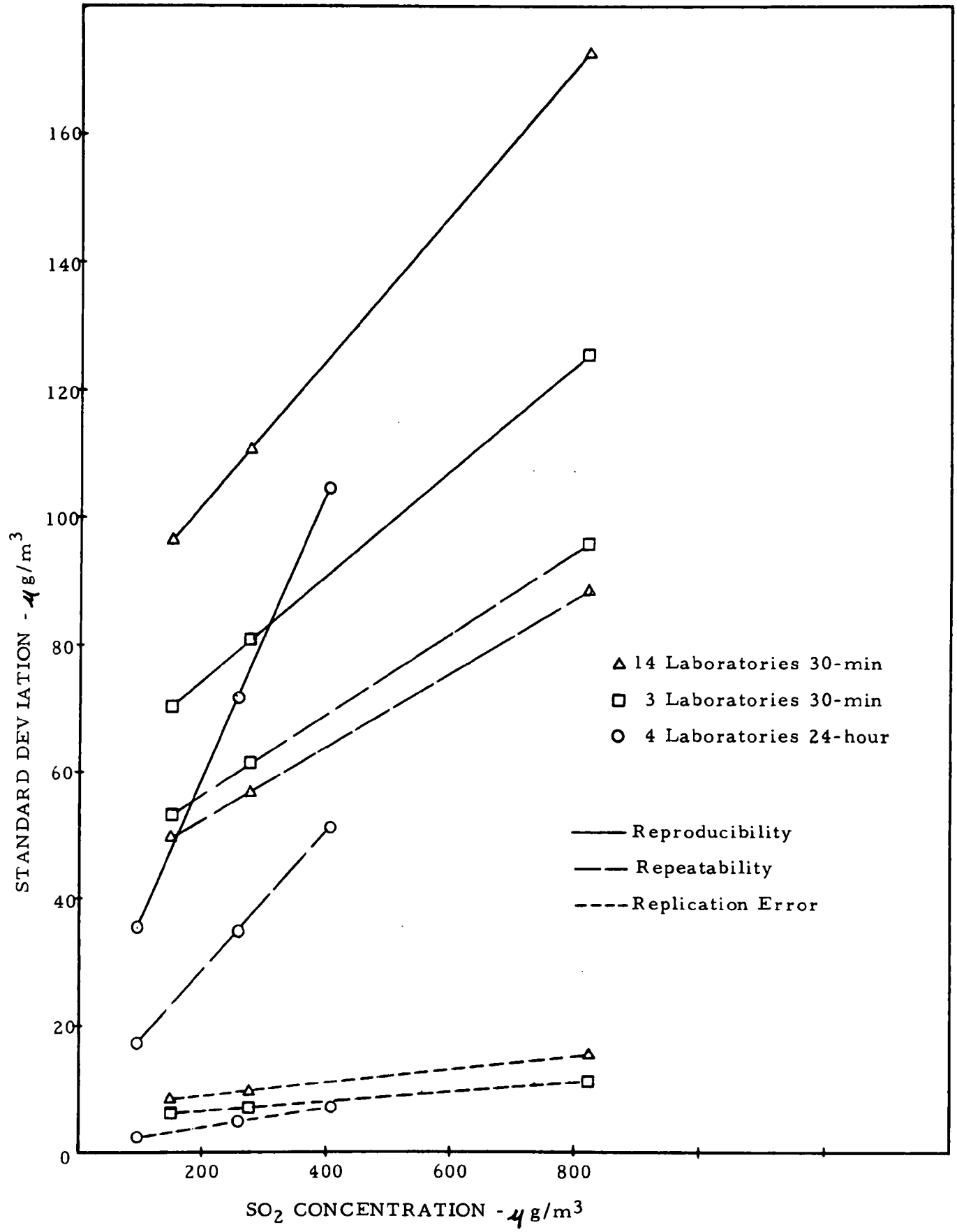


FIGURE 3. REPLICATION ERROR, REPEATABILITY, AND REPRODUCIBILITY VERSUS CONCENTRATION FOR 30-MINUTE SAMPLING AND 24- HOUR SAMPLING

Certain questions arose from a comparison of results from the 30-minute sampling study versus those of the 24-hour sampling study. The replication errors that resulted were quite similar for the two studies. However, the repeatability and reproducibility appeared to be much better (i.e., smaller standard deviations) for the 24-hour sampling study. The large differences between studies for both of these measures could be real; however, one immediately questions the various randomization processes which are so vital to the statistical analyses by which the data were treated.

Since three of the four laboratories which collaborated in the 24-hour sampling study had also participated in the 30-minute sampling study (numbers 927, 345 and 920), the possibility of a laboratory bias was immediately suspected. At this point, the data for the original 30-minute sampling study were examined. Just a quick look at the data reported by the three laboratories that are common to both studies seemed to indicate a unique similarity. The values for these three laboratories appeared to have less variability with respect to each other than was the case with the remaining eleven laboratories. Also, the means of these three laboratories appeared to be closer to the total concentration means than was true of other laboratories.

On the basis of these examinations, an analysis of variance was performed on the transformed 30-minute sampling values reported by laboratories 927, 345 and 920. The results of this analysis are shown

graphically in Figure 3, and in comparison to the curves for all fourteen laboratories analyzed together, a limited bias is evident.

Agreement between the curves for replication error and those for repeatability is quite good, and only the curves describing reproducibility indicate a significant difference. Since repeatability and reproducibility differ by only the lab-to-lab variance component as defined in the expression (B-9) of Appendix B, this difference in reproducibility must be caused by laboratory bias. A more detailed discussion of the laboratory variability component may be found on p. 344 of Mandel[2]. For example, the laboratory component, in the transformed scale, for all concentrations analysed together from Table B-6 is simply:

$$\text{laboratory component} = \sqrt{V(L) + V(LC)} = \sqrt{107.90 + 12.43} = 10.97$$

The variability among the three laboratories analyzed separately is obviously less than that which exists among all fourteen laboratories analyzed together. The laboratory variability component which resulted from each of the three analyses was isolated and is shown in Figure 4 in order to emphasize this fact. The laboratory component which resulted from analyzing all fourteen laboratories together is considered to be a more accurate representation for the entire population of laboratories.

Since these three laboratories--927, 345 and 920--collaborated in the four-laboratory 24-hour test, the reproducibility results of the 24-hour study are similarly biased. The difference between the two lower curves in Figure 4 is thought to be a real between-laboratory component which

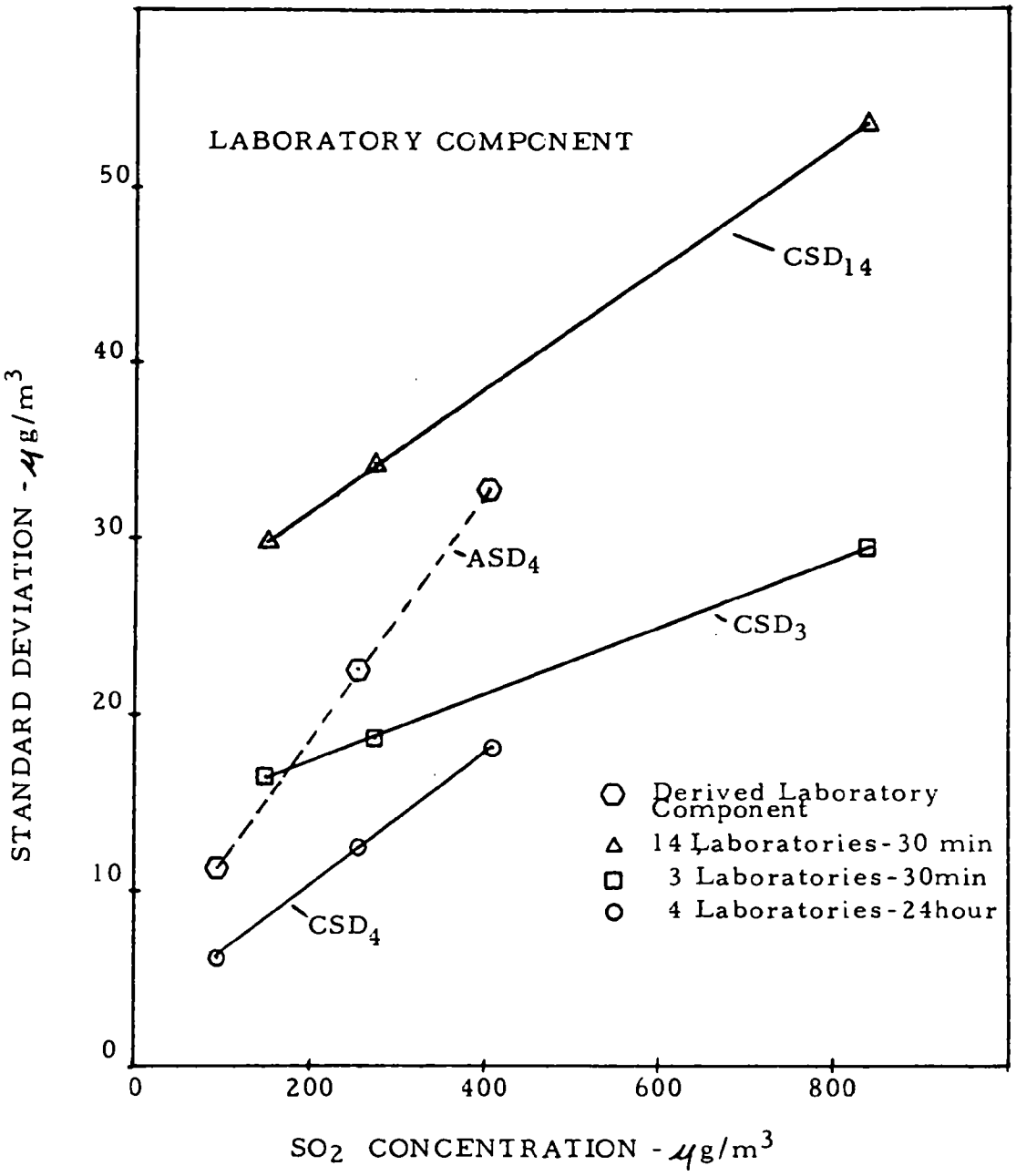


FIGURE 4. BETWEEN LABORATORY VARIABILITY COMPONENT (STANDARD DEVIATION) VERSUS CONCENTRATION FOR 30-MINUTE SAMPLING AND 24-HOUR SAMPLING

is a function of sampling time period and as such is included in the quoted reproducibility of the 24-hour method. This difference could result from these laboratories becoming increasingly proficient in conducting the test, operating the generating equipment and/or acquiring improved measuring equipment. It was not possible, however, to either identify or quantitatively define the effects of these factors.

But the true between-laboratory component exclusive of laboratory bias for the 24-hour method must lie close to the upper curve in Figure 4. A reasonable estimate was made of the laboratory component, and the result is illustrated by the dashed curve in Figure 4. This adjusted lab-to-lab component value has been included in the quoted reproducibility for the 24-hour method, and all subsequent calculations involving reproducibility are based on this assumption. The derived reproducibility curve for the 24-hour sampling method is illustrated by the dashed line in Figure 2, and details for the calculation of this curve are to be found in Appendix B.

A comparison of the curves for repeatability indicates little difference between the 30-minute sampling results of the three common laboratories analyzed separately and the fourteen collaborating laboratories analyzed together. However, there is considerable difference between the results of those two analyses and the results of the 24-hour sampling repeatability curve. This would indicate that a real difference in repeatability is attributable to the length of time over which the sample is taken. For this study the dilution air flow for the generating system was constant over the 24-hour period. The improved repeatability of the 24-hour sample is thought to be due primarily to the normal averaging of day-to-day variability factors. The better repeatability would tend to recommend the 24-hour sampling method.

C. Various Sources of Error Within the Analytical Method

The various calibration procedures required by the analytical method were documented by each of the collaborating laboratories. The following discussion describes the analysis which was conducted on each of these tasks, and the calibration data provided by the participants are summarized in Tables C-4 and C-5.

1. Calibration Curves

Each laboratory was required to prepare only one calibration curve as described in the Instructions to Collaborators (see Appendix D). The slopes and Y-intercepts of these curves were investigated to determine interlaboratory variability.

The overall mean slope was 0.030 absorbance unit per microgram (3 degrees of freedom), while the standard deviation for between-laboratory variation was 0.004. The 95 percent confidence interval for between-laboratory variability was therefore 0.030 ± 0.013. The overall mean is very close to the figure which is claimed for the method.

The overall mean Y-intercept was 0.201 absorbance unit, while the standard deviation was 0.020 absorbance unit (3 degrees of freedom). This results in a 95 percent confidence interval of 0.201 ± 0.064. The information in these two measures is limited by the fact that only one calibration curve was made by only four collaborating laboratories.

2. Control Samples

The control samples of standard sulfite solutions were recorded by each laboratory on each day on the basis of concentration added and concentration measured. The differences between these two figures were subjected to an analysis of variance to determine the day-to-day within-laboratory variability as well as the between-laboratory variability. These data consist of twenty-four individual values (four laboratories x six days) and are included in Table C-5.

The analysis of the control samples revealed that between-laboratory variability accounted for 72 percent of the total, while within-laboratory variability was responsible for the remaining 28 percent. The standard deviation for between-laboratory variability was 0.868μg (3 degrees of freedom) which gives a 95 percent confidence interval of ± 2.76μg. The standard deviation for within-laboratory variability was found to be 0.543μg (20 degrees of freedom), so that the 95 percent confidence interval of this measure was ± 1.13μg. For a 30-l air sample, these standard deviations correspond to concentrations of 38μg/m^3 and 92μg/m^3, respectively.

3. Reagent Blanks

Each of the collaborating laboratories prepared a reagent blank on each of the six sampling days. The values for the reagent blanks together with the differences between the reagent blanks

and the Y-intercepts of the calibration curves in absorption units are shown in Table C-5. An analysis of variance was conducted on the intercept/reagent blank differences, and the overall mean was not significantly different from zero. The standard deviation of the within-laboratory variability was 0.019 absorbance unit (20 degrees of freedom), representing 82 percent of the total variability. The 95 percent confidence interval was thus $\pm$ 0.040 absorbance unit. The between-laboratory variability accounted for the remaining 18 percent of the total, and the standard deviation of this component was 0.009 absorbance unit (3 degrees of freedom). The 95 percent confidence limit of this component was $\pm$ 0.028 absorbance unit.

In certain cases, the above measures for the 24-hour sampling method differ from corresponding results of the 30-minute sampling method. Part of this disagreement is thought to be due to the limited number of collaborators (four) participating in the 24-hour study. On the basis of only four laboratories, the tests for outlying observations become inconclusive, and there was hesitancy to eliminate observations which proved to be marginal. Thus, all observed values were retained, and the results are quoted on the basis of an analysis on the complete set of data.

D. Application of the Results

It was necessary to employ a number of techniques in analyzing the data that were submitted by the collaborating laboratories. The details

of these individual analyses are documented in Appendix B, and only the important results are summarized here. In all instances, the following results are based on a 0.05 level of significance. This allows the results of this study of the 24-hour sampling study to be compared directly with the results of the 30-minute study for which a 0.05 significance level was chosen.

The following expressions define the replication error ($\hat{\sigma}_{\epsilon}$), the repeatability ($\hat{\sigma}_{D}$), and the derived reproducibility ($\hat{\sigma}_{L}$) of the 24-hour method as a function of SO_2 concentration. The graphical representation of these expressions appears in Figure 2, and both the standard deviation ($\hat{\sigma}$) and concentration level (y) are in units of $\mu g/m^3$.

$$\hat{\sigma}_{\epsilon} = (.2312 + .0035\ y)(4.31)$$

$$\hat{\sigma}_{D} = 2.77\ (.2312 + .0035\ y)\ (11.26)$$

$$\hat{\sigma}_{L} = 2.77\ (.2312 + .0035\ y)\ (22.91)$$

Various measures of precision can be computed on the basis of these equations. Some of the more fundamental statements of precision are given below based on results from the analysis of variance treating the three concentrations together.

With respect to replication, the maximum permissible difference between duplicates is given by

$$R_{max} = (2.82)(.2312 + .0035\,y)(4.31)$$

If two replicates differ by more than R_{max}, there is less than one chance in twenty that they belong to the same population. R_{max} has been calculated for the three nominal SO_2 concentrations which were sampled in this study, and the results expressed as a percentage of concentration. These replication percentages are presented in the first row of Table I-1.

TABLE I-1. R_{max} AS A PERCENTAGE OF CONCENTRATION

Parameter	Concentration, $\mu g/m^3$		
	100	250	400
Replication Error	7.1	5.4	5.0
Repeatability	25.7	19.5	18.0
Reproducibility	59.9	45.6	42.0

From this, we see that 7.1 is the smallest percentage difference between two replicates that is significant in the 24-hour test at concentration levels of $100 \mu g/m^3$.

The following expression is used to compare two single-replicate observations made by the same analyst on different days.

$$R_{max} = (3.92)(.2312 + .0035y)(11.26)$$

At a concentration level of $100\mu g/m^3$, it is seen from Table I-1 that a difference of less than 25.7 percent cannot be detected between two such observations.

The expression which allows comparison of two observations made in separate laboratories on the same sample is:

$$R_{max} = (4.50)(.2312 + .0035\,y\,)(22.91)$$

For this measure, the method is unable to distinguish a real difference of less than 59.9 percent between observations at concentration levels of $100\mu g/m^3$. For each measure, the percentage difference that can be detected decreases with concentration; however, the absolute difference that is detectable increases with concentration.

LIST OF REFERENCES

1. McKee, H.C., Childers, R.E., and Saenz, O., Jr., Collaborative Study of Reference Method for Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method), prepared for Office of Measurement Standardization, Division of Chemistry and Physics, National Environmental Research Center, Environmental Protection Agency, Research Triangle Park, N.C. Contract CPA 70-40, September 1971.

2. Mandel, John, The Statistical Analysis of Experimental Data, John Wiley and Sons, Inc. New York, Chapter 9, pp 213-18 (1964).

3. Youden, W.J., Statistical Techniques for Collaborative Tests, A.O.A.C. Publication 1969.

APPENDIX A

Reference Method for the Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method)

APPENDIX A.—REFERENCE METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE (PARAROSANILINE METHOD)

1. *Principle and Applicability.* 1.1 Sulfur dioxide is absorbed from air in a solution of potassium tetrachloromercurate (TCM). A dichlorosulfitomercurate complex, which resists oxidation by the oxygen in the air, is formed (*1, 2*). Once formed, this complex is stable to strong oxidants (e.g., ozone, oxides of nitrogen). The complex is reacted with pararosaniline and formaldehyde to form intensely colored pararosaniline methyl sulfonic acid (*3*). The absorbance of the solution is measured spectrophotometrically.

1.2 The method is applicable to the measurement of sulfur dioxide in ambient air using sampling periods up to 24 hours.

2. *Range and Sensitivity.* 2.1 Concentrations of sulfur dioxide in the range of 25 to 1,050 $\mu g/m.^3$ (0.01 to 0.40 p.p.m.) can be measured under the conditions given. One can measure concentrations below 25 $\mu g./m.^3$ by sampling larger volumes of air, but only if the absorption efficiency of the particular system is first determined. Higher concentrations can be analyzed by using smaller gas samples, a larger collection volume, or a suitable aliquot of the collected sample. Beer's Law is followed through the working range from 0.03 to 1.0 absorbance units (0.8 to 27 $\mu g.$ of sulfite ion in 25 ml. final solution computed as SO_2).

2.2 The lower limit of detection of sulfur dioxide in 10 ml. TCM is 0.75 $\mu g.$, (based on twice the standard deviation) representing a concentration of 25 $\mu g./m^3$ SO_2 (0.01 p.p.m.) in an air sample of 30 liters.

3. *Interferences.* 3.1 The effects of the principal known interferences have been minimized or eliminated. Interferences by oxides of nitrogen are eliminated by sulfamic acid (*4, 5*), ozone by time-delay (*6*), and heavy metals by EDTA (ethylenediaminetetraacetic acid, disodium salt) and phosphoric acid (*4, 6,*). At least 60 $\mu g.$ Fe (III), 10 $\mu g.$ Mn(II), and 10 $\mu g.$ Cr(III) in 10 ml. absorbing reagent can be tolerated in the procedure. No significant interference was found with 10 $\mu g.$ CU (II) and 22 $\mu g.$ V(V).

4. *Precision, Accuracy, and Stability.* 4.1 Relative standard deviation at the 95 percent confidence level is 4.6 percent for the analytical procedure using standard samples. (*5*)

4.2 After sample collection the solutions are relatively stable. At 22° C. losses of sulfur dioxide occur at the rate of 1 percent per day. When samples are stored at 5° C. for 30 days, no detectable losses of sulfur dioxide occur. The presence of EDTA enhances the stability of SO_2 in solution, and the rate of decay is independent of the concentration of SO_2. (*7*)

5. *Apparatus.*

5.1 *Sampling.*

5.1.1 *Absorber.* Absorbers normally used in air pollution sampling are acceptable for concentrations above 25 $\mu g./m.^3$ (0.01 p.p.m.). An all-glass midget impinger, as shown in Figure A1, is recommended for 30-minute and 1-hour samples.

For 24-hour sampling, assemble an absorber from the following parts:

Polypropylene 2-port tube closures, special manufacture (available from Bel-Art Products, Pequannock, N.J.).

Glass impingers, 6 mm. tubing, 6 inches long, one end drawn to small diameter such that No 79 jewelers will pass through, but No 78 jewelers will not. (Other end fire polished.)

Polypropylene tubes, 164 by 32 mm. Nalgene or equal).

5.1.2 *Pump.* Capable of maintaining an air pressure differential greater than 0.7 atmosphere at the desired flow rate.

5.1.3 *Air Flowmeter or Critical Orifice.* A calibrated rotameter or critical orifice capable of measuring air flow within ±2 percent. For 30-minute sampling, a 22-gauge hypodermic needle 1 inch long may be used as a critical orifice to give a flow of about 1 liter/minute. For 1-hour sampling, a 23-gauge hypodermic needle five-eighths of an inch long may be used as a critical orifice to give a flow of about 0.5 liter/minute. For 24 hour sampling, a 27-gauge hypodermic needle three-eighths of an inch long may be used to give a flow of about 0.2 liter/minute. Use a membrane filter to protect the needle (Figure A1a).

6.2 *Analysis.*

5.2.1 *Spectrophotometer.* Suitable for measurement of absorbance at 548 nm. with an effective spectral band width of less than 15 nm. Reagent blank problems may occur with spectrophotometers having greater spectral band width. The wavelength calibration of the instrument should be verified. If transmittance is measured, this can be converted to absorbance:

$$A = \log_{10}(1/T)$$

6. *Reagents.*

6.1 *Sampling.*

6.1.1 *Distilled water.* Must be free from oxidants.

6.1.2 *Absorbing Reagent [0.04 M Potassium Tetrachloromercurate (TCM)].* Dissolve 10.86 g. mercuric chloride, 0.066 g. EDTA (thylenediaminetetraacetic acid, disodoum salt), and 6.0 g. potassium chloride in water and bring to mark in a 1,000-ml. volumetric flask. (Caution: highly poisonous. If spilled on skin, flush off with water immediately). The pH of this reagent should be approximately 4.0, but it has been shown that there is no appreciable difference in collection efficiency over the range of pH 5 to pH 3.(*7*) The absorbing reagent is normally stable for 6 months. If a precipitate forms, discard the reagent.

5.2 *Analysis.*

6.2.1 *Sulfamic Acid (0.6 percent).* Dissolve 0.6 g. sulfamic acid in 100 ml. distilled water. Prepare fresh daily.

6.2.2 *Formaldehyde (0.2 percent).* Dilute 5 ml. formaldehyde solution (36–38 percent) to 1,000 ml. with distilled water. Prepare daily.

6.2.3 *Stock Iodine Solution (0.1 N).* Place 12.7 g. iodine in a 250-ml. beaker; add 40 g. potassium iodide and 25 ml. water. Stir until all is dissolved, then dilute to 1,000 ml. with distilled water.

6.2.4 *Iodine Solution (0.01 N).* Prepare approximately 0.01 N iodine solution by diluting 50 ml. of stock solution to 500 ml. with distilled water.

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

6.2.6 *Stock Sodium Thiosulfate Solution (0.1 N).* Prepare a stock solution by dissolving 25 g. sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 1,000 ml. freshly boiled, cooled, distilled water and add 0.1 g. sodium carbonate to the solution. Allow the solution to stand 1 day before standardizing. To standardize, accurately weigh, to the nearest 0.1 mg., 1.5 g. primary standard potassium iodate dried at 180° C. and dilute to volume in a 500-ml. volumetric flask. To a 500-ml. iodine flask, pipet 50 ml. of iodate solution. Add 2 g. potassium iodide and 10 ml. of 1 N hydrochloric acid. Stopper the flask. After 5 minutes, titrate with stock thiosulfate solution to a pale yellow. Add 5 ml. starch indicator solution and continue the titration until the blue color disappears. Calculate the normality of the stock solution:

$$N = \frac{W}{M} \times 2.80$$

N = Normality of stock thiosulfate solution.

M = Volume of thiosulfate required, ml.

W = Weight of potassium iodate, grams.

$$2.80 = \frac{10^3 (\text{conversion of g. to mg.}) \times 0.1 \text{ (fraction iodate used)}}{35.67 \text{ (equivalent weight of potassium iodate)}}$$

6.2.7 *Sodium Thiosulfate Titrant (0.01 N).* Dilute 100 ml. of the stock thiosulfate solution to 1,000 ml. with freshly boiled distilled water.

$$\text{Normality} = \text{Normality of stock solution} \times 0.100.$$

6.2.8 *Standardize Sulfite Solution for Preparation of Working Sulfite-TCM Solution.* Dissolve 0.3 g. sodium metabisulfite ($Na_2S_2O_5$) or 0.40 g. sodium sulfite (Na_2SO_3) in 500 ml. of recently boiled, cooled, distilled water. (Sulfite solution is unstable; it is therefore important to use water of the highest purity to minimize this instability.) This solution contains the equivalent of 320 to 400 $\mu g./ml.$ of SO_2. The actual concentration of the solution is determined by adding excess iodine and back-titrating with standard sodium thiosulfate solution. To back-titrate, pipet 50 ml. of the 0.01 N iodine into each of two 500-ml. iodine flasks (A and B). To flask A (blank) add 25 ml. distilled water, and to flask B (sample) pipet 25 ml. sulfite solution. Stopper the flasks and allow to react for 5 minutes. Prepare the working sulfite-TCM Solution (6.2.9) at the same time iodine solution is added to the flasks. By means of a buret containing standardized 0.01 N thiosulfate, titrate each flask in turn to a pale yellow. Then add 5 ml. starch solution and continue the titration until the blue color disappears.

6.2.9 *Working Sulfite-TCM Solution.* Pipet accurately 2 ml. of the standard solution into a 100 ml volumetric flask and bring to mark with 0.04 M TCM. Calculate the concentration of sulfur dioxide in the working solution:

$$\mu g\ SO_2/ml. = \frac{(A - B)\ (N)\ (32{,}000)}{25} \times 0.02$$

A = Volume thiosulfate for blank, ml.

B = Volume thiosulfate for sample, ml.

N = Normality of thiosulfate titrant.

32,000 = Milliequivalent wt. of SO_2, $\mu g.$

25 = Volume standard sulfite solution, ml.

0.02 = Dilution factor.

This solution is stable for 30 days if kept at 5° C. (refrigerator). If not kept at 5° C., prepare daily.

6.2.10 *Purified Pararosaniline Stock Solution (0.2 percent nominal).*

6.2.10.1 *Dye Specifications.* The pararosaniline dye must meet the following performance specifications: (1) the dye must have a wavelength of maximum absorbance at 540 nm. when assayed in a buffered solution of 0.1 M sodium acetate-acetic acid; (2) the absorbance of the reagent blank, which is temperature-sensitive (0.015 absorbance unit/°C), should not exceed 0.170 absorbance unit at 22° C. with a 1-cm. optical path length, when the blank is prepared according to the prescribed analytical procedure and to the specified concentration of the dye; (3) the calibration curve (Section 6.2.1) should have a slope of 0.030 ± 0.002 absorbance units/$\mu g.$ SO_2 at this path length when the dye is pure and the sulfite solution is

properly standardized.

6.2.10.2 *Preparation of Stock Solution.* A specially purified (99–100 percent pure) solution of pararosaniline, which meets the above specifications, is commercially available in the required 0.20 percent concentration (Harleco*). Alternatively, the dye may be purified, a stock solution prepared and then assayed according to the procedure of Scaringelli, et al. (*4*)

6.2.11 *Pararosaniline Reagent.* To a 250-ml. volumetric flask, add 20 ml. stock pararosaniline solution. Add an additional 0.2 ml. stock solution for each percent the stock assays below 100 percent. Then add 25 ml. 3 M phosphoric acid and dilute to volume with distilled water. This reagent is stable for at least 9 months.

7. *Procedure.*

7.1 *Sampling.* Procedures are described for short-term (30 minutes and 1 hour) and for long-term (24 hours) sampling. One can select different combinations of sampling rate and time to meet special needs. Sample volumes should be adjusted, so that linearity is maintained between absorbance and concentration over the dynamic range.

7.1.1 *30-Minute and 1-Hour Samplings.* Insert a midget impinger into the sampling system, Figure A1. Add 10 ml. TCM solution to the impinger. Collect sample at 1 liter/minute for 30 minutes, or at 0.5 liter/minute for 1 hour, using either a rotameter, as shown in Figure A1, or a critical orifice, as shown in Figure A1a, to control flow. Shield the absorbing reagent from direct sunlight during and after sampling by covering the impinger with aluminum foil, to prevent deterioration. Determine the volume of air sampled by multiplying the flow rate by the time in minutes and record the atmospheric pressure and temperature. Remove and stopper the impinger. If the sample must be stored for more than a day before analysis, keep it at 5° C. in a refrigerator (see 4.2).

7.1.2 *24-Hour Sampling.* Place 50 ml. TCM solution in a large absorber and collect the sample at 0.2 liter/minute for 24 hours from midnight to midnight. Make sure no entrainment of solution results with the impinger. During collection and storage protect from direct sunlight. Determine the total air volume by multiplying the air flow rate by the time in minutes. The correction of 24-hour measurements for temperature and pressure is extremely difficult and is not ordinarily done. However, the accuracy of the measurement will be improved if meaningful corrections can be applied. If storage is necessary, refrigerate at 5° C. (see 4.2).

7.2 *Analysis.*

7.2.1 *Sample Preparation.* After collection, if a precipitate is observed in the sample, remove it by centrifugation.

7.2.1.1 *30-Minute and 1-Hour Samples.* Transfer the sample quantitatively to a 25-ml. volumetric flask; use about 5 ml. distilled water for rinsing. Delay analyses for 20 minutes to allow any ozone to decompose.

7.2.1.2 *24-Hour Sample.* Dilute the entire sample to 50 ml. with absorbing solution. Pipet 5 ml. of the sample into a 25-ml. volumetric flask for chemical analyses. Bring volume to 10 ml. with absorbing reagent. Delay analyses for 20 minutes to allow any ozone to decompose.

7.2.2 *Determination.* For each set of determinations prepare a reagent blank by adding 10 ml. unexposed TCM solution to a 25-ml. volumetric flask. Prepare a control solution by adding 2 ml. of working sulfite-TCM solution and 8 ml. TCM solution to a 25-ml. volumetric flask. To each flask containing either sample, control solution, or reagent blank, add 1 ml. 0.6 percent sulfamic acid and allow to react 10 minutes to destroy the nitrite from oxides of nitrogen. Accurately pipet in 2 ml. 0.2 percent formaldehyde solution, then 5 ml. pararosaniline solution. Start a laboratory timer that has been set for 30 minutes. Bring all flasks to volume with freshly boiled and cooled distilled water and mix thoroughly. After 30 minutes and before 60 minutes, determine the absorbances of the sample (denote as A), reagent blank (denote as A_0) and the control solution at 548 nm. using 1-cm. optical path length cells. Use distilled water, not the reagent blank, as the reference. (NOTE: This is important because of the color sensitivity of the reagent blank to temperature changes which can be induced in the cell compartment of a spectrophotometer.) Do not allow the colored solution to stand in the absorbance cells, because a film of dye may be deposited. Clean cells with alcohol after use. If the temperature of the determinations does not differ by more than 2° C. from the calibration temperature (8.2), the reagent blank should be within 0.03 absorbance unit of the y-intercept of the calibration curve (8.2). If the reagent blank differs by more than 0.03 absorbance unit from that found in the calibration curve, prepare a new curve.

7.2.3 *Absorbance Range.* If the absorbance of the sample solution ranges between 1.0 and 2.0, the sample can be diluted 1:1 with a portion of the reagent blank and read within a few minutes. Solutions with higher absorbance can be diluted up to sixfold with the reagent blank in order to obtain onscale readings within 10 percent of the true absorbance value.

8. *Calibration and Efficiencies.*

8.1 *Flowmeters and Hypodermic Needle.* Calibrate flowmeters and hypodermic needle (*8*) against a calibrated wet test meter.

8.2 *Calibration Curves.*

8.2.1 *Procedure with Sulfite Solution.* Accurately pipet graduated amounts of the working sulfite-TCM solution (6.2.9) (such as 0, 0.5, 1, 2, 3, and 4 ml.) into a series of 25-ml. volumetric flasks. Add sufficient TCM solution to each flask to bring the volume to approximately 10 ml. Then add the remaining reagents as described in 7.2.2. For maximum precision use a constant-temperature bath. The temperature of calibration must be maintained within ±1° C. and in the range of 20° to 30° C. The temperature of calibration and the temperature of analysis must be within 2 degrees. Plot the absorbance against the total concentration in μg. SO_2 for the corresponding solution. The total μg. SO_2 in solution equals the concentration of the standard (Section 6.2.9) in μg. SO_2/ml. times the ml. sulfite solution added (μg. SO_2= μg./ml. SO_2× ml. added). A linear relationship should be obtained, and the y-intercept should be within 0.03 absorbance unit of the zero standard absorbance. For maximum precision determine the line of best fit using regression analysis by the method of least squares. Determine the slope of the line of best fit, calculate its reciprocal and denote as B_s. B_s is the calibration factor. (See Section 6.2.10.1 for specifications on the slope of the calibration curve). This calibration factor can be used for calculating results provided there are no radical changes in temperature or pH. At least one control sample containing a known concentration of SO_2 for each series of determinations, is recommended to insure the reliability of this factor.

8.2.2 *Procedure with SO_2 Permeation Tubes.*

8.2.2.1 *General Considerations.* Atmospheres containing accurately known amounts of sulfur dioxide at levels of interest can be prepared using permeation tubes. In the systems for generating these atmospheres, the permeation tube emits SO_2 gas at a known, low, constant rate, provided the temperature of the tube is held constant (±0.1° C.) and provided the tube has been accurately calibrated at the temperature of use. The SO_2 gas permeating from the tube is carried by a low flow of inert gas to a mixing chamber where it is accurately diluted with SO_2-free air to the level of interest and the sample taken. These systems are shown schematically in Figures A2 and A3 and have been described in detail by O'Keeffe and Ortman (*9*), Scaringelli, Frey, and Saltzman (*10*), and Scaringelli, O'Keeffe, Rosenberg, and Bell (*11*).

8.2.2.2 *Preparation of Standard Atmospheres.* Permeation tubes may be prepared or purchased. Scaringelli, O'Keeffe, Rosenberg, and Bell (*11*) give detailed, explicit directions for permeation tube calibration. Tubes with a certified permeation rate are available from the National Bureau of Standards. Tube permeation rates from 0.2 to 0.4 μg./minute inert gas flows of about 50 ml./minute and dilution air flow rates from 1.1 to 15 liters/minutes conveniently give standard atmospheres containing desired levels of SO_2 (25 to 390 μg./m.³; 0.01 to 0.15 p.p.m. SO_2). The concentration of SO_2 in any standard atmosphere can be calculated as follows:

$$C = \frac{P \times 10^3}{R_d + R_i}$$

Where:

C = Concentration of SO_2, μg./m.³ at reference conditions.
P = Tube permeation rate, μg./minute.
R_d = Flow rate of dilution air, liter/minute at reference conditions.
R_i = Flow rate of inert gas, liter/minute at reference conditions.

8.2.2.3 *Sampling and Preparation of Calibration Curve.* Prepare a series (usually six) of standard atmospheres containing SO_2 levels from 25 to 390 μg. SO_2/m.³. Sample each atmosphere using similar apparatus and taking exactly the same air volume as will be done in atmospheric sampling. Determine absorbances as directed in 7.2. Plot the concentration of SO_2 in μg./m.³ (x-axis) against $A - A_0$ values (y-axis), draw the straight line of best fit and determine the slope. Alternatively, regression analysis by the method of least squares may be used to calculate the slope. Calculate the reciprocal of the slope and denote as B_c.

8.3 *Sampling Efficiency.* Collection efficiency is above 98 percent; efficiency may fall off, however, at concentrations below 25 μg./m.³. (*12, 13*)

9. *Calculations.*

9.1 *Conversion of Volume.* Convert the volume of air sampled to the volume at reference conditions of 25° C. and 760 mm. Hg. (On 24-hour samples, this may not be possible.)

$$V_R = V \times \frac{P}{760} \times \frac{298}{t + 273}$$

V_R = Volume of air at 25° C. and 760 mm. Hg, liters.
V = Volume of air sampled, liters.
P = Barometric pressure, mm. Hg.
t = Temperature of air sample, °C.

9.2 *Sulfur Dioxide Concentration.*

9.2.1 When sulfite solutions are used to prepare calibration curves, compute the concentration of sulfur dioxide in the sample:

$$\mu g.\ SO_2/m.^3 = \frac{(A - A_0)\ (10^3)\ (B_s)}{V_R} \times D$$

A = Sample absorbance.
A_0 = Reagent blank absorbance.
10^3 = Conversion of liters to cubic meters.
V_R = The sample corrected to 25° C. and 760 mm. Hg, liters.

*Hartmen-Leddon, 60th and Woodland Avenue, Philadelphia, PA 19143.

B_s = Calibration factor, μg./absorbance unit.

D = Dilution factor.

For 30-minute and 1-hour samples, D=1.

For 24-hour samples, D=10.

9.2.2 When SO_2 gas standard atmospheres are used to prepare calibration curves, compute the sulfur dioxide in the sample by the following formula:

$$SO_2, \mu g./m.^3 = (A - A_o) \times B_s$$

A = Sample absorbance.

A_o = Reagent blank absorbance.

B_s = (See 8.2.2.3).

9.2.3 *Conversion of μg./m.³ to p.p.m.* = If desired, the concentration of sulfur dioxide may be calculated as p.p.m. SO_2 at reference conditions as follows:

$$\text{p.p.m. } SO_2 = \mu g.\ SO_2/m.^3 \times 3.82 \times 10^{-4}$$

10. *References.*

(1) West, P. W., and Gaeke, G. C., "Fixation of Sulfur Dioxide as Sulfitomercurate III and Subsequent Colorimetric Determination", *Anal. Chem. 28*, 1816 (1956).

(2) Ephraims, F., "Inorganic Chemistry," p. 562, Edited by P.C.L. Thorne and E. R. Roberts, 5th Edition, Interscience. (1948).

(3) Lyles, G. R., Dowling, F. B., and Blanchard, V. J., "Quantitative Determination of Formaldehyde in Parts Per Hundred Million Concentration Level", *J. Air Poll. Cont. Assoc. 15*, 106 (1965).

(4) Scaringelli, F. P., Saltzman, B. E., and Frey, S. A., "Spectrophotometric Determination of Atmospheric Sulfur Dioxide", *Anal. Chem. 39*, 1709 (1967).

(5) Pate, J. B., Ammons, B. E., Swanson, G. A., Lodge, J. P., Jr., "Nitrite Interference in Spectrophotometric Determination of Atmospheric Sulfur Dioxide", *Anal. Chem. 37*, 942 (1965).

(6) Zurlo, N. and Griffini, A. M., "Measurement of the SO_2 Content of Air in the Presence of Oxides of Nitrogen and Heavy Metals", *Med. Lavoro, 53*, 330 (1962).

(7) Scaringelli, F. P., Elfers, L., Norris, D., and Hochheiser, S., "Enhanced Stability of Sulfur Dioxide in Solution", *Anal. Chem. 42*, 1818 (1970).

(8) Lodge, J. P. Jr., Pate, J. B., Ammons, B. E. and Swanson, G. A., "Use of Hypodermic Needles as Critical Orifices in Air Sampling," *J. Air Poll. Cont. Assoc. 16*, 197 (1966).

(9) O'Keeffe, A. E., and Ortman, G. C., "Primary Standards for Trace Gas Analysis", *Anal. Chem. 38*, 760 (1966).

(10) Scaringelli, F. P., Frey, S. A., and Saltzman, B. E., "Evaluation of Teflon Permeation Tubes for Use with Sulfur Dioxide", *Amer. Ind. Hygiene Assoc. J. 28*, 260 (1967).

(11) Scaringelli, F. P., O'Keeffe, A. E., Rosenberg, E., and Bell, J. P., "Preparation of Known Concentrations of Gases and Vapors with Permeation Devices Calibrated Gravimetrically", *Anal. Chem. 42*, 871 (1970).

(12) Urone, P., Evans, J. B., and Noyes, C. M., "Tracer Techniques in Sulfur Dioxide Colorimetric and Conductiometric Methods", *Anal Chem. 37*, 1104 (1965).

(13) Bostrom, C. E., "The Absorption of Sulfur Dioxide at Low Concentrations (p.p.m.) Studied by an Isotopic Tracer Method", *Intern. J. Air Water Poll. 9*, 33 (1965).

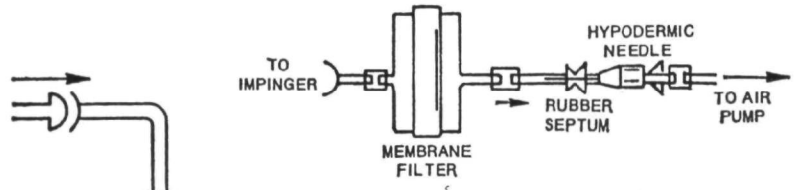


Figure A1a. Critical orifice flow control.

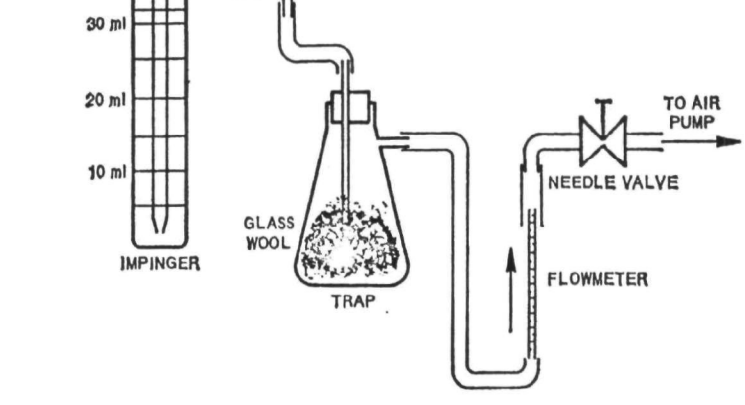


Figure A1. Sampling train.

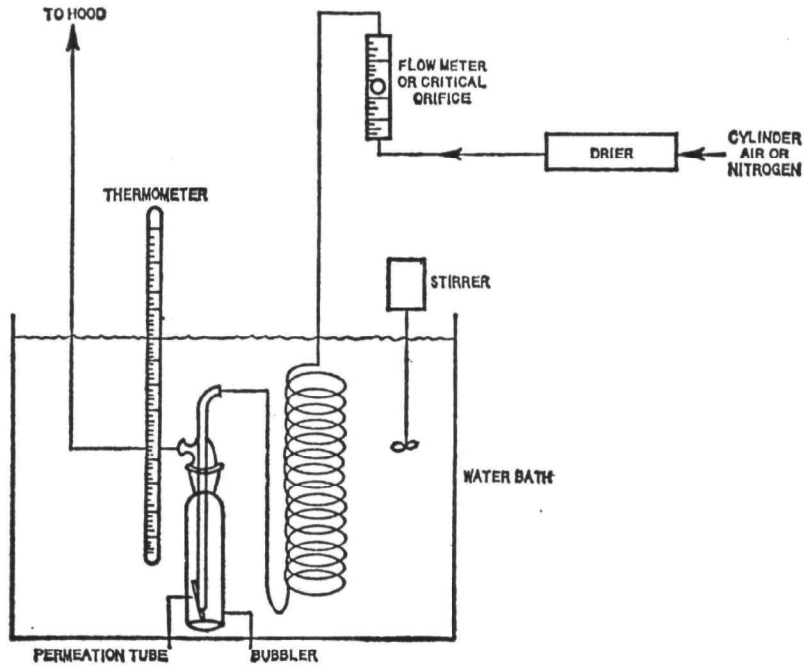


Figure A2. Apparatus for gravimetric calibration and field use.

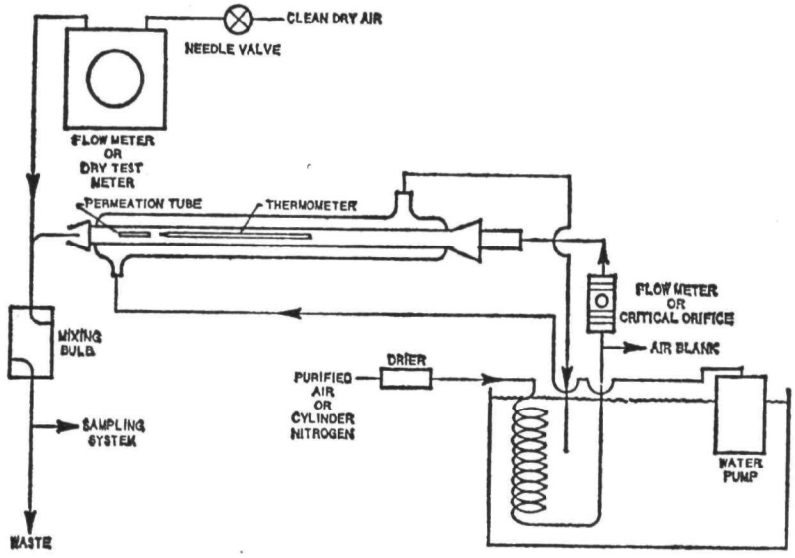


Figure A3. Permeation tube schematic for laboratory use.

APPENDIX B

Statistical Design and Analysis

APPENDIX B

Table of Contents

		Page
I.	Introduction	
	A. Purpose and Scope of the Experiment	B-1
	B. Design of the Experiment	B-2
II.	Preliminary Data Analysis	B-7
	A. Presentation of Data	B-7
	B. Tests for Outlying Observations	B-9
	C. Discussion of Results of Preliminary Data Analyses	B-11
III.	Analysis of Variance	B-13
	A. Analysis of Variance of Concentrations Separately	B-13
	B. Analysis of Variance for All Concentrations Analyzed Together	B-18
	C. Linear Model Analysis	B-21
IV.	Application of the Results	B-30
	A. Correction of Laboratory Bias	B-30
	B. Precision of Method	B-34
	C. Accuracy and Bias	B-38
List of References		B-42

APPENDIX B - STATISTICAL DESIGN AND ANALYSIS

I. INTRODUCTION

The present study of the pararosaniline method of measuring sulfur dioxide in the atmosphere is supplemental to and in support of an earlier similar study[1]. Primarily, the two studies differ only by the fact that the present study used a sampling time period of 24 hours, while the earlier study investigated the method using 30-minute sampling periods. For the present study, no familiarization session was conducted since three of the four collaborating laboratories had participated in the earlier study and were, therefore, completely familiar with the method. Southwest Research Institute acted as the fourth laboratory and was, of course, familiar with the method by way of having experimented with the method while organizing both collaborative studies.

A. Purpose and Scope of the Experiment

The purpose of the present study was twofold; (1) to determine the reliability of the method using sampling periods of 24 hours, and (2) to compare these measures with corresponding results for the 30-minute sampling study. In order to facilitate comparisons between the two studies, it was desirable to duplicate the analysis wherever the experimental design, the format of the data, and other considerations permitted.

The experimental collaborative study should be designed so that a straightforward analysis of variance can be conducted on the resulting data. This type of analysis gains the greatest amount of information that can be obtained from a given amount of data. Resources are thus optimized by requiring fewer collaborators, samples and replicate observations. Such an approach requires careful selection of laboratories, randomization of sample testing, and somewhat confines the analysis of outlying observations.

Although it was desired that a minimum of six laboratories participate in the study, the services of only four laboratories could be secured because of the large manhour requirement to run the tests. Since these laboratories had provided reliable results in previous studies, there was no reason to expect an unusually large scatter in the observations they would make for the present study.

Each laboratory was required to analyze three separate concentrations. Because individual equipment for generating the sample atmospheres was supplied to each laboratory, the concentrations could not be identical for all laboratories. However, calibration points at which the generating equipment was to be operated were specified so that the expected concentrations would be very similar for all laboratories. The expected mean concentrations were nominally 98, 291 and 475$\mu g/m^3$.

B. Design of the Experiment

The experimental design of this study was structured so that analysis of variance techniques could be employed. Three such techniques

were employed in the present study:

(1) A four-factor analysis of variance with data in the original scale for each concentration separately.

(2) A five-factor analysis of variance with data in a transformed scale with all concentrations analyzed together.

(3) A linear model analysis with data in the transformed scale.

The experimental design is illustrated in Figure B-1. Each factor was present in the following quantity; laboratories (four), runs (two), concentrations (three), samples (three), and analyses (three). This design results in a total of 216 individual observations. Comparing the design of the 24-hour study with that of the 30-minute study, the following analogies between factors should be noted:

Prior 30-minute Study	Current 24-hour Study
laboratories (14)	laboratories (4)
days (3)	runs (2)
concentrations (3)	concentrations (3)
replications (3)	samples (3)
	analyses (3)

The analytical design of this experiment considers the four laboratories and the three concentrations to be fixed factors, each randomly selected from a very large population, and crossed with respect to one another. The run, sample and analysis are random factors each nested within laboratories.

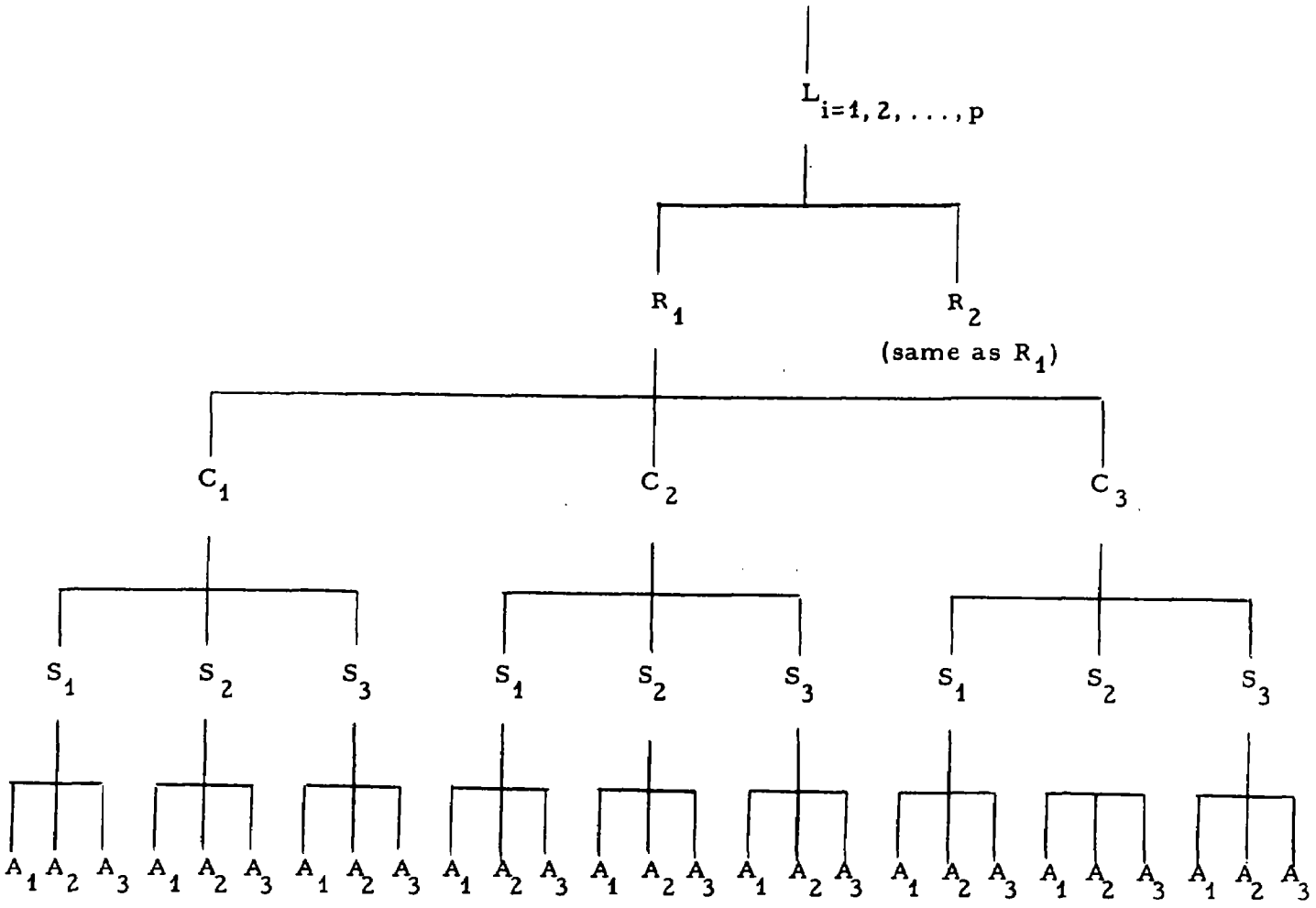


FIGURE B-1. DESIGN OF COLLABORATIVE EXPERIMENT. L, LABORATORIES; R, RUNS; C, CONCENTRATIONS; S, SAMPLES; A, ANALYSES.

Three general sources of variability were analyzed in the present study. Because of the 24-hour sampling requirement, only one concentration could be tested per day. The most fundamental measurement of the method was therefore due to variations among observations recorded by a laboratory during a single day. This variation is referred to as the replication error. The second level of variability is that which occurs within the observations recorded by a single laboratory on successive days of testing. This measurement is a combination of day-to-day variability and the previously defined replication error and, for this study, shall be termed the repeatability. The third measure is called reproducibility, and in addition to replication error and repeatability, it includes the component which describes laboratory-to-laboratory variability.

All three measures were developed by each of the analysis techniques. Taken together they describe the source and magnitude of measurement errors that are inherent within the method. With one exception, the definitions of these measures are consistent with those used in the 30-minute study so that comparisons between these studies are valid. The exception is that repeatability and reproducibility as defined in the 30-minute study have been multiplied by the factor 2.77 in the present study so as to conform with Mandel's[6] definition.

In addition to the analysis of the observations of the sample concentrations, a large volume of supplemental data was also analyzed.

These data pertain to calibration procedures required by the method and include the individual points for each calibration curve, the concentration and absorbance of all control samples, and the absorbances of all blanks.

II. PRELIMINARY DATA ANALYSIS

Each of the collaborating laboratories was able to conduct the entire series of measurements called for by the experimental design with only limited equipment difficulties. These equipment malfunctions will be dealt with in more detail in the section which discusses the handling of outlying observations.

The data provided by the collaborators were checked for internal consistency. No obvious deviations from the prescribed method were noted. The calculations which the collaborators were required to conduct were checked for arithmetic errors and none were identified beyond the acceptable disagreements due to rounding.

A. Presentation of Data

The observed values recorded during the tests by each of the collaborating laboratories are documented in Table B-1. The expected concentration values based on the calibrated performance of the SO_2 generating equipment are given in Table C-1. The observed values, Table B-1, were adjusted to compensate for the difference in the expected concentrations for the four laboratories. The adjusted values are found in Table C-3.

It was not appropriate to conduct an analysis of variance on the original observations, since the SO_2 levels for each of the three concentration ranges were not identical among laboratories. It was possible, however, to analyze the differences between the observed and expected values for each concentration, since the expected values for the four laboratories for each concentration range were quite similar to one another. These difference values are recorded in Table C-2 with

Laboratory	Run #1 Analysis 1	Run #1 Analysis 2	Run #1 Analysis 3	Run #2 Analysis 1	Run #2 Analysis 2	Run #2 Analysis 3
LOW CONCENTRATION SO_2						
#799 Sample #1	90	85	85	85	87	82
Sample #2	92	96	96	111	102	102
Sample #3	83	83	88	96	94	98
#927 Sample #1	101.9	101.9	101.9	96.9	96.9	96.9
Sample #2	103.5	103.5	103.5	99.2	96.0	99.2
Sample #3	104.2	107.3	104.2	99.2	102.2	102.2
#345 Sample #1	81	81	84	85	84	87
Sample #2	84	82	84	88	90	89
Sample #3	86	84	88	98	97	97
#920 Sample #1	95.2	97.2	93.0	90.2	93.4	89.3
Sample #2	96.7	99.4	95.2	93.3	98.7	93.3
Sample #3	91.9	99.8	97.2	92.4	97.9	93.8
MEDIUM CONCENTRATION SO_2						
#799 Sample #1	304*	304*	313*	265	265	256
Sample #2	308*	321*	321*	264	256	264
Sample #3	294*	308*	304*	244	234	244
#927 Sample #1	270.4	270.4	270.4	271.3	271.3	268.1
Sample #2	269.3	269.3	269.3	279.7	279.7	279.7
Sample #3	264.0	264.0	264.0	280.2	280.2	280.2
#345 Sample #1	241	240	240	228	231	228
Sample #2	243	243	243	234	234	238
Sample #3	247	246	249	239	237	243
#920 Sample #1	205*	208*	207*	149*	154*	149*
Sample #2	270	277	270	254	261	254
Sample #3	271	282	275	252	257	252
HIGH CONCENTRATION SO_2						
#799 Sample #1	389	389	389	424	420	429
Sample #2	404	404	404	417	426	426
Sample #3	392	382	421	412	412	403
#927 Sample #1	406.3	409.6	409.6	426.4	426.4	429.6
Sample #2	407.4	407.4	407.4	425.6	425.6	422.4
Sample #3	410.9	410.9	407.8	425.0	425.0	425.0
#345 Sample #1	383	382	388	382	377	383
Sample #2	390	390	385	387	393	391
Sample #3	397	393	384	385	387	388
#920 Sample #1	405	416	405	222*	227*	220*
Sample #2	417	424	417	383	386	379
Sample #3	410	422	418	378	383	375

* Outlying Observations

Table B-1. Observed Values by Collaborating Laboratories, Micrograms per Cubic Meter

observations that ultimately proved to be outliers marked with asterisks. Table C-3 contains the adjusted values of Table B-1. Finally, Table B-2 gives the values of Table C-3 in a transformed scale with appropriate substitutions made for the outlying observations as explained in the following section.

The transformation of the values of Table C-3 was necessary because of lack of homogeneity of variances between concentrations. It was not worthwhile to perform the analysis of variance on all concentrations together until the requirement of homogeneity between concentrations was established. The details of this transformation are discussed in the section dealing with the analysis of all concentrations together. The analysis of variance for all concentrations together was performed on the data in Table B-2 and appears in Table B-5.

B. Tests for Outlying Observations

Outlier tests were conducted on the data in Table C-2 after a preliminary review revealed several suspicious observations. Tests for outliers were conducted among laboratory means, among day means within laboratories, among sample means, and among analyses. The tests employed were those developed by Dixon[2] and David[3].

Nine observations recorded by laboratory No. 920 and nine additional observations reported by laboratory No. 799 proved to be outliers according to these criteria. These outlying observations are noted by asterisks in Tables B-1 and C-2. The values recorded by these laboratories on these days were significantly different from the values recorded by the other participating laboratories at these concentration levels.

It was possible to associate the outlying observations for laboratory No. 920 with equipment malfunctions. This collaborator reported that unusual flow rates prompted an investigation which revealed a leak in the absorber of one of the samples at the cap and tube junction. This leak was repaired at this time, and subsequent observations did not prove to be outliers.

In the case of laboratory No. 799, poor agreement was noted between the added control solution and the measured quantity. This would indicate a calibration problem, and the mean of this set of observations made on this day proved to be an outlier above other means at this concentration level.

The complete elimination of these outlying observations was rejected, since one of two undesirable circumstances would have resulted; either an unequal number of values would remain for each laboratory, or a large amount of otherwise useful data would have to be discarded. The inclusions of the outliers in the analysis as they were reported would have the undesirable effect of incorrectly influencing the ultimate measures of accuracy. It was therefore decided that substitutions for these outlying values would be the best solution to the problem in this case.

The pattern of the outliers reported by laboratory No. 920 was on the basis of analyses conducted on a single sample during each of three days. The remaining six observations on these days provide accurate measures of the concentration that was tested. The mean and variance

were calculated for each of the days on the basis of these six valid observations. Randomized substitutions were then made for the outlying values which would result in the same mean and variance when all nine values (i.e., the six valid observations plus the three substitute values) were analyzed together. In this way, the substitute values neither contribute nor delete information for the testing during that day.

In the case of laboratory No. 799, all nine values reported for the first day of measuring the medium concentration were outliers. Thus, the only remaining valid observations by this collaborator for this concentration are those made during the second run. The logical substitution in this case was to duplicate those values observed during the second day of testing the medium concentration. This substitution would have a minimal effect on the analyses and sample variance components for laboratory No. 799.

C. Discussion of Results of Preliminary Data Analyses

As noted previously, a preliminary examination was made of all data submitted by the collaborating laboratories. Each calculation made by the participants was checked for consistency with the instructions given to the collaborators as well as with the requirements of the test method. No errors were found beyond very insignificant rounding differences.

In the case of handling outlying observations, the methods employed were those considered to have the least influence on the final results of the analysis without undue elaboration or expenditure of effort.

Such compromises in data analysis are always dependent upon the judgment of the analyst. In the present study, it was possible to establish a reasonable physical cause for each outlying observation so that the outlier test result only confirms and does not dictate the problem data points.

III. ANALYSIS OF VARIANCE

Three distinct analyses were conducted on the data submitted by the collaborators after they had been corrected to eliminate the effects of outlying observations. An initial analysis of variance was conducted (Table B-3) on the adjusted data in the original scale (Table C-3) for each concentration level. A second analysis of variance was performed which treated all concentrations together (Table B-5) with the data in a transformed scale (Table B-2). The final linear model analysis (Table B-8) was conducted primarily to confirm the results of the first two analyses. A discussion follows which treats each analysis separately with a final section in which the techniques are compared and the results are summarized.

A. Analysis of Variance of Concentrations Separately

A separate analysis of variance was performed on the data for each of the three individual concentrations as though there were three distinct collaborative studies being analyzed. In this analysis, the variance components of four factors were compared among the three concentrations. The mathematical treatment of the data for this analysis was performed by a flexible computer program [4]. The inputs to this program could be formatted according to the design of the desired mathematical model of the experiment. For this analysis, the mathematical model was:

$$y_{ikms} = M + L_i + R_{k(i)} + S_{m\,[\bar{k}(i)]} + e_{s\left\{m\,[\bar{k}(i)]\right\}} \qquad \text{(B-1)}$$

LOW CONCENTRATION SO_2

Laboratory	Run #1 Analysis 1	Run #1 Analysis 2	Run #1 Analysis 3	Run #2 Analysis 1	Run #2 Analysis 2	Run #2 Analysis 3
799 Sample #1	83.0	74.2	74.2	74.2	78.0	67.7
Sample #2	86.7	94.0	94.0	120.3	104.6	104.6
Sample #3	70.3	70.3	79.3	94.0	90.4	97.6
#927 Sample #1	106.9	106.9	106.9	97.6	97.6	97.6
Sample #2	110.3	110.3	110.3	101.1	96.4	101.1
Sample #3	110.3	114.8	110.3	101.1	106.9	106.9
#345 Sample #1	70.3	70.3	75.5	78.0	75.5	81.8
Sample #2	75.5	71.6	75.5	83.0	86.7	85.5
Sample #3	79.3	75.5	83.0	101.1	99.9	99.9
#920 Sample #1	103.4	106.9	99.9	94.0	99.9	92.8
Sample #2	106.9	110.3	103.4	99.9	110.3	99.9
Sample #3	97.6	111.4	106.9	97.6	108.0	101.1

MEDIUM CONCENTRATION SO_2

#799 Sample #1	295.1	295.1	286.7	295.1	295.1	286.7
Sample #2	276.0	266.3	276.0	294.5	287.3	294.5
Sample #3	294.5	294.5	287.3	276.0	266.3	276.0
#927 Sample #1	305.6	305.6	305.6	306.8	306.8	303.9
Sample #2	305.1	305.1	305.1	314.1	314.1	314.1
Sample #3	300.4	300.4	300.4	314.1	314.1	314.1
#345 Sample #1	282.3	281.7	281.7	270.2	272.8	270.2
Sample #2	284.2	284.2	284.2	276.0	276.0	279.8
Sample #3	287.9	287.3	289.7	280.5	278.6	284.2
#920 Sample #1	315.2	325.0	320.2	300.4	303.9	307.3
Sample #2	316.9	322.4	316.9	303.3	309.1	303.3
Sample #3	317.5	326.7	320.8	301.6	305.6	301.6

HIGH CONCENTRATION SO_2

#799 Sample #1	394.9	394.9	394.9	416.0	413.7	419.1
Sample #2	404.0	404.0	404.0	410.9	417.2	417.2
Sample #3	396.6	390.2	414.4	408.9	408.9	403.6
#927 Sample #1	400.3	402.8	402.8	412.5	412.5	414.8
Sample #2	401.1	401.1	401.1	412.5	412.5	410.1
Sample #3	403.6	403.6	401.5	412.1	412.1	412.1
#345 Sample #1	388.9	388.5	392.3	388.5	385.0	388.9
Sample #2	393.6	393.6	390.2	391.5	395.3	394.0
Sample #3	397.8	395.3	389.8	390.2	391.5	392.3
#920 Sample #1	412.5	419.1	412.5	394.8	401.1	397.8
Sample #2	419.5	423.7	419.5	399.1	401.1	396.6
Sample #3	415.6	422.6	420.3	396.1	399.1	394.0

Table B-2. Transformed Values, Micrograms Per Cubic Meter

where

$i = 1, 2, 3 \ldots p$ designates a laboratory

$k = 1, 2, 3 \ldots w$ designates a run

$m = 1, 2, 3 \ldots n$ designates a sample

$s = 1, 2, 3 \ldots t$ designates an individual analysis

The term y_{ikms} represents the individual observations recorded by the collaborating laboratories, M represents the overall average, L_i represents the effect of the ith laboratory, $R_{k(i)}$ represents the effect of the kth run nested in the ith laboratory, $S_{m\left[k(i)\right]}$ is the effect of sample m nested in the kth run, and $e_{s\left\{m\left[k(i)\right]\right\}}$ represents the random deviation associated with an individual measurement.

For this study, there were $p = 4$ laboratories, $w = 2$ runs, $n = 3$ samples, and $t = 3$ analyses.

The analysis of variance technique was applied to the data in Table C-3. The results of this analysis are shown in Table B-3. The degrees of freedom and mean squares of Table B-3 have been suitably adjusted in consideration of the substitutions made for outlying observations. While all of the effects shown in B-3 are significant at the 95 percent level of confidence for at least one concentration, only the sample effect is significant at all three concentrations.

The variance components for each of the experimental factors were calculated and appear in Table B-4. The 95 percent confidence intervals were calculated using a method described by Dixon and Massey[2].

TABLE B-3. ANALYSES OF VARIANCE OF INDIVIDUAL CONCENTRATIONS UNTRANSFORMED DATA

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Expected Mean Square
		Low Concentration		
L	2231.93	3	743.98	$\sigma_A^2 + 3\sigma_S^2 + 9\sigma_R^2 + 18\sigma_L^2$
R(L)	544.61	4	136.15	$\sigma_A^2 + 3\sigma_S^2 + 9\sigma_R^2$
S(LR)	1123.78	16	70.24	$\sigma_A^2 + 3\sigma_S^2$
A(LRS)	260.67	48	5.43	σ_A^2
		Medium Concentration		
L	16709.15	3	5569.72	Same
R(L)	2363.61	3	787.87	as
S(LR)	2305.78	14	164.70	Low
A(LRS)	354.00	38	9.32	Concentration
		High Concentration		
L	8752.71	3	2917.57	Same
R(L)	8686.17	4	2171.54	as
S(LR)	1229.33	15	81.96	Low
A(LRS)	1422.67	46	30.93	Concentration

TABLE B-4. COMPONENTS OF VARIANCE FOR THE INDIVIDUAL CONCENTRATIONS UNTRANSFORMED DATA

Source of Variation	Component	Percent of Total	Degrees of Freedom	Standard Deviation	95% Confidence Interval
		Low Concentration			
L	33.77	49.57	3	5.81	3.29 to 21.66
R (L)	7.32	10.75	4	2.71	1.62 to 7.78
S (LR)	21.60	31.71	16	4.65	3.46 to 7.07
A (LRS)	5.43	7.97	48	2.33	1.95 to 2.90
Repeat.	34.36			5.86	
Reprod.	68.12			8.25	
		Medium Concentration			
L	265.66	67.08	3	16.30	9.23 to 60.74
R (L)	69.24	17.48	3	8.32	4.71 to 31.01
S (LR)	51.79	13.08	14	7.20	5.26 to 11.35
A (LRS)	9.32	2.35	38	3.05	2.51 to 3.91
Repeat.	130.35			11.42	
Reprod.	396.01			19.90	
		High Concentration			
L	41.45	12.89	3	6.44	3.65 to 23.99
R (L)	232.18	72.20	4	15.24	9.12 to 43.80
S (LR)	17.01	5.29	15	4.12	3.05 to 6.38
A (LRS)	30.93	9.62	46	5.56	4.62 to 7.01
Repeat.	280.12			16.74	
Reprod.	321.57			17.93	

Note: To be consistent with repeatability and reproducibility as defined by Mandel[6], the above standard deviations were multiplied by the factor $1.96\sqrt{2}$ resulting in the values which are plotted in Figure B-2

The results of this analysis were somewhat inconclusive in their inconsistency among concentrations. For example, the run (or day) effect for the low and medium concentrations contributed only minimally to the total variability. However, for the high concentration, the run effect proved to be the dominant component. The variance component due to sample effects is very nearly the same for all concentrations, whereas the component due to analysis variability is obviously concentration dependent. Since the replication error does vary with concentration level, a data transformation is necessary before the data for all concentrations can be analyzed simultaneously. The transformation will be discussed in detail in the following section.

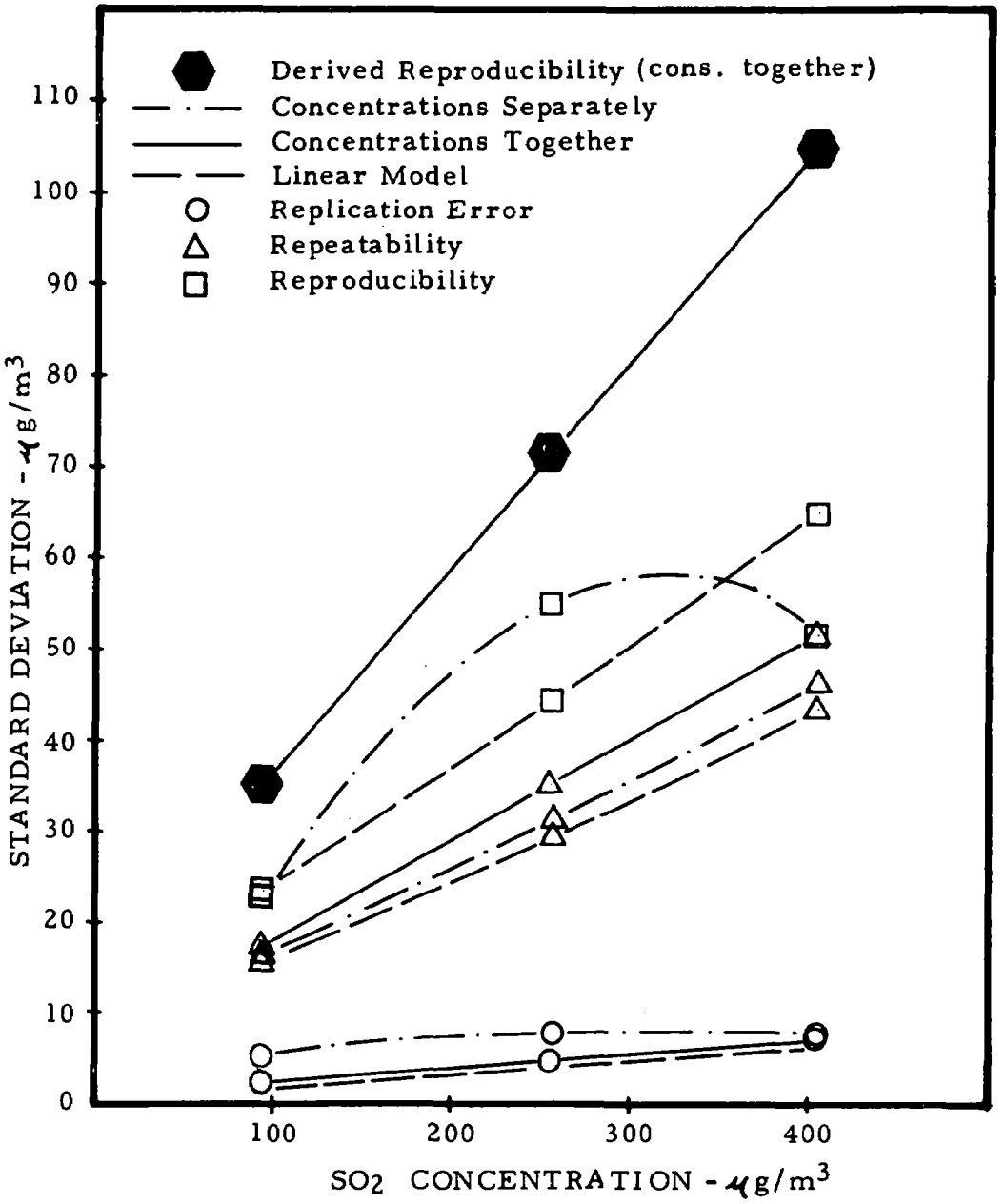
In addition to the variance components, Table B-4 contains the standard deviations for repeatability and reproducibility for the method as it applies to the individual concentrations. These measures multiplied by the factor 2.77 are displayed graphically in Figure B-2.

B. Analysis of Variance for All Concentrations Analyzed Together

In order to analyze the data for all three concentrations simultaneously, it is necessary that the variances at the different concentration levels be equal. The necessary homogeneity of variances can be accomplished by performing a transformation of the data using a technique described by Mandel[5][6].

The purpose of the data transformation is to force the standard deviation among replicates to be constant with respect to concentration.

FIGURE B-2. THE REPRODUCIBILITY, REPEATABILITY, AND REPLICATION ERROR STANDARD DEVIATIONS OBTAINED BY THREE DISTINCT ANALYSES



The line which describes the replication standard deviation versus concentration relationship is defined in terms of its slope and intercept as

$$\text{Standard Deviation} = 1.0 + 0.015 \times \text{Concentration}$$

The constants for this linear transformation were established by linear regression applied to the standard deviation of the adjusted original observations at each concentration level. Each observation is transformed by the following expression:

$$z = K \log_e (X_o + By) - G \qquad \text{(B-2)}$$

where z is the transformed variable, K and G locate the transformed range of the observations, $X_o = 1.0$ and $B = 0.015$, being the intercept and slope, respectively. K and G were chosen so that the range of the original observations would be maintained under the transformation. Their respective values become $K = 288.4$ and $G = 159.7$. This transformation was applied to the adjusted original data, Table C-3, followed by tests for homogeneity of variances and tests for outlying observations[2][3]. In addition, another analysis of variance was conducted on the transformed data for each of the three concentrations. This analysis confirmed the fact that the replication variance for the transformed data was now independent of concentration.

At this point, an analysis of variance was conducted on the transformed data for all concentrations simultaneously. The mathematical model for this analysis was:

$$Y_{ijkms} = M + L_i + C_j + R_{k(i)} + (LC)_{ij} + S_{m[k(i)]} + (CR)_{k(i)j} +$$

$$e_s\{m[k(i)]\} + (CS)_{m[k(i)]} + (CA)_s\{m[k(i)]\}\ j \qquad \text{(B-3)}$$

where $j = 1,2,3...q$ designates a concentration, and all other subscripts remain as previously defined. The term C_j represents the main effect of the SO_2 concentrations, $(LC)_{ij}$ represents the laboratory-concentration interaction, $(CR)_{k(i)j}$ represents the concentration-run interaction, $(CS)_{m[k(i)]}$ represents the concentration-sample interaction, and $(CA)_s\{m[k(i)]\}\ j$ represents the concentration analysis interaction. For this analysis, the factor quantities were $p = 4$ laboratories, $q = 3$ concentrations, $w = 2$ runs, $n = 3$ samples, and $t = 3$ analyses. The results of this analysis are tabulated in Table B-5, and the individual variance components are listed in Table B-6. The degrees of freedom and mean squares for this analysis have been adjusted to correct for the substitutions that were made for outlying observations. All the effects except the LC interaction are significant at the 0.05 level of significance. The results in Table B-6 are presented in the transformed scale which can easily be decoded back to the original scale by the linear approximation [5]:

$$\sigma y = \frac{X_o + By}{KB}\,\sigma z \qquad = (.2312 + .0035\ y)\,\sigma z$$

The values for replication error, repeatability [6] and reproducibility [6] which resulted from this analysis are presented graphically in the original scale in Figure B-2.

C. Linear Model Analysis

A number of unique assumptions are made with respect to observations recorded during an interlaboratory collaborative study when

TABLE B-5. ANALYSIS OF VARIANCE FOR ALL CONCENTRATIONS TOGETHER. DATA IN TRANSFORMED SCALE

Five Factors: L, Laboratories; C, Concentrations; R, Runs; S, Samples; and A, Analyses.

Source of Variations	Sum of Squares	Degrees of Freedom	Mean Square	Expected Mean Square
L	20219.18	3	6739.73	$3\sigma_A^2 + 9\sigma_S^2 + 27\sigma_R^2 + 54\sigma_L^2$
C	143637.76	2	81818.88	$\sigma_{CA}^2 + 3\sigma_{CS}^2 + 9\sigma_{CR}^2 + 72\sigma_C^2$
R (L)	3651.76	4	912.94	$3\sigma_A^2 + 9\sigma_S^2 + 27\sigma_R^2$
LC	3742.84	6	623.81	$\sigma_{CA}^2 + 3\sigma_{CS}^2 + 9\sigma_{CR}^2 + 18\sigma_{LC}^2$
S (LR)	2073.38	16	129.59	$3\sigma_A^2 + 9\sigma_S^2$
CR (L)	2800.56	7	400.08	$\sigma_{CA}^2 + 3\sigma_{CS}^2 + 9\sigma_{CR}^2$
A (LRS)	832.36	44	18.92	$3\sigma_A^2$
CS (LR)	3961.96	32	123.81	$\sigma_{CA}^2 + 3\sigma_{CS}^2$
CA (LRS)	1031.34	96	10.74	σ_{CA}^2

TABLE B-6. COMPONENTS OF VARIANCE FOR ALL CONCENTRATIONS TOGETHER. DATA IN TRANSFORMED SCALE.

Source of Variation	Component	Percent of Total	Degrees of Freedom	Standard Deviation	95% CI
L	107.90	7.83	3	10.39	5.88 to 38.71
C	1130.82	82.07	2	33.63	17.51 to 212.68
R (L)	29.01	2.11	4	5.39	3.22 to 15.48
LC	12.43	0.90	6	3.53	2.27 to 7.77
S (LR)	12.30	0.89	16	3.51	2.61 to 5.34
CR (L)	30.70	2.23	7	5.54	3.66 to 11.29
A (LRS)	6.31	0.46	44	2.51	2.09 to 3.17
CS (LR)	37.69	2.74	32	6.14	4.90 to 8.20
CA (LRS)	10.74	0.78	96	3.28	2.87 to 3.80
Repeatability	126.75			11.26	
Reproducibility	247.08			15.72	

Five Factors:

L - Laboratories
C - Concentrations
R - Runs
S - Samples
A - Analyses

Note: To be consistent with repeatability and reproducibility as defined by Mandel[6], the above standard deviations were multiplied by the factor $1.96\sqrt{2}$ resulting in the values which are plotted in Figure B-2.

analyzed by the linear model technique[1, 5, 6 and 9]. Basically, the linear model assumes that systematic differences exist between sets of measurements made by the same observer at different times or by different observers in different laboratories, and that these differences are linear functions of the magnitude of the measurements. The linear model allows for nonconstant, nonrandom differences between laboratories, and the method is not as sensitive to outlying observations as is the conventional analysis of variance.

The design of the experiment with respect to the 24-hour sampling SO_2 measuring method is as follows: each of p laboratories has measured each of q concentrations a total of n times. For the present case, the number of laboratories remains at 4. However, because the linear model as formulated by Mandel is limited to two factors with replicates, concentrations measured during successive runs are now considered to be individual materials. This results in q = 6 concentrations having been analyzed by each laboratory. For this analysis, the total number of replicate measurements conducted by each laboratory on each concentration is n = 9; i.e., 3 analyses recorded for each of 3 samples taken.

The linear model analysis was conducted by use of an efficient computer program written specifically for collaborative test method studies[9].

The criterion for homogeneity of data applies in the case of the linear model as it does for the more conventional analysis of variance. A preliminary investigation of these data was performed in order to determine relationships between various parameters among the collaborating laboratories. These parameters--the mean, slope and standard error of estimate--appear in Table B-7 and are graphically displayed together with 95 percent control limits in Figure B-3.

The mathematical model for the linear analysis is as follows:

$$y_{ij} = M + L_i + C_j + (LC)_{ij} \qquad \text{(B-4)}$$

where

$i = 1, 2, 3\ldots, p$ designates a laboratory

$j = 1, 2, 3\ldots, q$ designates a concentration

The term y_{ij} represents an individual measurement, M represents the overall average, L_i represents the effect of laboratory i, C_j represents the effect of concentration j, and $(LC)_{ij}$ represents the interaction effect between laboratory i and material j and includes the replication error.

The final linear model analysis is shown in Table B-8 with data in the transformed scale. The concurrence and nonconcurrence terms are shown even though it was apparent that no appreciable correlation existed between the means and slopes.

TABLE B-7. MEANS, SLOPES AND STANDARD ERRORS OF ESTIMATE FOR LINEAR MODEL ANALYSIS.DATA IN TRANSFORMED SCALE.

Laboratory Code Number	Mean	Slope	Standard Error of Estimate
799	259.5	1.0275	8.1
927	273.3	0.9792	7.3
345	251.2	1.0000	4.5
920	274.3	0.9933	10.4
Mean	264.6	1.0000	9.1*

* pooled estimate

An investigation of the correlation between the means and slopes revealed practically no correlation.

FIGURE B-3. CONTROL CHARTS FOR MEANS, SLOPES, AND STANDARD ERRORS OR ESTIMATE FOR LINEAR MODEL ANALYSIS.DATA IN TRANSFORMED SCALE.

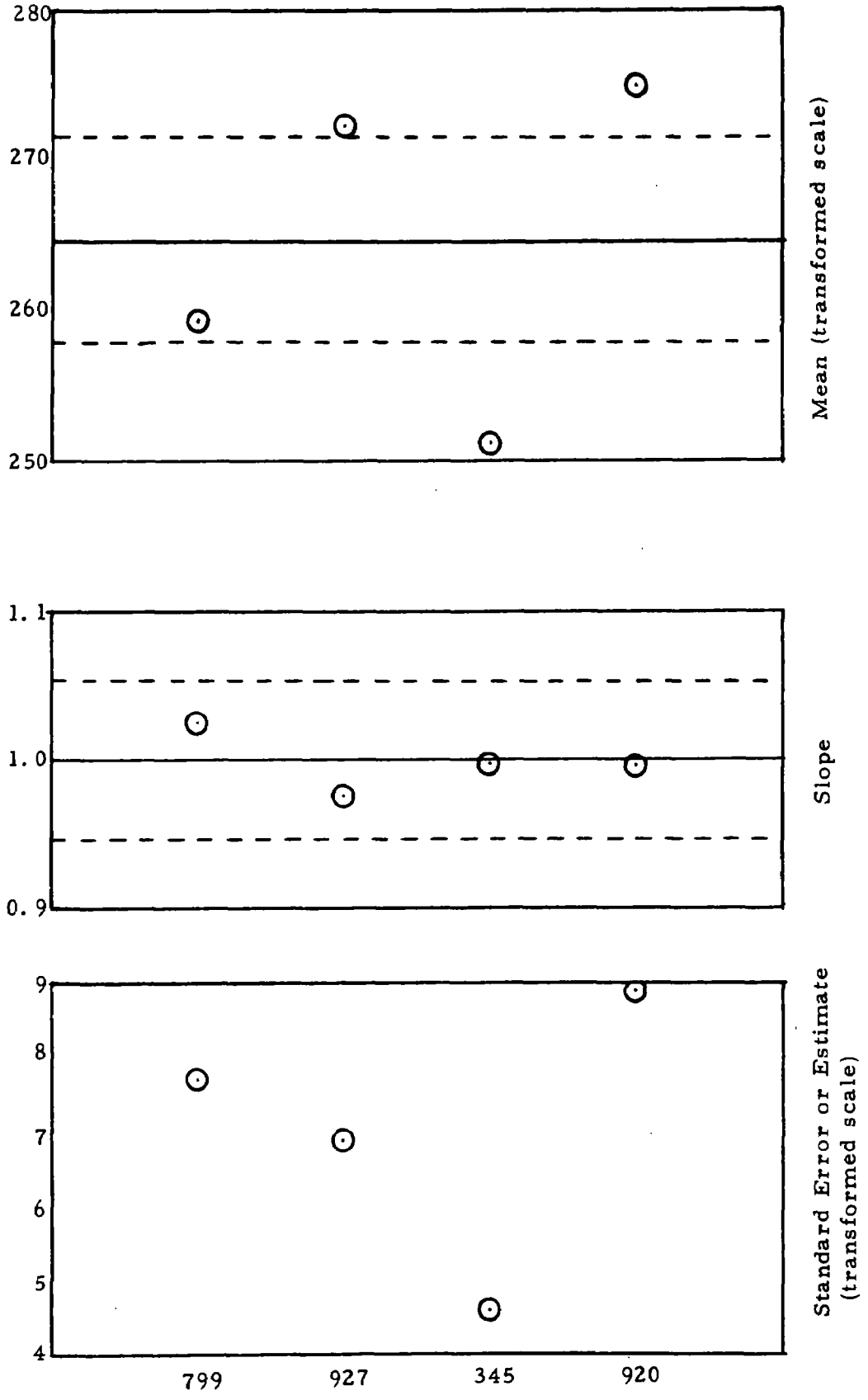


TABLE B-8. ANALYSIS OF VARIANCE FOR LINEAR MODEL.DATA IN TRANSFORMED SCALE.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square
Laboratories	2247.67	3	749.22
Concentrations	394769.41	5	78953.88
Laboratory x Concentration	1115.06	15	74.34
Linear	121.61	3	40.54
Concurrence	39.30	1	39.30
Nonconcurrence	82.31	2	41.16
Deviation from Linearity	993.45	12	82.79

The data from Table B-8 were used to compute the variance components which appear in Table B-9. In addition to the individual component variations, the repeatability and reproducibility for the method were calculated from these data and are displayed graphically in Figure B-2.

TABLE B-9. COMPONENTS OF VARIANCE FOR THE LINEAR MODEL ANALYSIS. COMPONENTS ARE EXPRESSED AS STANDARD DEVIATIONS IN THE ORIGINAL SCALE

Concentration $\mu g/m^3$	Std. Dev. ϵ	Std. Dev. λ	Std. Dev. δ	Std. Dev. μ	Std. Dev. Total
10	1.41	2.16	0	2.89	3.87
20	1.60	2.45	0	3.27	4.39
50	2.15	3.30	0	4.42	5.92
100	3.08	4.73	0	6.32	8.47
150	4.01	6.15	0	8.22	11.02
200	4.94	7.57	0	10.12	13.57
250	5.86	8.99	0	12.03	16.12
300	6.79	10.42	0	13.93	18.67
350	7.72	11.84	0	15.83	21.22
400	8.65	13.26	0	17.74	23.77
450	9.58	14.69	0	19.64	26.33
500	10.50	16.11	0	21.54	28.87

For definitions of ϵ, λ, δ and μ, the reader is referred to Mandel[10].

Note: The total standard deviation is the estimated standard deviation of reproducibility for the linear model. These estimates are to be multiplied by the factor 2.77 in order to reconcile them with the curve for reproducibility in Figure B-2.

IV. APPLICATION OF THE RESULTS

The results developed in previous sections will be applied in this section to describe the precision between replicates, the precision between days and the precision between laboratories for the 24-hour SO_2 sampling method. Only those results from the analysis of variance technique applied to the transformed data of all three concentrations simultaneously will be examined. Also, a 95 percent level of confidence will be adopted for each measure so that a direct comparison of these results can be made with the results from the 30-minute sampling study.

A. Correction of Laboratory Bias

Before applying the results from the analysis of variance technique, it will be necessary to correct for a laboratory bias which was found to exist. The general argument for the detection and isolation of this bias was presented in Part III of this report. The bias resulted from the fact that three of the four laboratories which collaborated in the 24-hour study demonstrate less laboratory-to-laboratory variability than is true for the general population of laboratories of which they are a subset. This can be demonstrated by isolating and comparing the laboratory-to-laboratory variability component which was developed by individual analyses of variance of (1) the 30-minute sampling data for all 14 collaborating laboratories, (2) the 30-minute sampling data for the 3 laboratories which were common to both studies, and (3) the 24-hour

sampling data for the four participating laboratories. The standard deviations for these individual components are displayed graphically in Figure B-4.

For discussion purposes, the causes describing these laboratory components from top to bottom in Figure B-4 have been given the following labels:

CSD_{14}	calculated standard deviation, 14 laboratories, 30-minute sampling study
ASD_4	adjusted standard deviation, 4 laboratories, 24-hour sampling study
CSD_3	calculated standard deviation, 3 laboratories, 30-minute sampling study
CSD_4	calculated standard deviation, 4 laboratories, 24-hour sampling study

The large difference between CSD_3 and CSD_{14}, both resulting from the same set of data analyzed by identical techniques, must result from the fact that this subset of three laboratories display a lab-to-lab variability component that is not typical (i. e., it is much lower) of the general population of laboratories. This laboratory bias obviously occurred also in the 24-hour sampling study as evidenced by the similarity between CSD_3 and CSD_4. This is a reasonable assumption, since three of the four laboratories that participated in the 24-hour study are responsible for the laboratory component CSD_3.

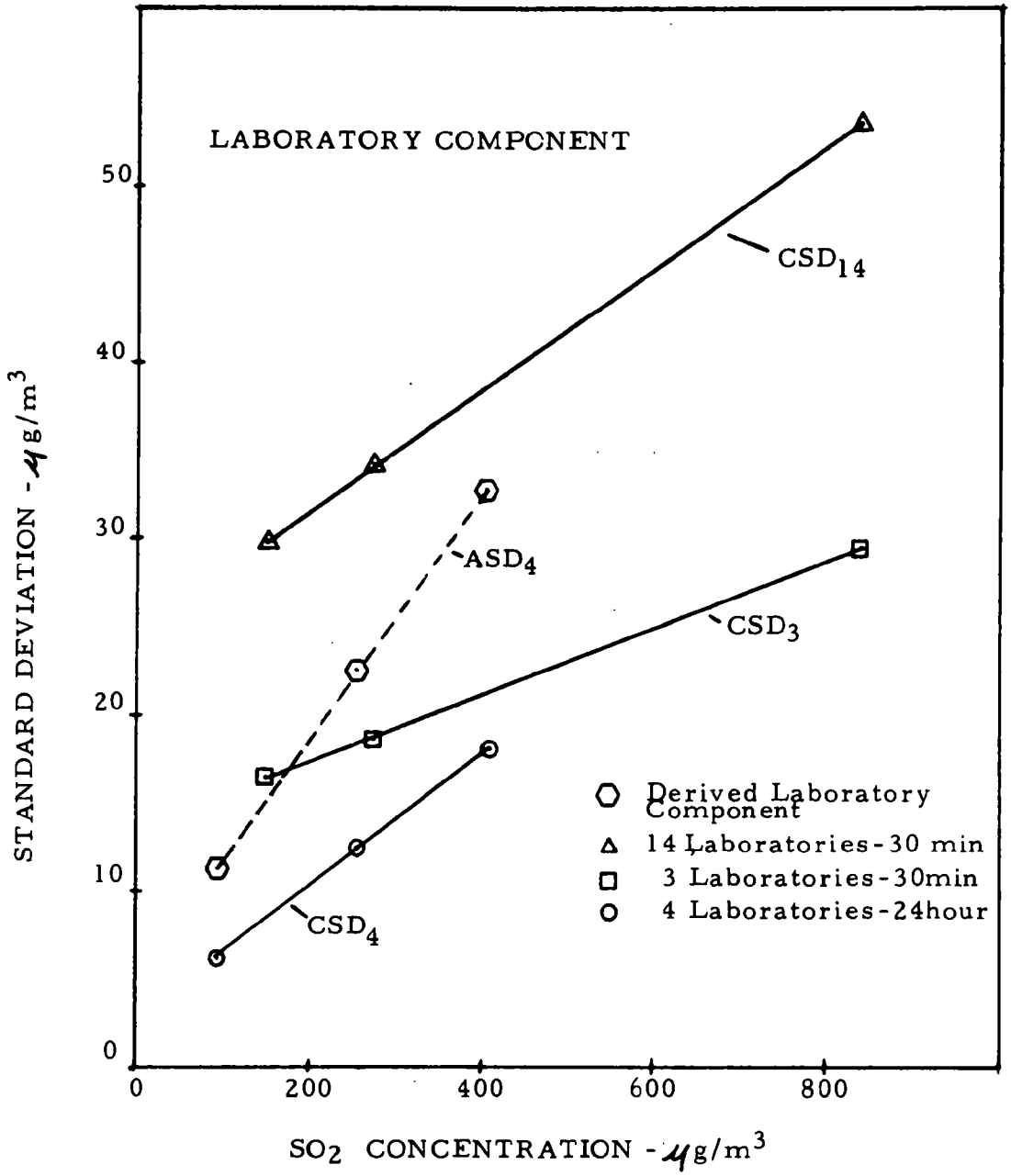
Because of this bias, it was necessary to estimate a "true" laboratory standard deviation component for the 24-hour sampling study by adjusting CSD_4. This adjusted component was derived from the ratio of components for the 30-minute study applied to the 24-hour component as follows:

$$ASD_4 = \frac{CSD_{14}}{CSD_3} \times CSD_4 \qquad \text{(B-5)}$$

The magnitude of the adjusted component was calculated by equation B-5 at various point estimates over the common concentration range from 150 $\mu g/m^3$ to 402 $\mu g/m^3$. An average adjustment of $ASD_4 = 1.82\ CSD_4$ was obtained. The adjusted laboratory component for the 24-hour study is shown by the dashed line in Figure B-4.

Since for this study, reproducibility is defined in terms of the variance components for repeatability and the laboratory-to-laboratory variability, the adjusted laboratory component will change the previously calculated value for reproducibility. The derived reproducibility is illustrated by the dashed curve in Figure B-2. This derived reproducibility curve is the sum of the derived laboratory component from Figure B-4 and the repeatability curve in Figure B-2. In all cases, the summation is carried out on variance components, although repeatability and reproducibility are defined and presented here in terms of standard deviations.

FIGURE B - 4. COMPARISON OF CALCULATED AND ADJUSTED LABARATORY COMPONENT STANDARD DEVIATIONS



B. Precision of Method

With the laboratory selection bias corrected, it is now possible to write expressions which will allow the pertinent standard deviations obtained from the analysis of variance for the three concentrations together in the transformed scale to be returned to the scale of the original data. These expressions for the replication error ($\hat{\sigma}_\epsilon$), repeatability ($\hat{\sigma}_D$) and reproducibility ($\hat{\sigma}_L$) standard deviation estimates are:

$$\hat{\sigma}_\epsilon = (.2312 + .0035y)(4.31) \qquad \text{(B-6)}$$

$$\hat{\sigma}_D = 2.77\,(.2312 + .0035y)(11.26) \qquad \text{(B-7)}$$

$$\hat{\sigma}_L = 2.77\,(.2312 + .0035y)(22.91) \qquad \text{(B-8)}$$

The replication, repeatability, and reproducibility standard deviation estimates in the transformed scale (4.31, 11.26, and 22.91, respectively) are derived from the Table B-6 component variances and standard deviations:

Replication error =

$$\sqrt{\text{Var(A)} + \text{Var(S)}} = \sqrt{6.31 + 12.30} = 4.31$$

Repeatability standard deviation =

$$\sqrt{\text{Var(CA)} + \text{Var(CS)} + \text{Var(A)} + \text{Var(CR)} + \text{Var(S)} + \text{Var(R)}} = 11.26$$

The reproducibility standard deviation estimate requires correction of the Table B-6 value to account for the adjustment in the laboratory

components dictated by the laboratory bias correction equation $ASD_4 = 1.82\,CSD_4$:

$$\text{Reproducibility std. dev.} = \sqrt{\text{Var (Repeat.)} + 1.82^2\,[\text{Var(LC)} + \text{Var(L)}]} \quad \text{(B-9)}$$

$$= \sqrt{126.75 + 3.31\quad [12.43 + 107.90\quad]} = 22.91$$

Equations (B-6), (B-7), and (B-8) allow one to express the precision of the 24-hour SO_2 sampling method for any desired case. The following examples have been chosen to coincide with those developed for the 30-minute SO_2 sampling study. The expression used to determine the range of two class means of equal sample size which would be accepted at the 95 percent confidence level as belonging to the same population is:

$$|\bar{x}_1 - \bar{x}_2|_{max} = t_{.025}(\nu)\,\sigma\sqrt{2/N} \quad \text{(B-10)}$$

where $\bar{x}_1$ is the highest mean, $\bar{x}_2$ is the lowest class mean, N represents the sample size, and σ based on ν degrees of freedom is an estimate of the standard deviation of the class means for which the range is to be determined. $t_{.025}(\nu)$ is the upper 2.5 percent point of the t distribution with ν degrees of freedom.

For the case when the two class means were derived from different sample sizes, the following expression was applied:

$$|\bar{x}_1 - \bar{x}_2|_{max} = t_{.025}(\nu)\,\sigma\sqrt{\frac{1}{N_1} + \frac{1}{N_2}} \quad \text{(B-11)}$$

Equation (B-11) reduces to equation (B-10) when $N_1 = N_2$.

The expression that was used in the earlier study to establish the maximum difference that could exist between a fixed value and an observed mean while still belonging to the same population (at the 95 percent level of confidence) was:

$$\left|\bar{x} - \mu_o\right|_{max} = 1.645\, \sigma / \sqrt{N} \qquad \text{(B-12)}$$

where $\bar{x}$ is the observed mean, μ_o is the fixed value, σ is an independent estimate of the standard deviation, and N is the size of the sample for which the mean is $\bar{x}$.

1. Precision Between Replicates

The precision with which the 24-hour method can distinguish between individual replicates is given by a combination of equations (B-6) and (B-10). Since $t_{.025}(48) = 2.01$ and $N = 1$, expression for this case becomes:

$$R_{max} = (2.84)(.2312 + .0035\,y)(4.31)$$

If two replicates differ by more than R_{max} they may be assumed with 95 percent confidence to belong to different populations.

At concentration levels below 400 $\mu g/m^3$, two replications which differ by more than 5.0 percent would be suspect, and at concentration levels below 100 $\mu g/m^3$ agreement of better than 7.1 percent should be expected between replicates of the same sample.

2. Precision Between Days

When measurements are made using the 24-hour method on different days by a single collaborator, the precision of the method is

described by a combination of equations (B-7) and (B-10). The expression for the precision between days is given by:

$$R_{max} = (3.92)(.2312 + .0035y)(11.26)$$

because $t_{.025}(4) = 2.776$ and N = 1. Two observations made on separate days by the same laboratory may not be considered to belong to the same population if they differ by R_{max}. Accordingly, we see that at concentration levels of 100 $\mu g/m^3$, R_{max} for repeatability of the method is 25.7 $\mu g/m^3$ which represents a percentage of concentration difference of 25.7 percent. At the other end of the scale, for a concentration level of 400 $\mu g/m^3$, one may accept with 95 percent confidence that two observations which differ by less than 72.0 $\mu g/m^3$ or 18.0 percent of concentration belong to the same population.

3. Precision Between Laboratories

The most important measure of the test method is that which describes the precision with which individual observations by different laboratories recorded on separate days can be distinguished. A combination of equations (B-8) and (B-10) with $t_{.025}(3) = 3.182$ and N = 1 results in the following expression by which this measure may be described.

$$R_{max} = (4.50)(.2312 + .0035y)(22.91)$$

R_{max} is again the maximum difference between two measures that can be said with 95 percent confidence to belong to the same population.

At a concentration level of 100 $\mu g/m^3$, R_{max} for reproducibility is 59.9 $\mu g/m^3$, which represents a concentration difference of 59.9 percent, while a concentration level of 400 $\mu g/m^3 R_{max}$ is 168.2 $\mu g/m^3$, which represents a concentration difference of 42 percent. Table B-10 summarizes R_{max} for the three precision measures at three concentration levels.

Equations (B-11) and (B-12) can be used to determine R_{max} between means of different sample size and between a mean and a fixed value, respectively. Equation (B-12) is also useful when it is desirable to determine the minimum number of observations required to determine agreement between an observed and a fixed mean. As an example of this application, a minimum of 9 observations would be required to determine with 95 percent confidence that the true mean for the high SO_2 concentration was less than 500 $\mu g/m^3$ when the actual value was 475 $\mu g/m^3$. This is determined when the expression is written as follows:

$$N = \left[\frac{1.645\,(.2312 + .0035\,\mu_o)\,(22.91)}{R}\right]^2$$

where R is the difference between the fixed and observed mean.

C. Accuracy and Bias

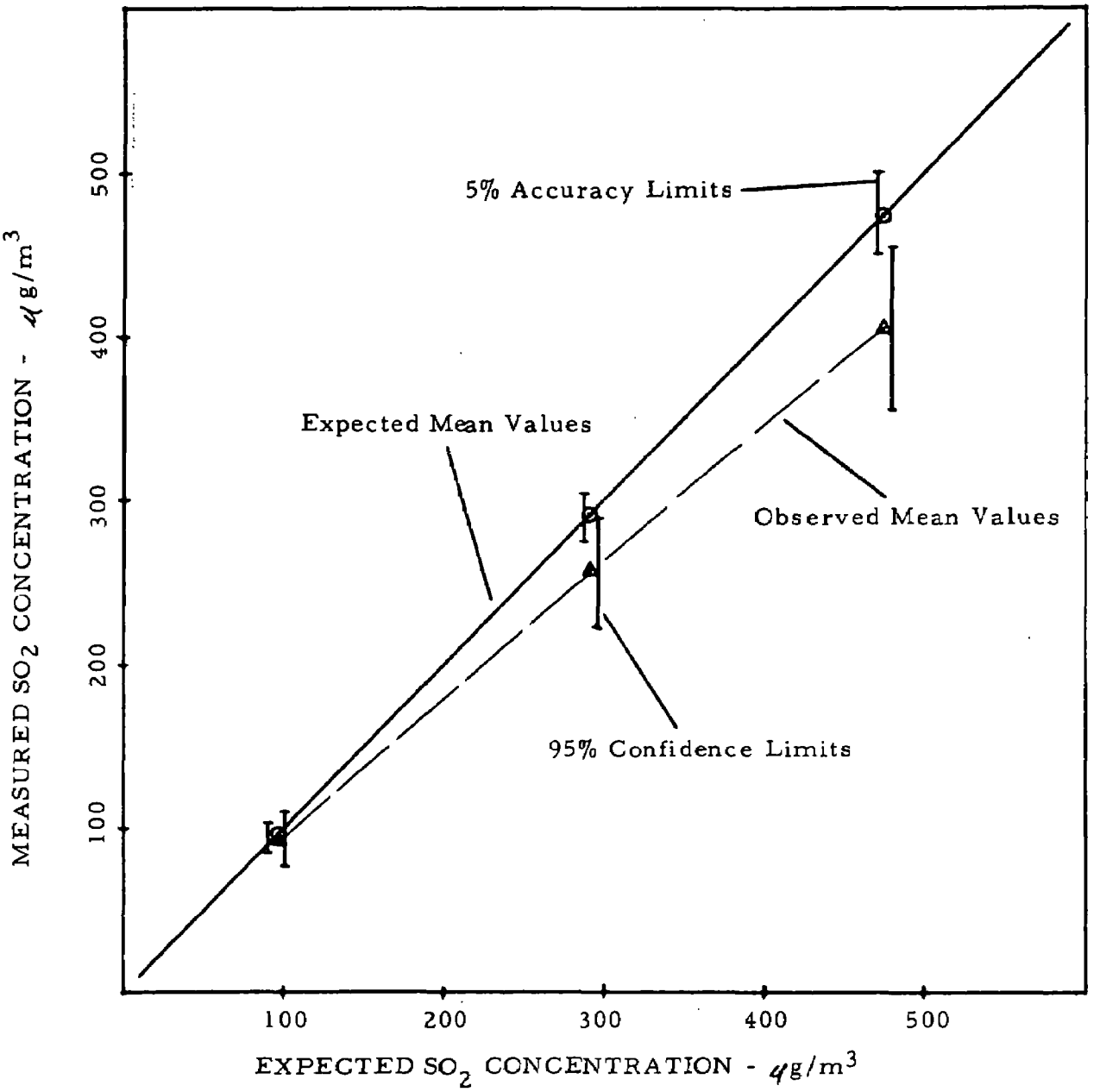
The values for the three SO_2 concentrations which were sampled in this study had expected means of 98, 291, and 475 $\mu g/m^3$. The values observed by the four participating laboratories had mean values which deviated from these expected values by -4.0, -33.1 and -72.0 $\mu g/m^3$, respectively. The resulting observed means are shown

together with their respective 95 percent confidence limits in Figure B-5. Figure B-5 also contains a plot of the expected mean values with their respective 5 percent accuracy limits representing the variability of the SO_2 generating equipment. This concentration dependent bias becomes significant at the 95 percent level of confidence for the high SO_2 concentration.

TABLE B-10. R_{max} AS A FUNCTION OF CONCENTRATION LEVEL

Concentration	Replication Error	Repeatability	Reproducibility
100 $\mu g/m^3$	7.1 $\mu g/m^3$	25.7 $\mu g/m^3$	59.9 $\mu g/m^3$
	7.1 percent	25.7 percent	59.9 percent
250 $\mu g/m^3$	13.5 $\mu g/m^3$	48.8 $\mu g/m^3$	114.0 $\mu g/m^3$
	5.4 percent	19.5 percent	45.6 percent
400 $\mu g/m^3$	20.0 $\mu g/m^3$	72.0 $\mu g/m^3$	168.1 $\mu g/m^3$
	5.0 percent	18.0 percent	42.0 percent

FIGURE B-5. THE ACCURACY OF THE 24-HOUR PARAROSANILINE METHOD



Appendix B

References

1. McKee, H. C., Childers, R. E., and Saenz, O., Jr., "Collaborative Study of Reference Method for Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method)," prepared for Office of Measurement Standardization, Division of Chemistry and Physics, National Environmental Research Center, Environmental Protection Agency, Research Triangle Park, N. C., Contract CPA 70-40, September 1971.

2. Dixon, Wilfred J., and Massey, Frank J., Jr., Introduction to Statistical Analysis, McGraw-Hill Book Company, Inc., New York, Chapter 9, p. 104 (1957).

3. 1968 Book of ASTM Standards, Part 30, Recommended Practice for Dealing with Outlying Observations, ASTM Designation: E 178-68, pp. 444-447.

4. Dixon, W. J., (ED.), BMD Biomedical Computer Programs, Second Edition, University of California Press, Berkeley and Los Angeles, pp. 586-600 (1968).

5. Mandel, J., "The Measuring Process," Technometrics, 1, pp. 251-267 (1959).

6. Mandel, J., and Lashof, P. W., "The Interlaboratory Evaluation of Testing Methods," ASTM Bulletin 239, pp. 53-61 (1959).

7. Dixon, Wilfred J., and Massey, Frank J., Jr., Introduction to Statistical Analysis, McGraw-Hill Book Company, Inc., New York, Chapter 10, pp. 179-180 (1957).

8. ASTM Manual for Conducting an Interlaboratory Study of a Test Method, ASTM SPP No. 335, American Society for Testing and Materials (1963).

9. Southwest Research Institute, Houston, Texas, Computer Program LINMOD, for Linear Model Analysis, Unpublished (1973).

10. Mandel, J., The Statistical Analysis of Experimental Data, John Wiley & Sons, New York, Chapter 13, p. 312 (1964).

APPENDIX C

Tabulation of Original Data

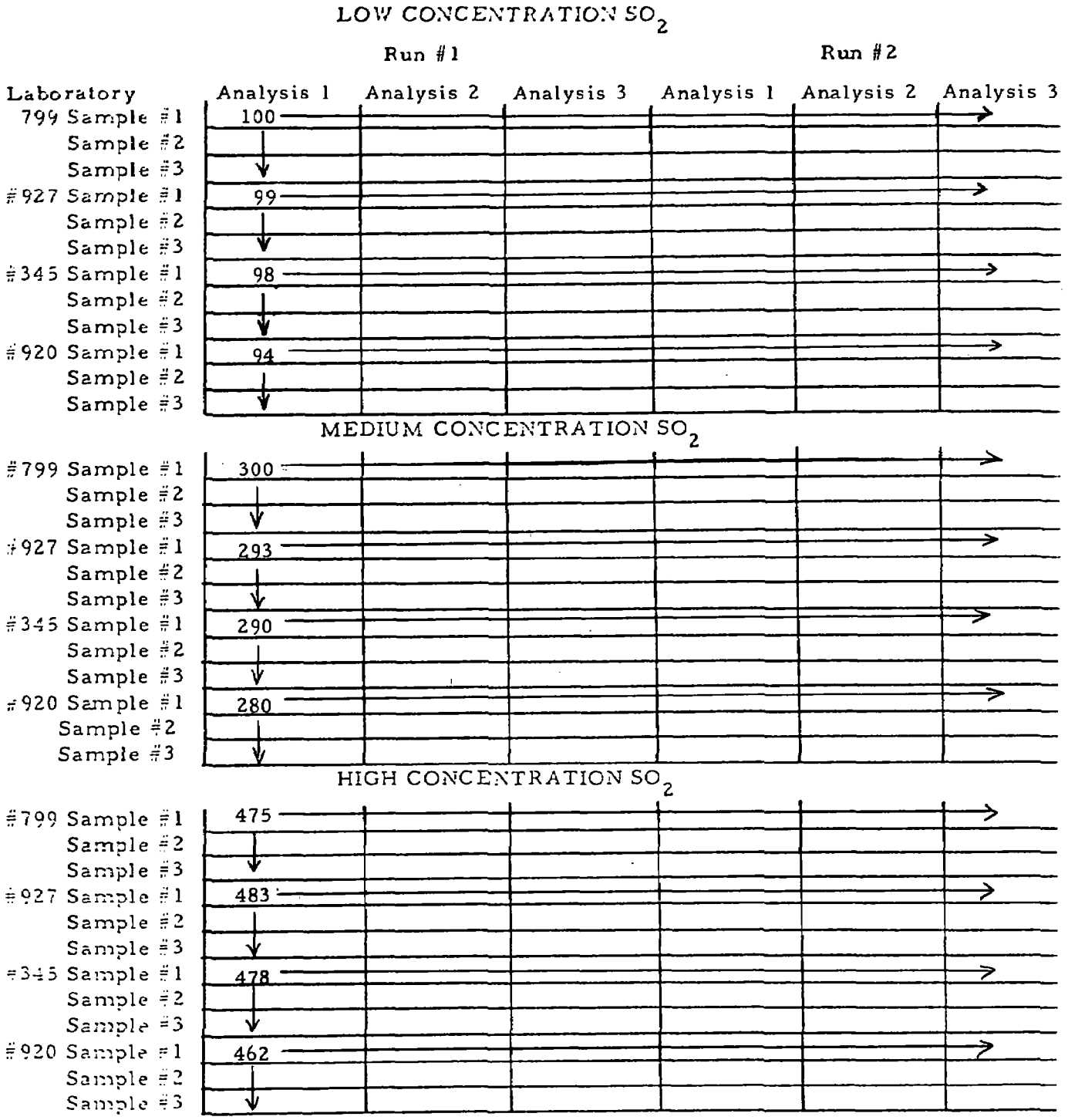


Table C-1. Expected Concentrations, Micrograms per Cubic Meter

LOW CONCENTRATION SO_2

Laboratory	Run #1 Analysis 1	Run #1 Analysis 2	Run #1 Analysis 3	Run #2 Analysis 1	Run #2 Analysis 2	Run #2 Analysis 3
799 Sample #1	- 10	- 15	- 15	- 15	- 13	- 18
Sample #2	- 8	- 4	- 4	11	2	2
Sample #3	- 17	- 17	- 12	- 4	- 6	- 2
#927 Sample #1	3	3	3	- 2	- 2	- 2
Sample #2	5	5	5	0	- 3	0
Sample #3	5	8	5	0	3	3
#345 Sample #1	- 17	- 17	- 14	- 13	- 14	- 11
Sample #2	- 14	- 16	- 14	- 10	- 8	- 9
Sample #3	- 12	- 14	- 10	0	- 1	- 1
#920 Sample #1	1	3	- 1	- 4	- 1	- 5
Sample #2	3	5	1	- 1	5	- 1
Sample #3	- 2	6	3	- 2	4	0

MEDIUM CONCENTRATION SO_2

#799 Sample #1	4 *	4 *	13 *	- 35	- 35	- 44
Sample #2	8 *	21 *	21 *	- 36	- 44	- 36
Sample #3	- 6 *	8 *	4 *	- 56	- 66	- 56
#927 Sample #1	- 23	- 23	- 23	- 22	- 22	- 25
Sample #2	- 24	- 24	- 24	- 13	- 13	- 13
Sample #3	- 29	- 29	- 29	- 13	- 13	- 13
#345 Sample #1	- 49	- 50	- 50	- 62	- 59	- 62
Sample #2	- 47	- 47	- 47	- 56	- 56	- 52
Sample #3	- 43	- 44	- 41	- 51	- 53	- 47
#920 Sample #1	- 75 *	- 72 *	- 73 *	-131 *	-126 *	-131 *
Sample #2	- 10	- 3	- 10	- 26	- 19	- 26
Sample #3	- 9	2	- 5	- 28	- 23	- 28

HIGH CONCENTRATION SO_2

#799 Sample #1	- 86	- 86	- 86	- 51	- 55	- 46
Sample #2	- 71	- 71	- 71	- 58	- 49	- 49
Sample #3	- 83	- 93	- 54	- 63	- 63	- 72
#927 Sample #1	- 77	- 73	- 73	- 57	- 57	- 53
Sample #2	- 76	- 76	- 76	- 57	- 57	- 61
Sample #3	- 72	- 72	- 75	- 58	- 58	- 58
#345 Sample #1	- 95	- 96	- 90	- 96	-101	- 95
Sample #2	- 88	- 88	- 93	- 91	- 85	- 87
Sample #3	- 81	- 85	- 94	- 93	- 91	- 90
#920 Sample #1	- 57	- 46	- 57	-240 *	-235 *	-242 *
Sample #2	- 45	- 38	- 45	- 79	- 76	- 83
Sample #3	- 52	- 40	- 44	- 84	- 79	- 87

*Outlying Observations

Table C-2. Deviations from Expected Values, Micrograms per Cubic Meter

LOW CONCENTRATION SO_2

Laboratory	Run #1 Analysis 1	Run #1 Analysis 2	Run #1 Analysis 3	Run #2 Analysis 1	Run #2 Analysis 2	Run #2 Analysis 3
799 Sample #1	88	83	83	83	85	80
Sample #2	90	94	94	109	100	100
Sample #3	81	81	86	94	92	96
#927 Sample #1	101	101	101	96	96	96
Sample #2	103	103	103	98	95	98
Sample #3	103	106	103	98	101	101
#345 Sample #1	81	81	84	85	84	87
Sample #2	84	82	84	88	90	89
Sample #3	86	84	88	98	97	97
#920 Sample #1	99	101	97	94	97	93
Sample #2	101	103	99	97	103	97
Sample #3	96	104	101	96	102	98

MEDIUM CONCENTRATION SO_2

#799 Sample #1	256	256	247	256	256	247
Sample #2	235	225	235	255	247	255
Sample #3	255	255	247	235	225	235
#927 Sample #1	268	268	268	269	269	266
Sample #2	267	267	267	278	278	278
Sample #3	262	262	262	278	278	278
#345 Sample #1	242	241	241	229	232	229
Sample #2	244	244	244	235	235	239
Sample #3	248	247	250	240	238	244
#920 Sample #1	280	290	285	262	266	270
Sample #2	281	288	281	265	272	265
Sample #3	282	293	286	263	268	263

HIGH CONCENTRATION SO_2

#799 Sample #1	389	389	389	424	420	429
Sample #2	404	404	404	417	426	426
Sample #3	392	382	421	412	412	403
#927 Sample #1	398	402	402	418	418	422
Sample #2	399	399	399	418	418	414
Sample #3	403	403	400	417	417	417
#345 Sample #1	380	379	385	379	374	380
Sample #2	387	387	382	394	390	388
Sample #3	394	390	381	382	384	385
#920 Sample #1	418	429	418	395	401	398
Sample #2	430	437	430	396	399	392
Sample #3	423	435	431	391	396	388

Table C-3. Observed Values (adjusted)

Note: The original observed values were adjusted by either adding or subtracting the amount necessary to put all observations on an equivalent basis regarding the means of the expected concentrations for low, medium and high levels.

Laboratory	Slope A/μg	Intercept A	Bs μg/A
799	0.0354	0.1945	28.2
927	0.0302	0.2229	33.1
345	0.0256	0.2109	39.1
920	0.0277	0.1770	35.7
Mean	0.02973	0.20133	34.025
Variance	0.00002	0.00040	21.116
Standard Deviation	0.00422	0.01996	4.5952
Degrees of Freedom	3	3	3
t0.95	3.182	3.182	3.182
Slope V_L	0.02973 ±	0.01343	
Intercept V_L	0.20133 ±	0.06351	
Bs V_L	34.025 ±	14.622	

Table C-4. Calibration Curve Parameters for Sulfur Dioxide 24-hour Sampling Study

Laboratory	Parameter	Units	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Mean	Std. Dev.
799	Bs	µg/A	28.2	28.2	28.2	28.2	28.2	28.2	28.2	
	Ao	A	.170	.210	.210	.160	.210	.185	.191	.032
	Yo-Ao	A	.015	−.025	−.025	.025	−0.25	.000	−.006	.001
	Δ Cont. Samp.	µg	1.79	2.74	0.69	1.59	1.95	0.02	1.46	.967
927	Bs	µg/A	33.1	33.1	33.1	33.1	33.1	33.1	33.1	
	Ao	A	.195	.190	.220	.202	.200	.208	.203	.011
	Yo-Ao	A	.020	.025	−.005	.013	.015	.007	.013	.011
	ΔCont. Samp.	µg	-0.06	-0.29	-0.03	-0.18	−0.13	0.10	−.098	.134
345	Bs	µg/A	39.1	39.1	39.1	39.1	39.1	39.1	39.1	
	Ao	A	.198	.195	.200	.213	.206	.195	.201	.007
	Yo-Ao	A	.007	.010	.005	-.008	-.001	.010	.004	.007
	ΔCont. Samp.	µg	-0.80	-0.49	-0.70	-0.45	-0.80	-0.40	-.607	.181
920	Bs	µg/A	35.7	35.7	35.7	35.7	35.7	35.7	35.7	
	Ao	A	.171	.168	.165	.165	.222	.220	.185	.028
	Yo-Ao	A	-.001	.002	.005	.005	-0.52	-.050	-.015	.028
	Δ Cont. Samp.	µg	-0.36	-0.32	-0.14	-0.54	0.36	0.58	-.070	.443

Table C-5. Calibration Data for Sulfur Dioxide 24-Hour Sampling Study

APPENDIX D

Instructions to Collaborators for Collaborative Test of Reference Method for the Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method) (24-hour sampling)

I. INTRODUCTION

A. Background

The Reference Method for the Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method) was published [1-2] by the Environmental Protection Agency as the method to be used in connection with federal ambient air quality standards for sulfur dioxide. The 30-minute sampling procedure of this method has been collaboratively tested and the resulting precision and accuracy information has been reported.[3]

B. Purpose and Scope

The purpose of this collaborative test is to broaden the previous information by testing the 24-hour sampling procedure. More specifically, the purpose is to evaluate the precision and accuracy characteristics of the method as it is published in the Federal Register. For this test, there is no interest in studying any modifications. Many similarities exist between the 24-hour procedure and the 30-minute procedure. Some of the precision parameters can be expected to be identical with those for the 30-minute procedure and need not be redetermined. The effects of four different factors will be evaluated using sulfur dioxide permeation tubes as standard reference materials. The collaborative test procedure is to be similar to that used for testing the 30-minute sampling procedure.

The estimated effort for a collaborator is 2-3 man-weeks.

---

1. Environmental Protection Agency, "National Primary and Secondary Ambient Air Quality Standards," Federal Register, Vol. 36, No.84, Part II, Appendix A, pp8187-8191, Friday, April 30, 1971.

2. Op cit, Federal Register, Vol. 36, No. 228, Appendix A, pp22385-22388, Thursday, November 25, 1971.

3. McKee et al, "Collaborative Study of Reference Method for Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method)," for Environmental Protection Agency, Contract CPA 70-40, Southwest Research Institute, September, 1971.

C. Experimental Design

The effects of laboratories, concentrations, samples, and analyses upon the precision and accuracy of the method will be determined using the experimental design shown in Figure 1.

An individual observation is denoted y_{ikjmn} which is to be interpreted as the nth analysis of the m th sample from the j th concentration during the k th run by the i th laboratory. From Figure 1, it can be seen that there are 2 runs, 3 concentrations, 3 samples, and 3 analyses. Consequently, each laboratory will generate 2 x 3 x 3 x 3 = 54 individual observations. The order in which the concentrations within a run are to be handled should be randomized and specific instructions will be issued in this regard.

To clarify certain features of the experiment design in Figure 1, the following definitions should be observed.

1. The two runs are identical (except for the randomized order of handling concentrations) and the first run should be completed before beginning the second.

2. The three concentrations (unknown to the collaborator) are the same for each run and represent the range of interest for this collaborative test. The order should be random.

3. The three samples for each concentration are to be taken simultaneously from a common manifold using similar sampling apparatus. The analysis of the three samples should be conducted simultaneously.

4. The three analyses for each sample are to be processed simultaneously. (Each analysis represents an identical aliquot from the same sample.)

Other specific instructions will be presented in the next section.

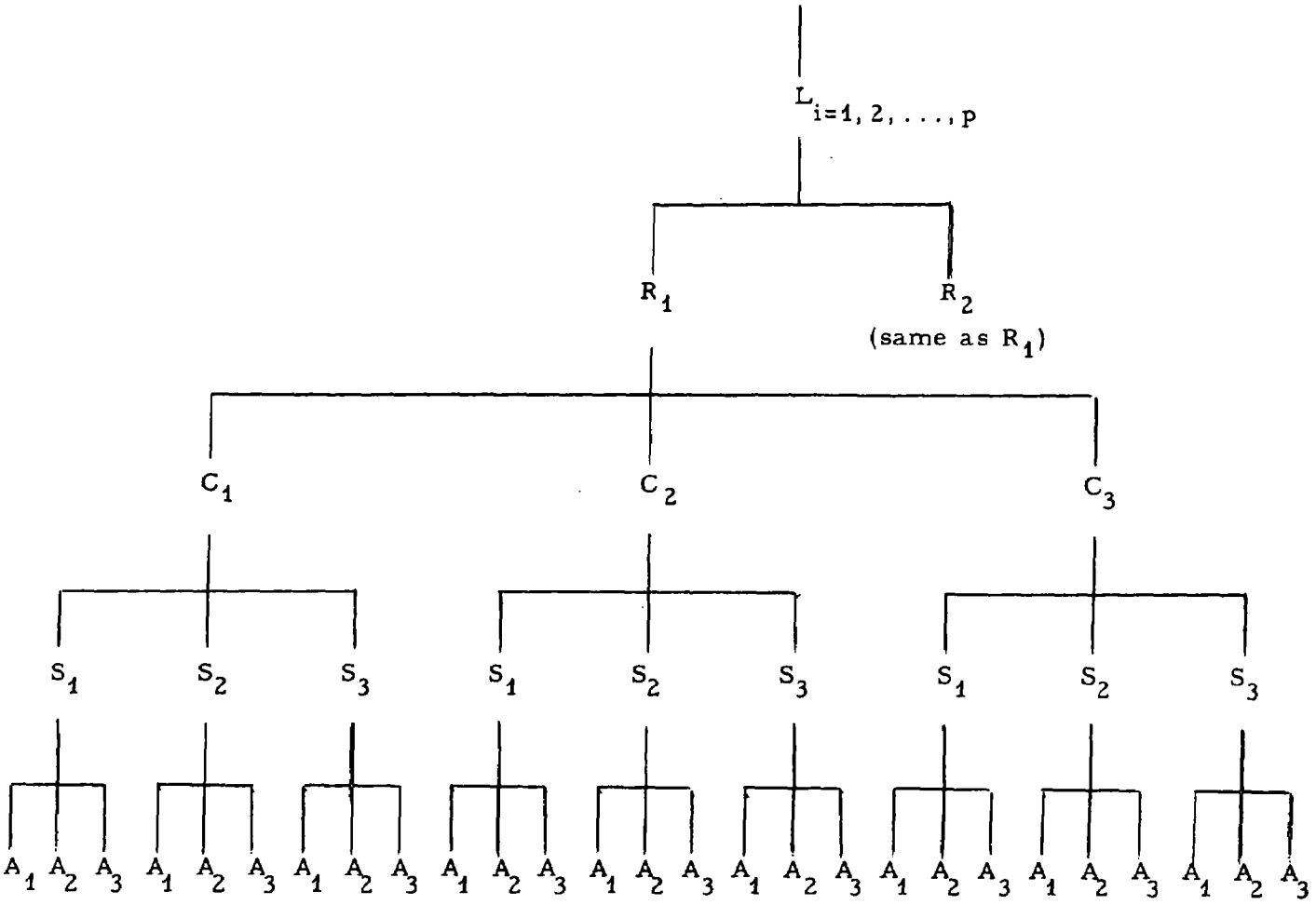


FIGURE 1. DESIGN OF COLLABORATIVE EXPERIMENT. L, LABORATORIES; R, RUNS; C, CONCENTRATIONS; S, SAMPLES; A, ANALYSES.

II. COLLABORATIVE TEST PROCEDURE

A. General Rules

1. Read the method carefully; if you have any questions, check them with Southwest Research Institute before you begin the collaborative determinations.

2. Make at least one practice run to familiarize yourself with the method so that you can avoid errors in manipulation.

3. Make the determinations as soon as possible after receiving the permeation tubes. Handle the permeation tubes according to instructions.

4. When you make the collaborative determination, follow the method exactly in every detail. Do not insert minor modifications, even though they may be in common use in your laboratory. You will destroy the value of the collaborative study if you depart from these instructions or those given in the method. If for any reason you are unable to follow all instructions to the letter, report the deviations to Southwest Research Institute.

5. Report all your results, unless you have been specifically instructed otherwise. Do not take the "best two out of three" values; do not report averages unless you were asked to do so.

6. Make only the number of determinations requested. (more or less data complicate the statistical analysis.)

7. Prepare a full report of your work on the forms provided, including all the data you obtained, and send it to Southwest Research Institute.

8. Return original data forms. Copies, no matter how legible, are not acceptable. You may make copies for your own re records.

9. You are invited to submit any comments, suggestions, criticisms, or description of difficulties that you feel are important. If you tried out a modification of the method, report your findings but keep these data separate from your collaborative report.

10. For this collaborative test, take the attitude that you, the analyst, will be asked to testify, under oath, that the results you submit are those obtained on the samples provided while following the method exactly in every detail.

B. Generation of Test Atmospheres

A special apparatus was developed[1] for generating test atmospheres using certified permeation tubes. The apparatus is described in the reference and a unit will be made available to each collaborator. The manifold of the apparatus has been modified to permit the simultaneous collection of three to six samples. A constant temperature bath with circulation pump (capable of ± 0.1°C temperature control) and a source of pure dry air are essential to complete the system. This system will be referred to as the standard system.

A certified sulfur dioxide permeation tube (permeation rate unknown to the collaborator) will be supplied to each collaborator. The system is to be operated at 25 ± 0.1°C. (Temperature variations greater than this will invalidate the results of a collaborator and jeopardize the success of the entire collaborative test.)

Keep the permeation tube in the system at 25 ± 0.1°C with both the air over the permeation tube and the dilution air flowing continuously. There will be no need to remove the tube once it has been installed in the system and equilibrium will be established at all times. Install the tube in the system as soon as possible and maintain constant temperature and air flow over the tube until the collaborative determination is complete. The air flow over the permeation tube should be maintained constant at a rate between 50 and 100 ml/minute. (A reading of 8 for the stainless steel ball in the rotameter in the standard system is recommended.) Constant dilution air flow is not required but a moderate flow is necessary at all times. (A dilution air flowmeter reading of 5 (stainless steel ball) for the standard system is suggested.) Do not make any modifications in the standard system without prior approval.

---

(1) McKee et al, "Collaborative Study of Reference Method for Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method)," for Environmental Protection Agency, Contract CPA 70-40, Southwest Research Institute, p 3-4, September, 1971.

Allow at least 48 hours after initial installation of the tube to reach equilibrium - more if the tube has been at a temperature very different from 25°C. Do not begin a collaborative determination within 24 hours following a temperature upset exceeding ± 0.5°C.

The dilution air flow rates to achieve the concentrations to be used in the test will be specifically prescribed in the following instructions.

C. Preparation of Calibration Curve

Prior to the sampling of test atmospheres, prepare a calibration curve using sulfite solution in accordance with Section 8.2.1 of the Reference Method. (A supply of pararosaniline in accordance with Section 6.2.10.2 will be provided.) Run triplicates at each of the six calibration points (0, 0.5, 1, 2, 3, and 4ml) and record each of the 18 individual observations on the data forms provided (see Form B). It is important that you prepare the calibration curve in this manner even though this may not be your usual practice. Do not run more or less calibration points or replicates. Please note that the calibration curves are to be in terms of gross rather than net absorbance.

Compute the slope and intercept of the curve (method on Form B suggested) and compare with the specifications in Sections 6.2.10.1 and 8.2.1 and recalibrate if there are gross departures from these specifications. Compute the calibration factor and retain for use in future analyses.

All collaborative determinations will be based on this calibration factor unless subsequent control samples indicate it to be unreliable. If this should occur, prepare a new calibration curve in accordance with the instructions above and notify Southwest Research Institute. Do not discard any calibration data. Report complete data on each calibration curve prepared.

D. Sampling and Analysis of Test Atmospheres

Refer to Figure 1 and the itemized instructions below for the sequence of steps in the sampling and analysis of the test atmospheres.

When you receive your data forms, they will be preassembled into what shall be referred to as packets. You will receive six packets (one for each concentration for each run) which will contain Preparation of Standard Atmospheres (Form D) and Sampling and Analysis Data (Form A). A separate form for calibration (Form B) is included but is not part of a

packet. Each packet will contain a green circled number on the upper right hand corner of Form D which indicates the chronological order in which the experiment is to be done. The order of the concentrations within a run has been randomized. Please follow this order, and do not separate the forms of a packet.

Each packet indicates the prescribed flow rate through the permeation system (on Form D in red) to achieve the desired concentration. See the next subsection of these instructions for a brief description of each data form.

Read the following instructions over carefully, and if there are any questions contact Southwest Research Institute before proceeding.

1. Be sure that the permeation system is in equilibrium and properly operating.

2. Be sure that the calibration curve is complete and that its slope and intercept meets specifications.

3. Begin a run. Make sure that all incompleted data form packets are in ascending numerical order. The lowest numbered incompleted data form packet is referred to as the next data form packet.

4. Begin processing a concentration. Consult the next data form packet and set permeation system dilution air flow to the setting shown in red on Form D of the respective data form packet. Commence monitoring the system and allow one hour for the system to stabilize.

5. Begin sampling. Prepare three absorbers according to Section 7.1.2 and connect them to the sampling manifold and sample flow rate control device (Section 5.1.3). Start sample flow and record time. Sampling from midnight to midnight as specified in Section 7.1.2 is not mandatory for this test.

6. Continue sampling. Complete 24-hour monitoring data is not required; however, the following data should be recorded as normal working hours permit. Monitor permeation system and record hourly on Form D. Monitor sample temperature (at manifold discharge) and pressure (barometric) and record hourly on the back of Form A.

7. Stop sampling. After 24 hours, stop sample flow and record time and flow rate for each sample on Form A. Disconnect absorbers and set aside for analysis.

8. If a subsequent run or concentration is to be initiated immediately, proceed simultaneously with Steps 9 and 12. Otherwise, proceed with Step 9.

9. Prepare samples for analysis. Follow instructions in Sections 7.2.1 and 7.2.1.2. Samples may be stored in accordance with Section 7.1.2; however, do not store all samples for analysis at one time. Samples are to be analyzed in batches corresponding to each concentration for each run (a data form packet). There will thus be six batches - three for each run. If samples are stored, record length of storage and temperature of storage in the bottom margin on the back of the respective Form A.

10. Begin determination. Follow the instructions of Section 7.2.2 exactly. Record data on Form A.

11. Calculate results according to Section 9 and record on Form A. It may not be possible to convert sample volume according to Section 9.1. Do so only if meaningful corrections can be applied.

12. Repeat from Step 4 if other concentrations within a run remain to be processed.

13. Repeat from Step 3 if a run remains to be made.

14. Prepare report. Your report will consist of all data forms plus any comments or criticisms you may care to make. Return original data forms in the addressed and stamped envelope provided. Because of color coding and double-sided data forms, it is imperative that original forms be returned. You may make whatever copies you wish for your own records.

15. Await acknowledgement of receipt of your results and further instructions if any are required.

You may be assured that your careful and complete execution of this test represents a significant contribution to the improvement of air quality measurement methods and to the resultant improvement in air quality. Your efforts are most appreciated. Thank you.

Following data analysis, you will receive a copy of the formal report on the collaborative testing of this method.

E. Description of Data Retrieval Forms

A series of data retrieval forms have been designed for use with the Pararosaniline Method for sulfur dioxide in the atmosphere, some of which are used in this collaborative test.

The actual information each form retrieves can be seen by inspection of the following samples; however, some additional comments on each form used are given below. In all cases, the notation and procedure is identical to and is keyed with the method published in the Federal Register.

Form A. Sampling and Analysis Data Form: This form accommodates the sampling and analysis of ambient or synthetic atmospheres with any sampling time and either sulfite or gaseous calibration. Up to twelve individual determinations can be recorded along with up to three control samples and the necessary calibration and reagent blank information. Where meaningful temperature and pressure corrections can be made, the back of the form provides for the required monitoring. Up to 24 observations on up to four samples can be recorded.

Form B. Calibration Procedure with Sulfite Solution: Space is provided for up to 18 individual sulfite standards in addition to the directions for calculating the slope by the method of least squares. A graph for plotting the curve is provided on the back of the form.

Form D. Preparation of Standard Atmospheres: The operating conditions of a permeation tube system can be recorded on this form. Up to 24 observations can be recorded.

REFERENCE METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE (PARAROSANILINE METHOD)

SAMPLING AND ANALYSIS DATA FORM

Laboratory Identification Number _____ Date _____

Name and Title of Analyst _____

Name and Address of Laboratory _____

_____

_____

_____

SAMPLE TEMPERATURE AND PRESSURE

Note: Use reverse side for monitoring if appropriate.

Temperature of air sample, t = _____ ° C. (Sec. 7.1.1)

Barometric pressure, P = _____ mm Hg (Sec. 7.1.1)

CALIBRATION

Note: Use Form B or Form C whichever is appropriate.

Calibration factor, B_s = _____ µg/absorbance unit (Sec. 8.2.1)

or B_g = _____ (µg/m³)/absorbance unit (Sec. 8.2.2.3)

REAGENT BLANK

Reagent blank absorbance, A_o = _____ absorbance units (Sec. 7.2.2)

Sample Number	SAMPLING (Secs. 7.1.1 & 9.1)				DETERMINATION (Secs. 7.2.2 & 9.2)				
	ℓ/min	min	V	V_R	A	A - A_o	D	µg	µg/m³
1									
2									
3									
Control	µg added = _____ (Sec. 7.2.2)						---		---
							---		---
							---		---

Reference: Environmental Protection Agency, "National Primary and Secondary Ambient Air Quality Standards," Federal Register, Vol 36, No. 84, Part II, Appendix A, pp 8187-8191, Friday, April 30, 1971.

SAMPLE TEMPERATURE AND BAROMETRIC PRESSURE

	Time	Sample Number _____		Sample Number _____		Sample Number _____		Sample Number _____	
		t	P	t	P	t	P	t	P
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									
22									
23									
24									
Average									

REFERENCE METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE (PARAROSANILINE METHOD)

CALIBRATION PROCEDURE WITH SULFITE SOLUTION
(Section 8.2.1)

Laboratory Identification Number _____ Date _____

Name and Title of Analyst _____

Name and Address of Laboratory _____

_____

_____

_____

Working Sulfite-TCM Solution Concentration = _____ μg/ml (Sec. 6.2.9)

	ml	X, μg	Y=A, abs.	X^2	XY
1	0				
2	0				
3	0				
4	0.5				
5	0.5				
6	0.5				
7	1				
8	1				
9	1				
10	2				
11	2				
12	2				
13	3				
14	3				
15	3				
16	4				
17	4				
18	4				
Summation		ΣX=	ΣY=	ΣX^2=	ΣXY=

Number of points, N = _____

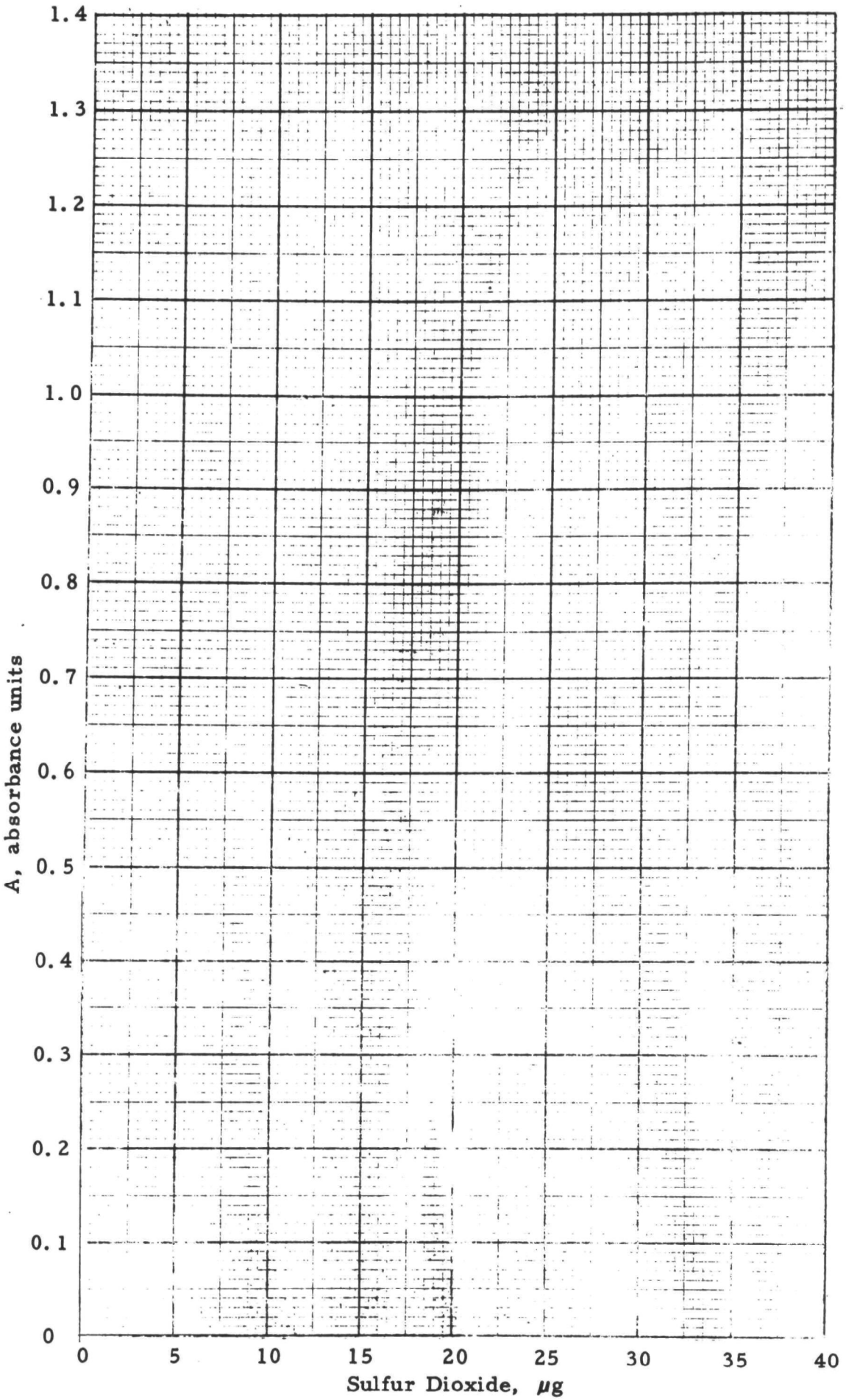
$$\text{Slope} = \frac{\Sigma XY - \frac{\Sigma X \, \Sigma Y}{N}}{\Sigma X^2 - \frac{\Sigma X \, \Sigma X}{N}} = \_\_\_\_\_ \text{ absorbance units/}\mu g$$

$$\text{Calibration Factor, } B_s = \frac{1}{\text{Slope}} = \_\_\_\_\_ \ \mu g/\text{absorbance unit}$$

Reference: Environmental Protection Agency, "National Primary and Secondary Ambient Air Quality Standards," Federal Register, Vol 36, No. 84, Part II, Appendix A, pp 8187-8191, Friday, April 30, 1971.

FORM B

CALIBRATION CURVE WITH SULFITE SOLUTION



FORM B (Back)

REFERENCE METHOD FOR THE DETERMINATION
OF SULFUR DIOXIDE IN THE ATMOSPHERE
(PARAROSANILINE METHOD)

PREPARATION OF STANDARD ATMOSPHERES
(Sections 8.2.2.1 & 8.2.2.2)

Laboratory Identification Number _____ Date _____

Name and Title of Analyst _____

Name and Address of Laboratory _____

_____

_____

_____

Permeation Tube Number _____ Permeation Rate, P = _____ μg/min

	Time	t	R_d	R_i	C
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					

Reference: Environmental Protection Agency, "National Primary and Secondary Ambient Air Quality Standards," Federal Register, Vol 36, No. 84, Part II, Appendix A, pp 8187-8191, Friday, April 30, 1971.