



R E S E A R C H T R I A N G L E I N S T I T U T E

Final Report

**AN EVALUATION OF THE HIGH-VOLUME METHOD FOR DETERMINING
SUSPENDED PARTICULATES OVER SHORT SAMPLING TIMES**

by

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ABSTRACT

Results of a field evaluation of the high volume method of measuring suspended particulates in the ambient air for 4- and 6-hour sampling periods and various combinations of equilibration parameters are reported. Under the conditions tested, a short-term sampling procedure--namely, a 4-hour sampling period and a 2-hour equilibration period at about 25°C and a relative humidity of 10 percent or less--is recommended. Results of this field evaluation indicate that the precision, expressed as a relative standard deviation, would be approximately 5.2 percent for the above short-term sampling procedure.

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EXECUTIVE SUMMARY

Background

In order to facilitate a shorter reaction time in applying control strategies during periods of air stagnation advisories, an acceptable short-term method for the determination of suspended particulates in the atmosphere is required. The objective of this study is to develop a guideline document outlining proper operating procedures for the use of a short-term method of measuring suspended particulates, following as closely as possible the Environmental Protection Agency (EPA) reference method for the determination of suspended particulates in the atmosphere.

The study was divided into three tasks as follows:

1. To estimate the precision associated with short-term (e.g., 4-hour and 6-hour) sampling periods and to determine the comparability of cumulative short-term sampling results to the 24-hour sampling period by conducting field tests in the local area using standard high-volume samplers and filters.
2. To evaluate the influence of the equilibration variables: a) relative humidity, b) temperature, and c) duration on measurement variability.
3. To specify a feasible procedure for short-term sampling based on the results of 1 and 2 above.

Test Plan

The test plan was designed and conducted in such a manner that the data could be subjected to statistical analysis allowing for the construction of confidence limits on the final results. Individual test plans were designed for the short-term sampling study and the filter equilibration study.

The short-term sampling test plan was designed to allow for estimating the precision of 4-hour, 6-hour, and 24-hour sampling periods and for comparing the average 24-hour suspended particulate concentration obtained by combining short-term samples with that resulting from one 24-hour sample. Six samplers were run concurrently with two collecting 24-hour samples, and the other four making consecutive short-term runs of 4, 4, 6, 6, and 4 hours over the same 24-hour period. The test

was replicated, resulting in a total of 44 samples, including six sets of four 4-hour samples, four sets of four 6-hour samples, and two sets of two 24-hour samples for estimating precisions. It also provided two sets of data for comparing cumulative short-term sampling period results with 24-hour sampling period results.

The equilibration study consisted of conditioning exposed filters (high-volume samples) in an environmental chamber set at 32°C and 100 percent relative humidity for a period of 24 hours. The filters were then placed in equilibration chambers with different combinations of relative humidity and temperature. Each filter was weighed after equilibration times of 1, 2, 4, and 24 hours. From these data, percent difference in the instantaneous weight and the correct weight versus equilibration time were determined for each equilibration environment. (The reference weight was taken as the weight obtained after 24 hours of equilibration in an environment of less than 50 percent relative humidity and about 25°C.)

Results

Results of this study are applicable only to the type of particulates in the local area. Particulates with different chemical and physical properties and/or atmospheres with different concentrations and combinations of gaseous pollutants may give markedly different results.

Four-hour sampling periods with 2 hours of equilibration in a controlled environment at 25°C and a relative humidity of less than 10 percent showed a precision, expressed as a relative standard deviation, of 5.2 percent. (A collaborative test of the high volume method using 24-hour sampling and equilibration periods showed a relative standard deviation of 3.0 percent).

Six-hour sampling periods with 2 hours of equilibration in a controlled environment at 25°C and a relative humidity of less than 10 percent showed a relative standard deviation of 3.5 percent.

A potential bias between short-term and 24-hour sampling was indicated by the second day's set of data showing the cumulative short-term concentrations to be an average 8.3 percent higher than that given by the 24-hour samplers. Only a 1.2 percent difference (in the same direction) was observed on the first day's set of data.

Suspended particulate concentrations calculated after a 2-hour equilibration period averaged 1.5 percent higher than when calculated after a 24-hour equilibration period.

Recommendations

The suggested short-term sampling procedure is a 4-hour sample collection period followed by a 2-hour equilibration period in a controlled environment at approximately 25°C and with a relative humidity of 10 percent or less. Test results indicate that the precision expressed as a relative standard deviation of such a short-term procedure would be about 5.2 percent. The shorter equilibration period (2 hours) results in an average positive relative bias of 1.5 percent in the measured concentrations when compared to 24-hour equilibrated samples. A detailed description of the suggested procedure is given in appendix A.

Results of this study are applicable only to the local area in which the measurements were made. Therefore, before recommending the short-term method for general use, it should be evaluated under the various extremes that will be encountered in the field. For example, atmospheres with high concentrations of particulates that plug the filter, causing a nonlinear drop in the flow rate over a 4-hour period, could result in errors in determining the average flow rate. Other errors can result due to unequal sampling rates if the particulate concentration as well as the flow rate is varying with time. Also, since the precision appears to be a function of the sampling period duration rather than the weight of collected particulates, the precision could possibly be improved using continuous flow-rate recorders so that a better estimate of the average flow rate could be obtained. This possibility could be investigated with further testing.

Further study could be undertaken to determine the reasons for differences in the concentrations determined by 24-hour sampling and those determined by consecutive short-term sampling over a 24-hour period. It appears from the results of this study that adverse weather conditions (high humidity, dense fog, air stagnation) can cause a higher daily average concentration to be measured by consecutive short-term sampling than by 24-hour sampling over the same period. However, at this point, there is no definite proof that 24-hour sampling results are

more accurate estimates of true concentrations than the consecutive short-term sampling. It is therefore recommended that further testing be done to examine the causes of differences in this type of comparison.

1.0 INTRODUCTION

In order to facilitate a shorter reaction time in applying control strategies during periods of air stagnation advisories, an acceptable short-term method for the determination of suspended particulates in the atmosphere is required. The objective of this study is to develop a guidelines document outlining proper operating procedures for the use of a short-term method of measuring suspended particulates, following as closely as possible the Environmental Protection Agency (EPA) reference method for the determination of suspended particulates in the atmosphere (ref. 1).

The study was divided into three tasks as follows:

1. Estimate the precision of short-term (e.g., 4-hour and 6-hour) sampling periods and determine the comparability of cumulative short-term sampling results to the 24-hour sampling period by conducting field tests in the local area using standard high-volume samplers and filters.
2. Evaluate the influence of the equilibration variables: a) relative humidity, b) temperature, and c) duration on measurement variability.
3. Specify a feasible procedure for short-term sampling based on the results of 1 and 2 above.

Techniques for dynamic calibration of high-volume samplers using test atmospheres containing known concentrations of particulates are not available. Therefore, there is no way of knowing the accuracy of the values derived from high-volume sampling. However, numerous experiments and studies have been performed to identify and evaluate factors that influence the final results (ref. 2) from which accuracy estimates can be deduced. This study then is designed to determine system precision for different sampling period durations and to determine the relative error, if any, in estimating a 24-hour average concentration by combining results from short-term sampling periods and comparing them with the value obtained from a 24-hour sampling period. Attached to this report as appendix A is a proposed reference method for short-term sampling and sample equilibration based on the results of this study.

Results of this study are applicable only to the type of particulates in the local area. Particulates with different chemical and physical properties and/or atmospheres with different concentrations and combinations of gaseous pollutants may give markedly different results.

2.0 TEST PLAN

The test plan was designed and conducted in such a manner that the data could be subjected to statistical analysis allowing for the construction of confidence limits on the final results. Individual test plans were designed for the short-term sampling study and the filter equilibration study.

The short-term sampling test plan was designed to allow for estimating the precision of 4-hour, 6-hour, and 24-hour sampling periods and for comparing the average 24-hour suspended particulate concentration obtained by combining short-term samples with that resulting from one 24-hour sample. Six samplers were run concurrently with two collecting 24-hour samples, and the other four making consecutive short-term runs of 4, 4, 6, 6, and 4 hours over the same 24-hour period. The test was replicated resulting in a total of 44 samples, including six sets of four 4-hour samples, four sets of four 6-hour samples, and two sets of two 24-hour samples for estimating precisions. It also provided two sets of data for comparing short-term sampling period results with 24-hour sampling period results.

The equilibration study consisted of conditioning exposed filters (high-volume samples) in an environmental chamber set at 32°C and 100 percent relative humidity for a period of 24 hours. The filters were then placed in an equilibration chamber with different combinations of relative humidity and temperature. Each filter was weighed after equilibration times of 1, 2, 4, and 24 hours. From these data, percent difference in the instantaneous weight and the correct weight versus equilibration time were determined for each equilibration environment. (The reference weight was taken as the weight obtained after 24 hours of equilibration in an environment of less than 50 percent relative humidity and about 25°C.) The curves developed from these data were validated by collecting fresh samples under various temperature and relative humidity combinations and equilibrating them as described above. A compilation of the data collected for the short-term sampling study and equilibration study is tabulated in appendix B.

2.1 Short-term Sampling Study

2.1.1 Apparatus. Apparatus used in the short-term sampling study included the following:

1. Six standard high volume samplers, each labeled and having a separate flow measuring device.
2. Standard 8 x 10 inch fiberglass filters having a collection efficiency of at least 99 percent for particles of 3 μ m diameter.
3. Orifice calibration unit with different resistance plates as shown in figure A-3 of appendix A.
4. Differential manometer capable of measuring 16 inches of water.
5. Relative humidity indicator.
6. Analytical balance capable of weighing to 0.1 mg.
7. Desiccating chamber.
8. Clean manila folders for the storage of filters.
9. Desiccant.

2.1.2 Description of Sampling Site. The sampling site was located near a heavily traveled, four-lane highway in Durham, North Carolina. In the immediate vicinity of the site was a large bus depot and some medium industry. At the site--the roof of a one-story EPA air testing station--the six samplers were placed approximately 10 feet apart in two rows of three. Weather conditions during the sampling dates varied from 20 to 100 percent RH and 7° to 30°C. The winds were variable in direction and speed, and during one short-term period a dense fog was present.

2.1.3 Procedure. The procedure followed in making high-volume measurements were essentially those recommended in the quality assurance document EPA-R4-73-028b (ref. 2). The procedure consisted of these primary operations:

1. Clean filters were inspected for pinholes, marked with an identification number, and equilibrated in an airtight desiccator chamber where a relative humidity of less than 50 percent was controlled by the presence of fresh Drierite (8 mesh). Each filter was equilibrated in this environment for a period of 24 hours, weighed to the nearest 0.1 mg, and the tare weight recorded. The equilibration temperature was 25°C \pm 2°C.

2. The samplers were calibrated in the laboratory using the orifice calibration unit and the differential manometer by the method described in subsection 8.1.1 of appendix A. Rotameters (one per sampler) were the flow-measuring devices used.

3. Filter changes for the short-term samplers were carried out as follows:

- a) Record rotameter indications for short-term samplers.
- b) Turn off short-term samplers and record the time.
- c) Remove exposed filters, fold, and place in clean manilla folders.
- d) Install new filters.
- e) Turn samplers on and record the time and relative humidity.
- f) Wait 5 minutes and record rotameter indications.

This procedure minimized the time of sampler shutdown to 15 minutes for filter changes for the short-term collecting period and allowed for samplers to be started or stopped within 1 minute of each other.

4. Exposed filters were equilibrated for 24 hours under the same conditions as described above for clean filters and then weighed to the nearest 0.1 mg.

2.1.4 Data Analysis for Short-term Sampling Periods. The data collected for this section are tabulated in tables B-1 and B-2 of appendix B, which contains a qualitative study for the data analysis performed in this section and in section 3.0.

Suspended particulate concentrations were calculated by

$$SP_M = \frac{(W_f - W_i) \times 10^6}{\frac{Q_i + Q_f}{2} \times T} \quad (1)$$

where

W_f = Weight of filter and particulates after 24 hours of equilibration, g

W_i = Tare weight of filter, g

Q_i = Flow rate at beginning of sampling period, m^3/min

Q_f = Flow rate at end of sampling period, m^3/min

T = Sampling time, min

SP_M = Measured suspended particulate concentration, $\mu g/m^3$.

Samplers designated as B, C, D, and E collected short-term samples over consecutive periods of 4, 4, 6, 6, and 4 hours, while samplers designated as A and F collected continuously over the same 24-hour period. The resulting information (presented in table B-1 of appendix B) was analyzed to a) estimate the precision of the weighted average concentrations based on suspended

particulate concentrations determined from 4-hour and 6-hour sampling periods, and b) compare the daily average concentration determined by consecutive short sampling periods to the concentration determined by the 24-hour sampling period.

The precision of the suspended particulate concentration measurements for the short-term sampling periods was determined by calculating the average concentration (\overline{SP}_j), the standard deviation (s_j), and the coefficient of variation (\widehat{CV}_j) for each time period according to equations (2), (3), and (4), respectively.

$$\overline{SP}_j = \sum_{i=1}^4 \frac{SP_{ji}}{4} \quad (2)$$

$$s_j = \left[\sum_{i=1}^4 \frac{(SP_{ji} - \overline{SP}_j)^2}{3} \right]^{1/2} \quad (3)$$

$$\widehat{CV}_j = \frac{s_j}{\overline{SP}_j} \quad (4)$$

where

SP_{ji} = Suspended particulate concentration measured by the i^{th} sampler ($i = 1 - 4$) during the j^{th} time period, $\mu\text{g}/\text{m}^3$. (Values of SP_{ji} determined during the short-term sampling study are reported in table B-1 of appendix B.)

Estimates of the true coefficients of variation for the short-term sampling periods were found by the following:

$$\widehat{CV}(4 \text{ hours}) = \sum_{j=1}^6 \frac{\widehat{CV}_j}{6} \quad (5)$$

where

\widehat{CV}_j = Estimated coefficient of variation of the j^{th} 4-hour sampling period,

and

$$\widehat{CV}(6 \text{ hours}) = \sum_{j=1}^4 \frac{\widehat{CV}_j}{4} \quad (6)$$

where

\widehat{CV}_j = Estimated coefficient of variation of the j^{th} 6-hour sampling period.

Values of \overline{SP}_j , s_j , and \widehat{CV}_j for 4-hour sampling are given in table 1; for 6-hour sampling, the values are listed in table 2,

Table 1. Results from 4-hour sampling periods

Sampling Day	Time Period	\overline{SP}_j ($\mu\text{g}/\text{m}^3$)	s_j ($\mu\text{g}/\text{m}^3$)	\widehat{CV}_j
May 28-29	10 a.m. - 2 p.m.	80.0	4.1	0.051
	2 p.m. - 6 p.m.	82.0	4.7	0.057
	6 a.m. - 10 a.m.	56.8	3.3	0.058
June 2-3	10 a.m. - 2 p.m.	77.2	3.7	0.048
	2 p.m. - 6 p.m.	94.8	4.2	0.044
	6 a.m. - 10 a.m.	90.1	4.5	0.050

Table 2. Results from 6-hour sampling periods

Sampling Day	Time Period	\overline{SP}_j ($\mu\text{g}/\text{m}^3$)	s_j ($\mu\text{g}/\text{m}^3$)	\widehat{CV}_j
May 28-29	6 p.m. - 12 p.m.	106.0	3.4	0.032
	12 p.m. - 6 a.m.	59.5	1.5	0.025
	6 p.m. - 12 p.m.	112.0	4.2	0.037
June 2-3	12 p.m. - 6 a.m.	68.8	2.8	0.041

Using the values from table 1 in equation (5), an estimate of the coefficient of variation for 4-hour sampling periods is

$$\widehat{CV}(4 \text{ hours}) = 0.051 = 5.1 \text{ percent}$$

For 6-hour sampling periods, an estimate of the coefficient of variation was calculated from the values in table 2 using equation (6):

$$\widehat{CV}(6 \text{ hours}) = 0.034 = 3.4 \text{ percent}$$

According to subsection 2.2 of appendix C, the 90 percent confidence interval for CV(4 hours) can be calculated in the following manner.

$$\frac{\widehat{CV}(4 \text{ hours})}{1 + r} < CV(4 \text{ hours}) < \frac{\widehat{CV}(4 \text{ hours})}{1 - r} \quad (7)$$

where

$$r = U_{\gamma} \frac{1}{\sqrt{2N}}$$

$$\widehat{CV}(4 \text{ hours}) = 0.051$$

$$\gamma = 0.90$$

$$U_{\gamma} = 1.645$$

N = Total number of 4-hour samples (no. of 4-hour sampling periods \times no. of samples collected in each period).

$$N = 24.$$

Therefore, the 90 percent confidence interval for CV(4 hours) is:

$$0.041 < CV(4 \text{ hours}) < 0.067.$$

The 90 percent confidence interval for CV(6 hours) was determined in the same manner. For this calculation

$$\widehat{CV}(6 \text{ hours}) = 0.0341$$

$$\gamma = 0.90$$

$$U_{\gamma} = 1.645$$

N = Total number of 6-hour samples

$$N = 16$$

yielding

$$0.026 < CV(6 \text{ hours}) < 0.048.$$

To compare the short-term with the 24-hour sampling period, an average 24-hour suspended particulate concentration was found for each short-term sampler by the following equation:

$$SP_{AVG} = \frac{\sum_{j=1}^5 W_j}{\sum_{j=1}^5 V_j} \times 10^6 \quad (8)$$

where

W_j = Particulate weight collected by the sampler during the j^{th} time period, g

V_j = Air volume sampled by the sampler during the j^{th} time period, m^3 .

Five consecutive time periods with a total elapsed time of 24 hours were sampled for this study. The values of SP_{AVG} for all short-term samplers were averaged and compared with the average suspended particulate concentration determined by the 24-hour samplers (see fig. 1).

The average daily particulate concentration levels as determined by short-term sampling and 24-hour sampling, as well as the relative difference of the concentration found by short-term sampling with respect to that found by 24-hour sampling, are listed below for the respective sampling dates.

May 28-29

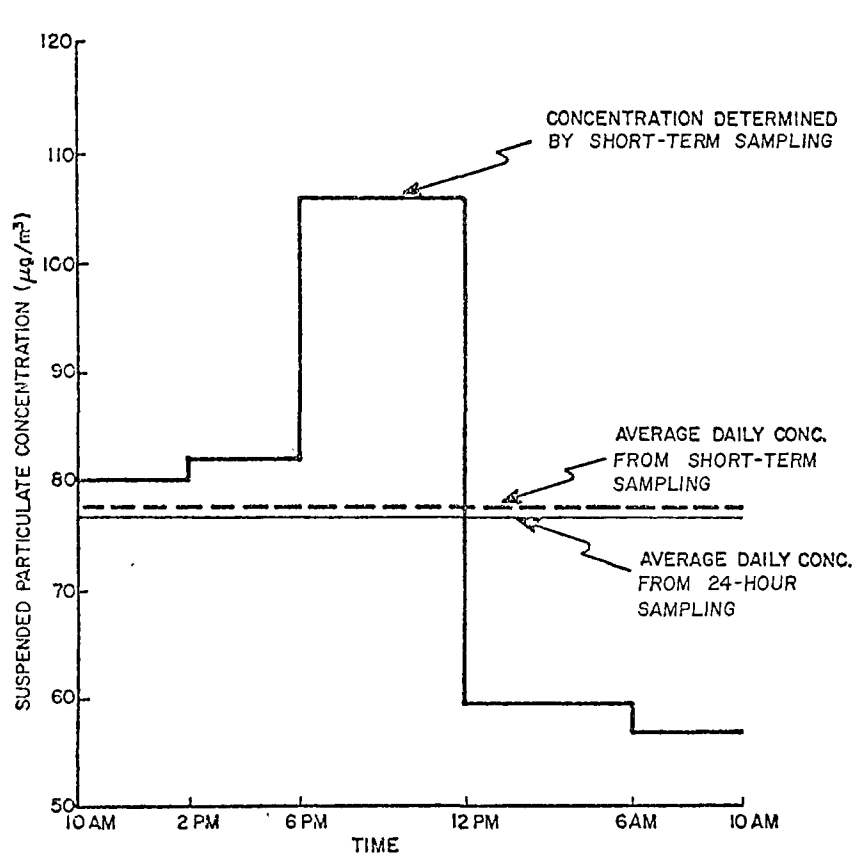
Average concentration from short-term sampling	77.6 $\mu g/m^3$
Average concentration from 24-hour sampling	76.7 $\mu g/m^3$
Relative difference	1.2 percent

June 2-3

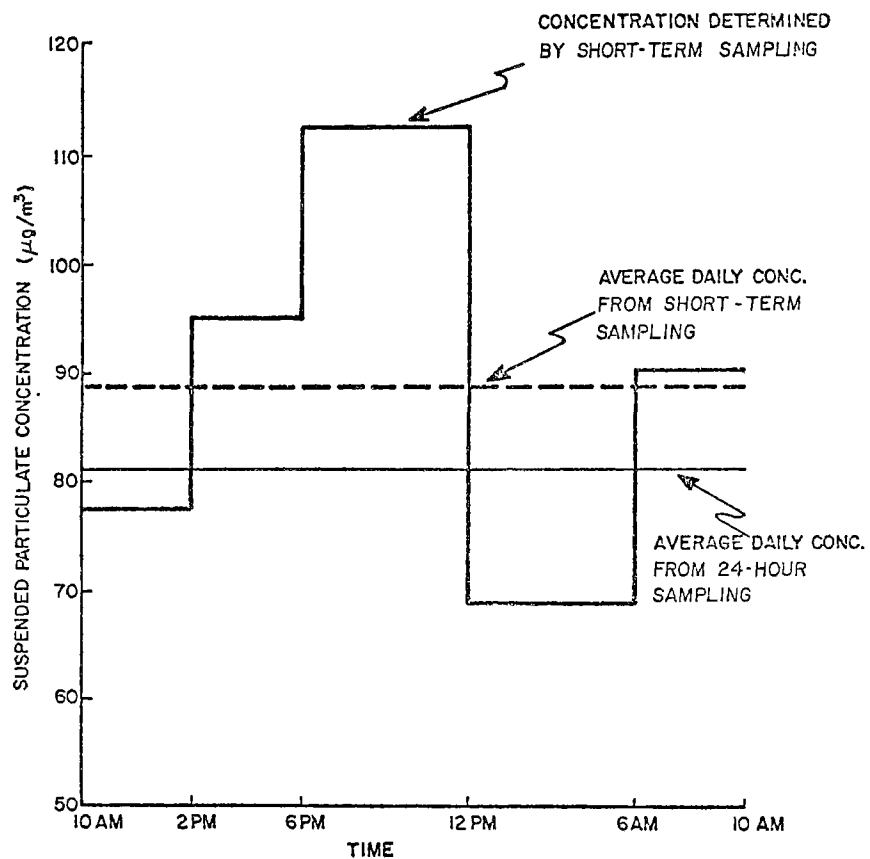
Average concentration from short-term sampling	88.7 $\mu g/m^3$
Average concentration from 24-hour sampling	81.3 $\mu g/m^3$
Relative difference	8.3 percent

The data show good agreement for the May 28-29 sampling period. The approximately 8-percent relative difference for the June 2-3 sampling period is not greater than would be expected due to normal imprecision of the method (at the .05 level). However, since the agreement was good among the short-term samplers and the two 24-hour samplers gave almost identical results (see table B-1 of appendix B for individual values), the assumption can be made that some condition adversely affected either all of the short-term samplers or the two 24-hour samplers equally.

Noticeable environmental differences in the two sampling periods were a much higher relative humidity and more stagnant atmospheric conditions during the June 2-3 sampling period than during the May 28-29 period. A possible explanation is that under the conditions of June 2-3 the short-term samplers were



(A) May 28-29, 1974, sampling period



(B) June 2-3, 1974, sampling period

Figure 1. Suspended particulate concentration levels, as determined from short-term and 24-hour sampling periods.

biased due to increased conversion of acid gases in the atmosphere to particulate matter at the surface of the clean alkaline filters (ref. 3).

(Filters used for the study had pH's ranging from about 8.5 to 9.) If this assumption is true, larger biases can be expected if 1) more alkaline filters are used, or 2) the atmosphere being tested has higher concentrations of acid gases. This possibility could be evaluated in future testing by using neutral filters and/or monitoring gaseous concentrations while sampling.

2.2 Filter Equilibration Study

2.2.1 Apparatus. Special apparatus used in the equilibration study included the following:

1. Two airtight ovens capable of maintaining a constant temperature ($\pm 2^{\circ}\text{C}$) and relative humidity (± 5 percent).
2. Two airtight desiccating chambers.
3. One airtight environmental chamber capable of maintaining a constant temperature ($\pm 2^{\circ}\text{C}$) and relative humidity (± 5 percent) at preset levels.
4. Four thermometers.
5. Four relative humidity indicators.
6. Clean manila folders.
7. Desiccant.
8. Analytical balance capable of measuring to 0.1 mg.

2.2.2 Procedure. After completion of the short-term sampling study, the samples collected during that study were conditioned in an environment of 32°C and 100 percent relative humidity for a period of 24 hours and used for the equilibration study. It was felt that this environment was representative of the more adverse conditions under which high volume sampling is conducted. For the short-term study, a total of 44 filters (11 per sampler) were used; therefore, in order to make the best comparison of equilibration conditions, the samples were equilibrated by sampler group in one of four conditions as listed below.

Filters from Sampler	Environment Number	Equilibration Condition
B	1	< 50% RH/ 25°C
C	2	< 10% RH/ 25°C
D	3	< 10% RH/ 50°C
E	4	< 50% RH/ 50°C

The exposed filters after being conditioned at 32°C and 100 percent RH were weighed and the weights recorded after 1, 2, 4, and 24 hours of equilibration. The filter weight after 24 hours of equilibration is defined and will be referred to throughout this report as the equilibrium weight. (Again the 24-hour weight achieved in environment 1 is defined as the correct weight against which all other weights are compared.)

2.2.3 Data Analysis for the Equilibration Study. The net collected particulate weight was found as a function of equilibration time, t_E ($t_E = 1, 2, 4, 24$ hours), by

$$W_{SP}(t_E) = W_f(t_E) - W_i \quad (9)$$

where

$W_{SP}(t_E)$ = Net particulate weight at equilibration time, t_E , g

$W_f(t_E)$ = Filter plus particulate weight at equilibration time, t_E , g

W_i = Tare weight of filter, g.

Blank filters subjected to the same equilibration procedures as the samples indicated a negligible filter weight change therefore, W_i for a given filter is considered a constant independent of the equilibration environment throughout the procedure.

The relative difference of the particulate weight at equilibration time t_E with respect to the equilibrium weight (the weight at $t_E = 24$ hours) for a given environment is given by

$$y(t_E) = \frac{W_{SP}(t_E) - W_{SP}(24)}{W_{SP}(24)} \quad (10)$$

where

$W_{SP}(t_E)$ = Particulate weight after equilibration for $t_E < 24$ hours, g

$W_{SP}(24)$ = Net particulate weight after 24 hours of equilibration, g

$y(t_E)$ = Error in particulate weight at $t_E < 24$ hours with respect to the weight at $t_E = 24$ hours.

For each environment, an average relative difference, $\bar{y}(t_E)$, and standard deviation, $s(y)$, were determined for $t_E = 1, 2$, and 4 hours. The average relative difference, $\bar{y}(t_E)$, is subscripted with the number of the

environment being considered, e.g., the average relative difference caused by equilibration in environment 1 for time t_E is termed $\bar{y}_1(t_E)$. Values of $\bar{y}(t_E)$ versus t_E for the respective environments were least-squares fitted to exponential functions and graphed in figure 2. The 90 percent confidence limits for the curves presented in figure 2 were determined such that a sample equilibration in a given environment for time t_E will yield a measured value of $y(t_E)$ that will fall within the interval $\bar{y}(t_E) \pm 1.645 s(y)$ approximately 90 percent of the time (1.645 is value of the standard normal variable, U_γ , whose absolute value is exceeded by $1 - \gamma$ where $\gamma = 0.90 =$ the confidence level).

Since the equilibrium weight of a sample equilibrated in environment 1 (< 50% RH/25°C) is considered to be the correct weight of the collected particulates (ref. 3), environment 1 is considered the reference equilibration environment. In order to compare the effect of equilibration in environments 2, 3, and 4 with the effect of equilibration in environment 1, the curves presented in figure 2 were shifted such that the initial values of $\bar{y}_2(t_E)$, $\bar{y}_3(t_E)$, and $\bar{y}_4(t_E)$ were equal to the initial value of $\bar{y}_1(t_E)$; i.e., $\bar{y}_1(1) = \bar{y}_2(1) = \bar{y}_3(1) = \bar{y}_4(1)$ (see figure 3).

The resulting values of $\bar{y}_2(24)$, $\bar{y}_3(24)$, and $\bar{y}_4(24)$ indicate that equilibration of a sample for 24 hours in environments 2, 3, or 4 will result in an equilibration weight less than the weight that would have been achieved by equilibration in the reference environment. The data analysis therefore becomes a matter of determining at what equilibration times $\bar{y}_2(t_E)$, $\bar{y}_3(t_E)$, and $\bar{y}_4(t_E)$ (as seen in figure 3) will be approximately equal to $\bar{y}_1(24)$.

While $\bar{y}_2(t_E)$ and $\bar{y}_3(t_E)$ are within ≈ 1 percent of $\bar{y}_1(24)$ after only 2 hours of equilibration, the standard deviation, $s(y)$ of $\bar{y}_3(2)$ is (from table B-8 in appendix B) 0.0179, while $s(y)$ for $\bar{y}_2(2)$ is only 0.0082. It appears, therefore, that the same equilibration for 2 hours in environment 2 (< 10% RH/25°C) will not only yield particulate weights that are within ≈ 1 percent of the reference weights, but the variability of this bias to the measured suspended particulate concentration will be negligible.

2.2.4 Validation of Data. The curves developed during the equilibration study of relative difference in particulate weight versus equilibration time (fig. 2) were validated in the following manner.

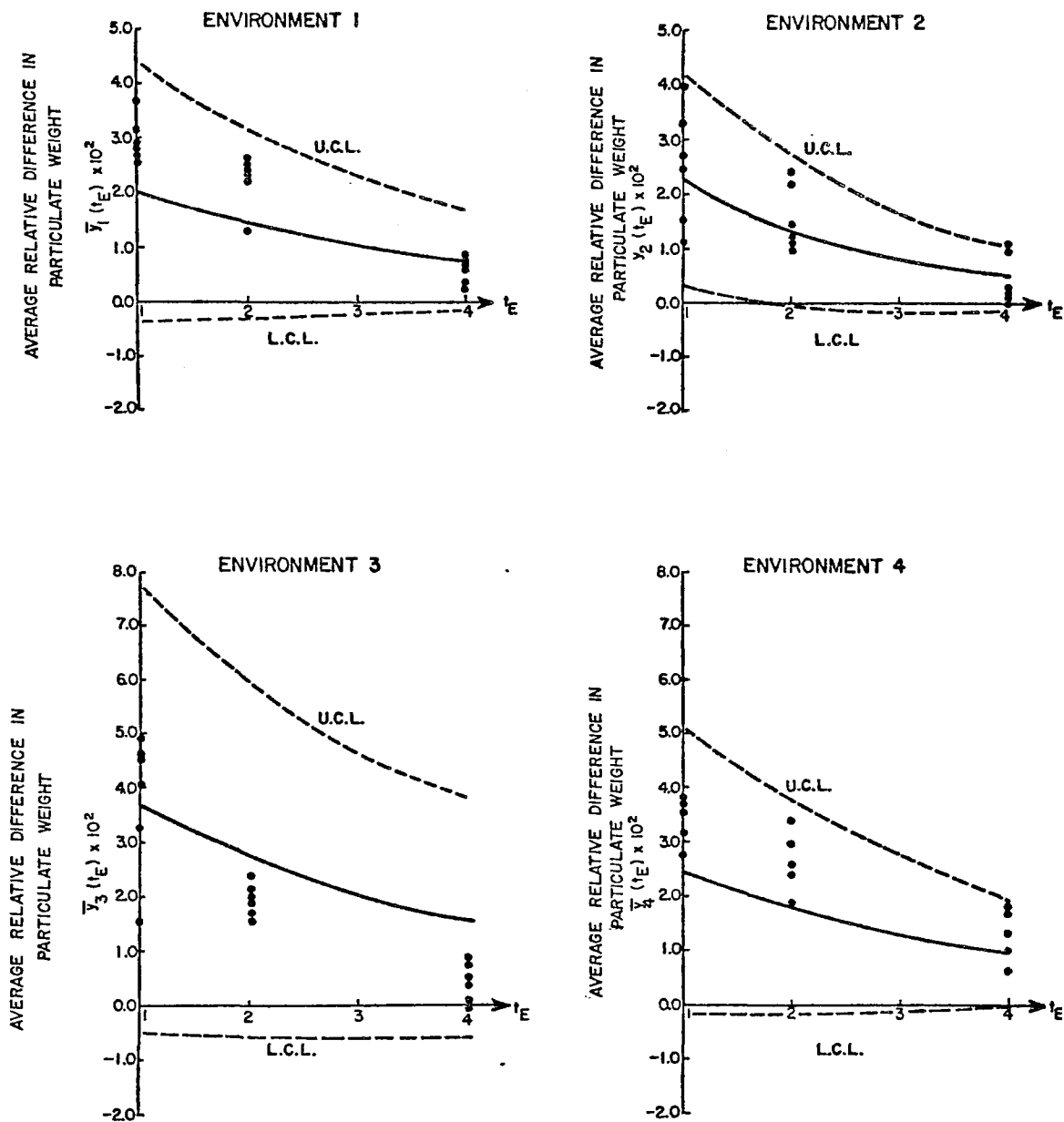


Figure 2. Average relative difference in particulate weight, $\bar{y}(t_E)$, versus equilibration time, t_E .

--- Limits of 90 percent Confidence Interval
 U.C.L. Upper Confidence Limit
 L.C.L. Lower Confidence Limit
 • validation data points

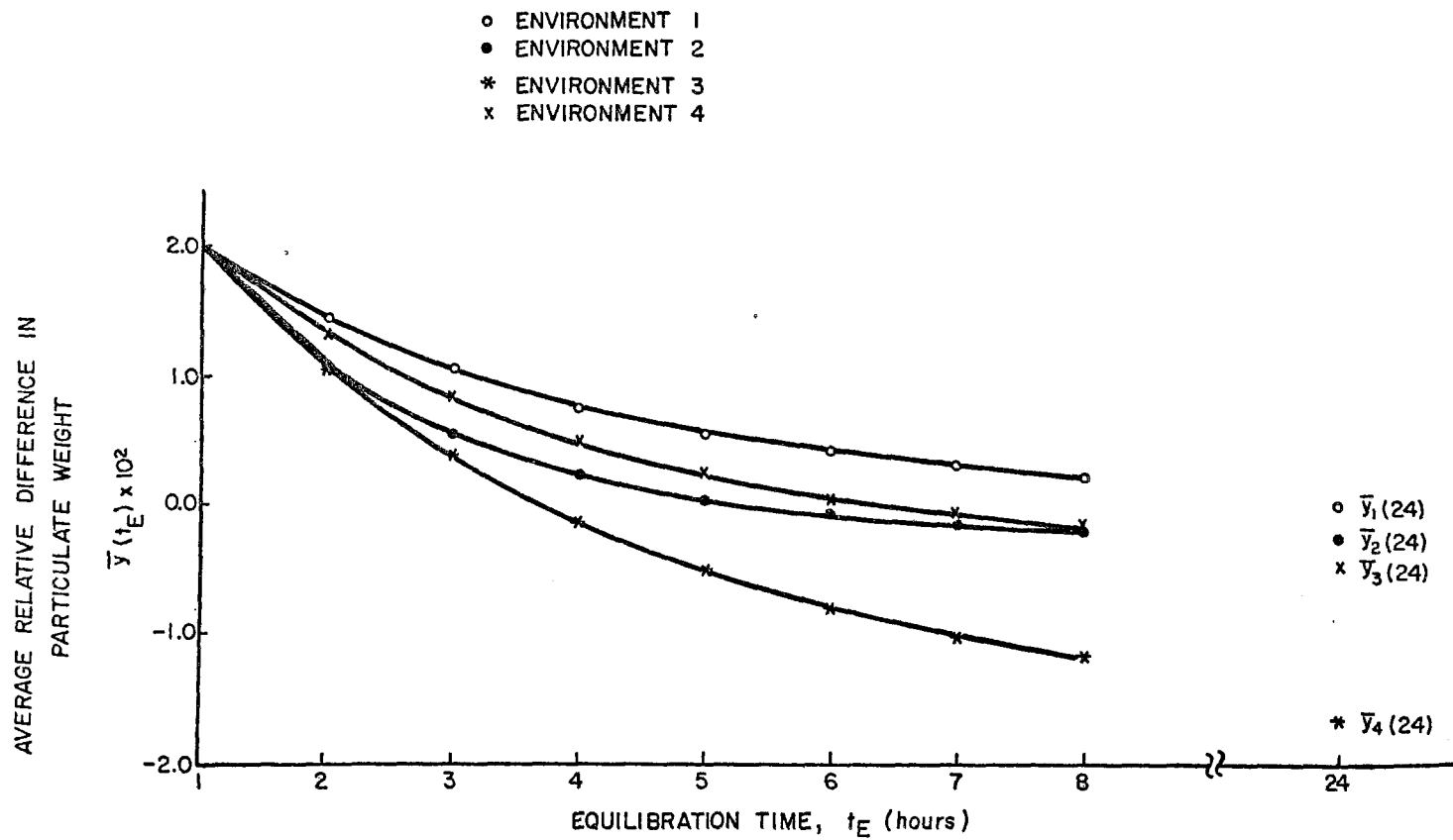


Figure 3. Average relative difference in particulate weight versus equilibration time: Environments 2, 3, and 4 compared with environment 1.

1. Fresh filters were placed in the six high-volume samplers at the sampling site and allowed to collect particulates for various sampling times to obtain samples of varying weight.

2. At the end of each sampling period, the samples were equilibrated in environments described in subsection 2.2.2. Since environment 1 was considered the reference environment, two filters were placed in that environment and the remaining four filters were distributed to two of the other environments for equilibration.

3. The exposed filters were weighed after 1, 2, 4, and 24 hours of equilibration and the data analyzed according to equations (9) and (10).

4. The values of $y(t_E)$ versus t_E resulting from step 3 above were plotted in figure 2 for the respective environments.

As can be seen, the data collected during this section of the study appear to validate all of the curves within the respective 90 percent confidence intervals.

3.0 RESULTS

When a suspended particulate concentration has been determined by sampling during a short sampling period and the sample has been equilibrated under specified conditions, the 90 percent confidence interval of the true average suspended particulate concentration for the specified sampling time, i.e., the interval in which one can be 90 percent confident that the true average concentration will fall, can be calculated (assuming no bias other than that due to equilibration) by the following:

$$SP_T = SP_M - \hat{\tau} \pm 1.645 \hat{\sigma} \quad (11)$$

where

SP_T = True average suspended particulate concentration, $\mu\text{g}/\text{m}^3$

SP_M = Measured average suspended particulate concentration, $\mu\text{g}/\text{m}^3$

$\hat{\tau}$ = Estimated bias introduced by equilibration for $t_E < 24$ hrs,
 $\mu\text{g}/\text{m}^3$

$\hat{\sigma}$ = Overall estimated standard deviation of measured samples; a
function of sampling period time and equilibration time.

Estimates of the bias, $\hat{\tau}$, and standard deviation, $\hat{\sigma}$, are calculated by equations (12) and (13), respectively

$$\hat{\tau} = SP_M \times \left[\frac{\bar{y}(t_E)}{1 + \bar{y}(t_E)} \right] \quad (12)$$

$$\hat{\sigma} = SP_M \times \{ \hat{CV}^2(\text{sampling time}) + \hat{CV}^2(1 + y(t_E)) \}^{1/2} \quad (13)$$

The square of the estimated relative standard deviation, \hat{CV}^2 , for single operator variation for 4-hour sampling periods is

$$\hat{CV}^2 = \hat{CV}^2(4 \text{ hours}) = (0.052)^2,$$

and for 6-hour sampling periods

$$\hat{CV}^2 = \hat{CV}^2(6 \text{ hours}) = (0.034)^2.$$

Values of

$$\hat{CV}^2[1 + y(t_E)] = \left[\frac{s(y)}{1 + y(t_E)} \right]^2$$

can be determined from table 3 for the designated equilibration environments and equilibration times.

The use of this method for determining the true average concentration from a measured average concentration is illustrated as follows.

A measured average suspended particulate concentration of $100 \mu\text{g}/\text{m}^3$ has been determined by sampling for 4 hours and equilibrating the sample for $t_E = 2$ hours in environment 2.

The true average suspended particulate concentration with 90 percent confidence limits can be found by

$$SP_T = SP_M - \hat{\tau} \pm 1.645 \hat{\sigma}.$$

Equations (12) and (13) state that

$$\hat{\tau} = SP_M \left[\frac{\bar{y}(t_E)}{1 + \bar{y}(t_E)} \right] \text{ and } \hat{\sigma} = SP_M \times \{ CV^2(\text{sampling time}) + \hat{CV}^2[1 + y(t_E)] \}^{1/2}$$

where from table 3 for $t_E = 2$ hours

Table 3. Values of $\bar{y}(t_E)/[1 + \bar{y}(t_E)]$ and $CV[1 + \bar{y}(t_E)]$ for varying t_E

Environment	t_E	$\bar{y}(t_E)/[1 + \bar{y}(t_E)]$	$CV[1 + \bar{y}(t_E)]$
1	1	0.0196	0.0142
	2	0.0143	0.0098
	4	0.0076	0.0060
2	1	0.0221	0.0115
	2	0.0134	0.0081
	4	0.0049	0.0037
3	1	0.0354	0.0242
	2	0.0267	0.0174
	4	0.0150	0.0150
4	1	0.0240	0.0156
	2	0.0177	0.0117
	4	0.0096	0.0057

$$\frac{\bar{y}(2)}{1 + \bar{y}(2)} = 0.0134 \text{ and } \widehat{CV}^2[1 + \bar{y}(2)] = (0.0081)^2$$

and for 4 hour sampling periods

$$\widehat{CV}^2 = \widehat{CV}^2(4 \text{ hours}) = (0.051)^2$$

Hence,

$$SP_T = SP_M - 0.0134 \times SP_M \pm 1.645 \times SP_M \times [(0.051)^2 + (0.0081)^2]^{1/2}.$$

Therefore, given a measured average suspended particulate concentration, SP_M , of $100 \mu\text{g}/\text{m}^3$, the true average concentration for the specified sampling time would fall within the following limits

$$90.1 \mu\text{g}/\text{m}^3 < SP_T < 107 \mu\text{g}/\text{m}^3$$

with approximately 90 percent confidence assuming no bias other than that due to equilibration times less than 24 hours.

4.0 CONCLUSIONS

The Short-Term Sampling Study indicates that the coefficient of variation for single operator variation is a function of sampling time. Short sampling times increase the variation from 3 percent for 24-hour sampling (ref. 4), to an average of approximately 3.4 percent for 6-hour sampling, and 5.2 percent for 4-hour sampling.

For the sampling dates studied, the plots in figures 1A and 1B show good agreement between the daily average particulate concentration determined by consecutive short-term sampling periods and that found by 24-hour sampling. The percent difference (expressed as the relative difference) between the results of the two methods varied from approximately 1 percent for May 28-29 to approximately 8 percent for June 2-3. It is felt, however, that further study will be necessary in order to draw any definite conclusions based on this type of comparison.

The recommended equilibration procedure for the type of particulates studied is 2 hours of postsampling conditioning in an environment comparable to environment 2 (i.e., at $\approx 25^{\circ}\text{C}$ and $\text{RH} \leq 10$ percent). While none of the environments studied, with the possible exception of environment 3, contributes extreme errors to the measured particulate concentration, environment 2 caused the instantaneous particulate weight to decrease more rapidly and with less variability toward an equilibrium weight (i.e., the weight after 24-hours of equilibration) for equilibration times less than 24 hours.

5.0 RECOMMENDATIONS

Recommendations are given in two areas. First, procedures for short-term high volume sampling are recommended based on the data obtained from this study. Secondly, recommendations are made for further evaluation of short-term sampling in different atmospheres where the chemical and physical properties of the particulate matter adequately cover the spectrum of particulates encountered in high-volume sampling.

5.1 Recommended Short-term Sampling Procedure

The recommended short-term sampling procedures differ from the procedures for the EPA reference method of measuring suspended particulates in ambient air only in the length of the sample collection period and the filter equilibration conditions. The recommended short-term method is given in detail in appendix A. In this section the specific recommendations are given along with the reasons for making the recommendation.

Results from this study indicate that if these recommended procedures are followed the reported values will be within ± 10 percent of the average value with 90 percent confidence. The average value as used here represents the average value that would result from several measurements made under similar conditions. The average value will be the true value if there is no bias in the measurement process.

5.1.1 Recommended Sampling Procedure. A 4-hour sampling period is recommended. The data analysis indicated that for collected particulate weights greater than about 20 mg the sampling period time is more critical to precision than is the actual particulate weight. A 4-hour sampling period appears to be about the shortest possible for the results to be within ± 10 percent of the average value with 90-percent confidence.

5.1.2 Recommended Equilibration Procedure. A 2-hour equilibration period in a controlled environment with a relative humidity of 10 percent or less and a temperature of approximately 25°C is recommended. These conditions are recommended. These conditions are recommended for several reasons. First, the desired conditions can be realized with simple equipment. A desiccator with fresh Drierite will maintain a less than 10 percent relative humidity, and the normal range of temperatures of a working area is acceptable. Also, this set of conditions was selected because of the smaller variability in the test data (see fig. 3, environment 2) and because the particulate weight after 24-hours of equilibration in this set of conditions was not significantly different from that obtained from the reference environment, i.e., that recommended in reference 1.

5.2 Recommendations for Further Testing

Results of this study are applicable only to the local area in which the measurements were made. Therefore, before recommending the short-term method for general use, it should be evaluated under the various extremes that will be encountered in the field. For example, atmospheres with high concentrations of particulates that plug the filter, causing a nonlinear drop in the flow rate over a 4-hour period, could result in errors in determining the average flow rate. Other errors can result due to unequal sampling rates if the particulate concentration as well as the flow rate is varying with time. Also, since the precision appears to be a function of

the sampling period duration rather than the weight of collected particulates, the precision could possibly be improved using continuous flow-rate recorders so that a better estimate of the average flow rate could be obtained. This possibility could be investigated with further testing.

Further study could be undertaken to determine the reasons for differences in the concentrations determined by 24-hour sampling and those determined by consecutive short-term sampling over a 24-hour period. It appears from the results of this study that adverse weather conditions (high humidity, dense fog, air stagnation) cause a higher daily average concentration to be measured by consecutive short-term sampling than by 24-hour sampling over the same period. However, at this point, there is no definite proof that 24-hour sampling results are more accurate estimates of true concentrations than the consecutive short-term sampling. It is therefore recommended that further testing be done to examine the causes of differences in this type of comparison.

6.0 REFERENCES

1. Appendix B, "National Primary and Secondary Ambient Air Standards." Federal Register 36, No. 84, Part II (April 30, 1971).
2. U.S. Environmental Protection Agency. Guidelines for Development of a Quality Assurance Program: Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method). EPA-R4-73-028b, Washington, D.C., June 1973.
3. Robert M. Burton et al. "Field Evaluation of the High-Volume Particle Fractionating Cascade Impactor—A Technique for Respirable Sampling." Presented at the 65th annual meeting of the Air Pollution Control Association, June 18-22, 1972.
4. Herbert C. McKee et al. Collaborative Study of Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method). Southwest Research Institute, Contract CAP 70-40, SwRI Project 21-2811, San Antonio, Texas, June 1971.

APPENDIX A PROPOSED REFERENCE METHOD FOR THE DETERMINATION OF SUSPENDED PARTICULATES IN THE ATMOSPHERE OVER SHORT SAMPLING TIMES. (HIGH VOLUME METHOD)

1.0 PRINCIPLE AND APPLICABILITY

1. Air is drawn into a covered housing and through a filter by means of a high-flow-rate blower at a flow rate (1.41 to 1.98 m³/min; 50 to 70 ft³/min) that allows suspended particles having diameters of less than 100 μm (Stokes equivalent diameter) to pass to the filter surface (ref. 1). Particles within the size range of 0.1 to 100 μm diameter are ordinarily collected on fiberglass filters. The mass concentration of suspended particulates in the ambient air (μg/m³) is computed by measuring the mass of collected particulates and the volume of air sampled.

2. This method is applicable to measurement of 4-hour average mass concentrations of suspended particulates in ambient air. To assure measurements of acceptable precision, this method should not be used to measure average concentrations of less than about 50 μg/m³ (this yields 4-hour samples of approximately 20 mg). The size of the sample collected is usually adequate for other analyses. Concentrations as low as 10 μg/m³ can be measured; however, the relative error would probably be larger than that given in section 4.0.

2.0 RANGE AND SENSITIVITY

Weights are determined to the nearest 0.1 mg, airflow rates are determined to the nearest 0.1 m³/min, times are determined to the nearest minute, and mass concentrations are reported to three significant digits, e.g., 102 μg/m³ and 50.6 μg/m³.

3.0 INTERFERENCES

1. Particulate matter that is oily, such as photochemical smog or wood smoke, may block the filter and cause a rapid drop in airflow at a nonuniform rate. Dense fog or high humidity in conjunction with certain types of particulates may severely reduce the airflow through the filter.

2. Fiberglass filters are comparatively insensitive to changes in relative humidity but collected particulates can be hygroscopic (ref. 2).

3. Acid gases in the sample air may be converted to particulate matter on the surface of alkaline filters (refs. 3, 4).

4.0 PRECISION, ACCURACY, AND STABILITY

4.1 Precision

Based on the Short-term High-Volume Study, the estimated relative standard deviation (coefficient of variation) for single analyst variation (repeatability) for 4-hour sampling and 2-hour equilibration periods is 5.2 percent.

4.2 Accuracy

The accuracy with which the sampler measures the true average concentration cannot be quantitatively determined. Measured values higher than the true values may result when alkaline filters are used. A functional analysis of the method indicates that other large biases should not occur in short-term sampling (ref. 5)

5.0 APPARATUS

5.1 Sampling

5.1.1 Sampler. The sampler consists of three units: 1) the faceplate and gasket, 2) the filter adapter assembly, and 3) the motor unit. Figure A-1 shows an exploded view of these parts, their relationship to each other, and how they are assembled. The sampler must be capable of passing environmental air through a 406.5 cm^3 (63 in.^2) portion of a clean 20.3 by 25.4 cm (8 by 10 in.) fiber-glass filter at a rate of at least $1.70 \text{ m}^3/\text{min}$ ($60 \text{ ft}^3/\text{min}$). The motor must

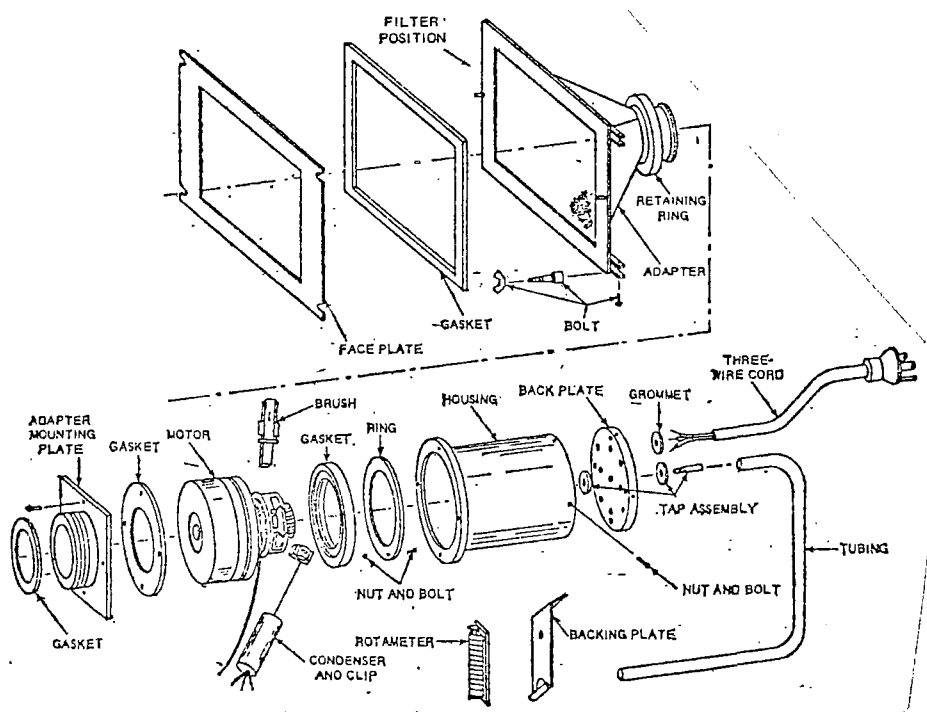


Figure A-1. Exploded view of typical high-volume air sampler parts.

be capable of continuous operation for 4-hour periods with input voltages ranging from 110 to 120 volts, 50-60 cycles alternating current and must have third-wire safety ground. The housing for the motor unit may be of any convenient construction so long as the unit remains airtight and leak free.

5.1.2 Sampler Shelter. It is important that the sampler be properly installed in a suitable shelter. The shelter is subjected to extremes of temperature, humidity, and all types of air pollutants. For these reasons the materials of the shelter must be chosen carefully. Properly painted exterior plywood or heavy gauge aluminum serve well. The sampler must be mounted vertically in the shelter so that the fiberglass filter is parallel with the ground. The shelter must be provided with a roof so that the filter is protected from precipitation and debris. The internal arrangement and configuration of a suitable shelter with a gable roof are shown in figure A-2. The clearance area between the main housing and the roof at its closest point should be $580.5 \pm 193.5 \text{ cm}^2$ ($90 \pm 30 \text{ in.}^2$). The main housing should be rectangular, with dimensions of about 29 by 36 cm (11-1/2 by 14 in.).

5.1.3 Rotameter. A rotameter marked in arbitrary units, frequently 0 to 70, and capable of being calibrated is acceptable for measuring sample flow rates. Other devices of at least comparable accuracy may be used (see addendum A).

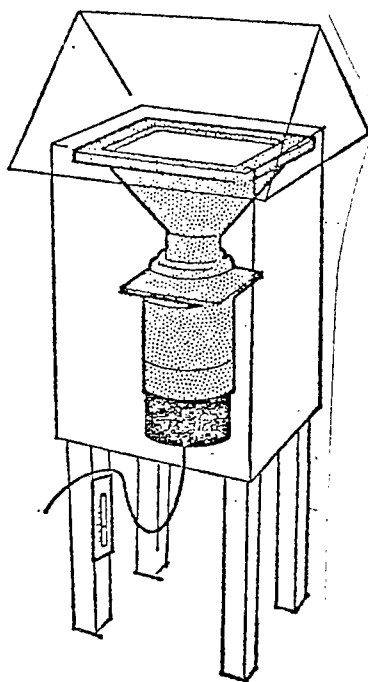


Figure A-2. Assembled sampler and shelter.

5.1.4 Orifice Calibration Unit. Consisting of a metal tube 7.6 cm (3 in.) ID and 15.9 cm (6-1/4 in.) long with a static pressure tap 5.1 cm (2 in.) from one end. See figure A-3. The tube end nearest the pressure tap is flanged to about 10.8 cm (4-1/4 in.) OD with a male thread of the same size as the inlet end of the high-volume air sampler. A single metal plate 9.2 cm (3-5/8 in.) in diameter and 0.24 cm (3/32 in.) thick with a central orifice 2.9 cm (1-1/3 in.) in diameter is held in place at the air inlet end with a female threaded ring. The other end of the tube is flanged to hold a loose female threaded coupling, which screws onto the inlet of the sampler. An 18-hole metal plate, an integral part of the unit, is positioned between the orifice and sampler to simulate the resistance of a clean fiber-glass filter. An orifice calibration unit is shown in figure A-3.

5.1.5 Differential Manometer. Capable of measuring to at least 40 cm (16 in.) of water.

5.1.6 Positive Displacement Meter. Calibrated in cubic meters or cubic feet, to be used as a primary standard.

5.1.7 Barometer. Capable of measuring atmospheric pressure to the nearest mm of Hg.

5.2 Analysis

5.2.1 Filter Conditioning Environment. Balance room or desiccator maintained

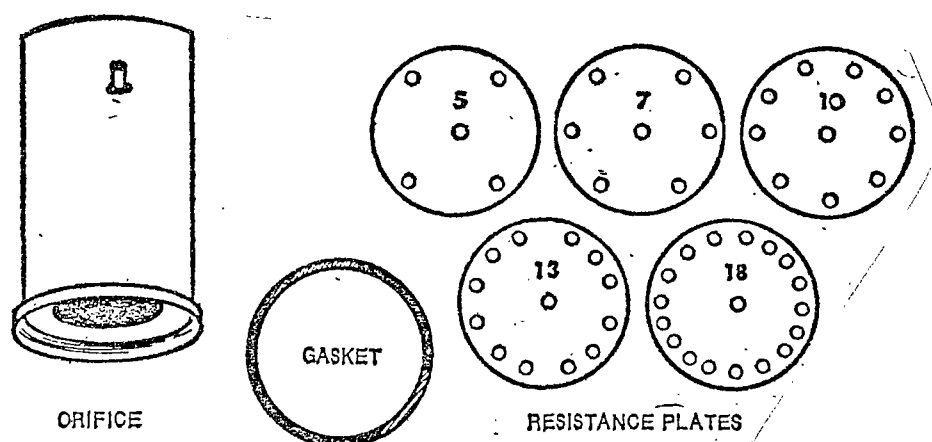


Figure A-3. Orifice calibration unit.

at approximately 25°C and less than 10 percent relative humidity. A desiccator with fresh desiccant such as Drierite maintained in an air-conditioned room provides a satisfactory conditioning environment.

5.2.2 Analytical Balance. Equipped with a weighing chamber designed to handle unfolded 20.3 by 25.4 cm (8 by 10 in.) filters and having a sensitivity of 0.1 mg.

5.2.3 Light Source. Frequently a table of the type used to view X-ray films.

5.2.4 Number Device. Capable of printing identification numbers on the filters.

6.0 REAGENTS

6.1 Filter Media

Neutral fiberglass filters having a collection efficiency of at least 99 percent for particles of 0.3 μ m diameter, as measured by the DOP test, are suitable for the quantitative measurement of concentrations of suspended particulates (ref. 6), although some other medium, such as paper, may be desirable for some analyses. If a more detailed analysis is contemplated, care must be exercised to use filters that contain low background concentrations of the pollutant being investigated. Careful quality control is required to determine background values of these pollutants.

7.0 PROCEDURE

7.1 Sampling

7.1.1 Filter Preparation. Expose each filter to the light source and inspect for pinholes, particles, or other imperfections. Filters with visible imperfections should not be used. A small brush is useful for removing particles. Print an identification number using the numbering device on the outer edge of the filters. Equilibrate the filters in the filter conditioning environment of section 7.2 for 2 hours. Weigh the filters to the nearest 0.1 mg; record tare weight and filter identification number. Do not bend or fold the filter before collection of the sample.

7.1.2 Sample Collection. Open the shelter, loosen the wing nuts, and remove the faceplate from the filter holder. Install a numbered, preweighed,

fiberglass filter in position (rough side up), replace the faceplate without disturbing the filter, and fasten securely. Undertightening will allow air leakage; overtightening will damage the sponge rubber faceplate gasket. A very light application of talcum powder may be used on the sponge rubber faceplate gasket to prevent the filter from sticking. During inclement weather the sampler may be removed to a protected area for filter change. Close the roof of the shelter, run the sampler for about 5 minutes, connect the rotameter to the nipple on the back of the sampler, and read the widest part of the rotameter float with the rotameter in a vertical position. Estimate to the nearest whole number. If the float is fluctuating rapidly, tip the rotameter and slowly straighten it until the float gives a constant reading. Disconnect the rotameter from the nipple; record the initial rotameter reading, the starting time, and the date on the filter or other suitable form folder. (The rotameter should never be connected to the sampler except when the flow is being measured.) Sample for 4 hours and take a final rotameter reading. Record the final rotameter reading, ending time, and date on the filter folder or other suitable form. Remove the faceplate as described above and carefully remove the filter from the holder, touching only the outer edges. Fold the filter lengthwise so that only surfaces with collected particulates are in contact, and place in a manila folder. Record on the folder or other suitable form the filter number, location, and any other factors, such as meteorological conditions or razing of nearby buildings, that might affect the results. If the sample is defective, void it at this time. In order to obtain a valid sample, the flow rate of a high-volume sampler must be measured with the same rotameter and tubing that were used during its calibration.

7.2 Analysis

Equilibrate the exposed filters for 2 hours in a low relative humidity (< 10 percent) and room temperature environment, then weigh to the nearest 0.1 mg. After they are weighed, the filters may be saved for detailed chemical analysis.

7.3 Maintenance

7.3.1 Sampler Motor. Replace brushes before they are worn to the point where motor damage can occur.

7.3.2 Faceplate Gasket. Replace when the margins of samples are no longer

sharp. The gasket may be sealed to the faceplate with rubber cement or double-sided adhesive tape.

7.3.3 Rotameter. Clean as required, using alcohol.

8.0 CALIBRATION

8.1 Purpose

Since only a small portion of the total air sampled passes through the rotameter during measurement, the rotameter must be calibrated against actual airflow with the orifice calibration unit. Before the orifice calibration unit can be used to calibrate the rotameter, the orifice calibration unit itself must be calibrated against the positive displacement primary standard.

8.1.1 Orifice Calibration Unit. Attach the orifice calibration unit to the intake end of the positive displacement primary standard and attach a high-volume motor blower unit to the exhaust end of the primary standard. Connect one end of a differential manometer to the differential pressure tap of the orifice calibration unit and leave the other end open to the atmosphere. Operate the high-volume motor blower unit so that a series of different, but constant, airflows (usually six) are obtained for definite time periods. Record the reading on the differential manometer at each airflow. The different constant airflows are obtained by placing a series of load-plates, one at a time, between the calibration unit and the primary standard. Placing the orifice before the inlet reduces the pressure at the inlet of the primary standard below atmospheric; therefore, a correction must be made for the increase in volume caused by this decreased inlet pressure. Attach one end of a second differential manometer to an inlet pressure tap of the primary standard and leave the other open to the atmosphere. During each of the constant airflow measurements made above, measure the true inlet pressure of the primary standard with this second differential manometer. Measure atmospheric pressure and temperature. Correct the measured air volume to true air volume as directed in subsection 9.1.1, then obtain true airflow rate, Q , as directed in subsection 9.1.3. Plot the differential manometer readings of the orifice unit versus Q .

8.1.2 High-volume Sampler. Assemble a high-volume sampler with a clean filter in place and run for at least 5 minutes. Attach a rotameter, read

the float, adjust so that the float reads 65, and seal the adjusting mechanism so that it cannot be changed easily. Shut off motor, remove the filter, and attach the orifice calibration unit in its place. Operate the high-volume sampler at a series of different, but constant, airflows (usually six). Record the reading of the differential manometer on the orifice calibration unit and record the readings of the rotameter at each flow. Measure atmospheric pressure and temperature. Convert the differential manometer reading to m^3/min , Q , then plot rotameter reading versus Q .

8.1.3 Correction for Differences in Pressure or Temperature. See Addendum B.

9.0 CALCULATIONS

9.1 Calibration of Orifice

9.1.1 True Air Volume. Calculate the air volume measured by the positive displacement primary standard.

$$V_a = \frac{(P_a - P_m)}{P_a} (V_M)$$

where

V_a = True air volume at atmospheric pressure, m^3

P_a = Barometric pressure, mm Hg

P_m = Pressure drop at inlet of primary standard, mm Hg

V_M = Volume measured by primary standard, m^3 .

9.1.2 Conversion Factors

Inches Hg $\times 25.4$ = mm Hg.

Inches water $\times 73.48 \times 10^{-3}$ = inches of Hg.

Cubic feet air $\times 0.0284$ = cubic meters air.

9.1.3 True Airflow Rate

$$Q = \frac{V_a}{T}$$

where

Q = Flow rate, m^3/min

T = Time of flow, min.

9.2 Sample Volume

9.2.1 Flow Rate Conversion. Convert the initial and final rotameter readings to true airflow rate, Q, using the calibration curve of subsection 8.1.2.

9.2.2 Volume of Air Sampled. Calculate the volume of air sampled by

$$V = \frac{Q_i + Q_f}{2} \times T$$

where

V = Air volume sampled, m³
Q_i = Initial airflow rate, m³/min
Q_f = Final airflow rate, m³/min
T = Sampling time, min.

9.3 Mass Concentration

Calculate mass concentration of suspended particulates by

$$SP = \frac{(W_f - W_i) \times 10^6}{V}$$

where

SP = Mass concentration of suspended particulates, µg/m³
W_i = Initial weight of filter, g
W_f = Final weight of filter, g
V = Air volume sampled, m³
10⁶ = Conversion of g to µg.

10.1 REFERENCES

1. C. D. Robson and K. E. Foster. "Evaluation of Air Particulate Sampling Equipment." Am. Ind. Hyg. Assoc. J. 24(1962): 404.
2. G. P. Tierney and W. D. Conner. "Hygroscopic Effects on Weight Determinations of Particulates Collected on Glass-Fiber Filters." Am. Ind. Hyg. Assoc. J. 28 (1967): 363.
3. Robert M. Burton et al. "Field Evaluation of the High-Volume Particle Fractionating Cascade Impactor--A Technique for Respirable Sampling." Presented at the 65th Annual Meeting of the Air Pollution Control Association, June 18-22, 1972.
4. Peter K. Mueller et al. "Selection of Filter Media: An Annotated

Outline." Presented at the 13th Conference on Methods in Air Pollution and Industrial Hygiene Studies, University of California, Berkeley, California, October 30-31, 1972.

5. F. Smith and A. C. Nelson, Jr., "Guidelines for Development of Quality Assurance Programs and Procedures Applicable to Measuring Pollutants for Which National Ambient Air Quality Standards Have Been Promulgated," Final Report, Research Triangle Institute, Contract No. EPA-Durham-68-02-0598, Environmental Protection Agency, Research Triangle Park, N.C. 27711, Aug. 1973.
6. J. B. Pate and E. C. Tabor. "Analytical Aspects of the Use of Glass-Fiber Filters for the Collection and Analysis of Atmospheric Particulate Matter." Am. Ind. Hyg. Assoc. J. 23 (1962): 144-50.

ADDENDA

A. ALTERNATIVE EQUIPMENT

A modification of the high-volume sampler incorporating a method for recording the actual airflow over the entire sampling period has been described, and is acceptable for measuring the concentration of suspended particulates (J. S. Henderson. Eighth Conference on Methods in Air Pollution and Industrial Hygiene Studies, Oakland, Calif. 1967). This modification consists of an exhaust orifice meter assembly connected through a transducer to a system for continuously recording airflow on a circular chart. The volume of air sampled is calculated by the following equation:

$$V = Q \times T$$

Q = Average sampling rate, m^3/min .

T = Sampling time, minutes.

The average sampling rate, Q , is determined from the recorder chart by estimation if the flow rate does not vary more than $0.11 \text{ m}^3/\text{min}$ ($4 \text{ ft}^3/\text{min}$) during the sampling period. If the flow rate does vary more than 0.11 m^3 ($4 \text{ ft}^3/\text{min}$) during the sampling period, read the flow rate from the chart at 2-hour intervals and take the average.

B. PRESSURE AND TEMPERATURE CORRECTIONS

If the pressure or temperature during high-volume sampler calibration is substantially different from the pressure or temperature during orifice calibration, a correction of the flow rate, Q , may be required. If the pressures differ by no more than 15 percent and the temperatures differ by no more than 100 percent ($^{\circ}\text{C}$), the error in the uncorrected flow rate will be no more than 15 percent. If necessary, obtain the corrected flow rate as directed below. This correction applies only to orifice meters having a constant orifice coefficient. The coefficient for the calibrating orifice described in 5.1.4 has been shown experimentally to be constant over the normal operating range of the high-volume sampler (0.6 to $2.2 \text{ m}^3/\text{min}$; 20 to $78 \text{ ft}^3/\text{min}$). Calculate corrected flow rate:

$$Q_2 = Q_1 \left[\frac{T_2 P_1}{T_1 P_2} \right]^{1/2}$$

where

Q_2 = Corrected flow rate, m³/min

Q_1 = Flow rate during high-volume sampler calibration (subsection 8.1.2), m³/min

T_1 = Absolute temperature during orifice unit calibration (subsection 8.1.1), K or °R.

P_1 = Barometric pressure during orifice unit calibration (subsection 8.1.1), mm. Hg.

T_2 = Absolute temperature during high-volume sampler calibration (subsection 8.1.2), K or °R.

P_2 = Barometric pressure during high-volume sampler calibration (subsection 8.1.2), mm. Hg.

APPENDIX B
COMPILATION OF DATA FOR THE SHORT-TERM HIGH-VOLUME SAMPLING STUDY

1.0 DATA COLLECTED FOR THE SHORT-TERM SAMPLING STUDY

Table B-1. Measured suspended particulate concentrations
from 4-, 6-, and 24-hour sampling periods

Sampler	Concentration ($\mu\text{g}/\text{m}^3$)					SP _{AVE}	24-hr. (10 a.m. 10 a.m.)
	10 a.m.- 2 p.m.	2 p.m.- 6 p.m.	6 p.m.- 12 p.m.	12 p.m.- 6 a.m.	6 a.m.- 10 a.m.		
May 28-29							
B	79.7	75.5	104.6	58.4	57.4	76.1	
C	74.5	82.6	102.2	58.1	52.4	74.9	
D	84.0	86.8	108.6	60.3	60.4	80.3	
E	81.8	83.0	108.6	61.2	57.1	79.3	
A	--	--	--	--	--	--	78.5
F	--	--	--	--	--	--	75.0
$\overline{\text{SP}}_j$	80.0	82.0	106.0	59.5	56.8	77.7	76.8
\hat{s}_j	4.1	4.7	3.2	1.5	3.3	2.6	
$\hat{\text{CV}}_j(\%)$	5.1	5.8	3.0	2.6	5.8	3.3	
June 2-3							
B	75.5	89.1	106.6	64.7	83.5	83.9	
C	76.2	95.4	117.2	71.3	92.9	90.9	
D	82.7	99.1	113.7	69.5	93.1	91.3	
E	74.5	95.8	111.9	69.7	91.0	88.8	
A	--	--	--	--	--	--	81.3
F	--	--	--	--	--	--	81.7
$\overline{\text{SP}}_j$	77.2	94.8	112.4	68.8	90.1	88.7	81.5
\hat{s}_j	3.7	4.2	4.5	2.8	4.5	3.4	
$\hat{\text{CV}}_j(\%)$	4.8	4.4	4.0	4.1	5.0	3.8	

Table B-2. Data Collected May 28-29, 1974

Equilibration Conditions: < 50% Relative Humidity/ 25°C \pm 2°C

Sampler	Filter No.	Sampling Period			Flow Rate (m ³ /min)	Weights (g)	
		Start	Stop	Elapsed Time (min)		W _i	W _f
A	5	2:00 p.m.	2:00 p.m.	1440	1.66	3.6460	3.8333
F	2	2:00 p.m.	2:00 p.m.	1440	1.80	3.8249	4.0198
B	3	2:00 p.m.	5:45 p.m.	225	1.72	3.6048	3.6341
C	7	2:00 p.m.	5:45 p.m.	225	1.98	3.6187	3.6556
D	4	2:00 p.m.	5:45 p.m.	225	1.79	3.8082	3.8432
E	1	2:00 p.m.	5:45 p.m.	225	1.89	3.6358	3.6711
B	8	6:00 p.m.	11:45 p.m.	345	1.71	3.8342	3.8958
C	10	6:00 p.m.	11:45 p.m.	345	1.95	3.8183	3.8871
D	6	6:00 p.m.	11:45 p.m.	345	1.79	3.8382	3.9053
E	9	6:00 p.m.	11:45 p.m.	345	1.86	3.6392	3.7089
B	12	12:00 p.m.	6:00 a.m.	360	1.67	3.8167	3.8518
C	14	12:00 p.m.	6:00 a.m.	360	1.95	3.8562	3.8970
D	11	12:00 p.m.	6:00 a.m.	360	1.86	3.6316	3.6721
E	13	12:00 p.m.	6:00 a.m.	360	1.86	3.6591	3.7001
B	15	6:15 a.m.	10:00 a.m.	225	1.72	3.5838	3.6061
C	20	6:15 a.m.	10:00 a.m.	225	1.93	3.8520	3.8748
D	16	6:15 a.m.	10:00 a.m.	225	1.80	3.8292	3.8537
E	19	6:15 a.m.	10:00 a.m.	225	1.87	3.5592	3.5833
B	18	10:15 a.m.	2:00 p.m.	225	1.65	3.8385	3.8681
C	21	10:15 a.m.	2:00 p.m.	225	1.95	3.5917	3.6244
D	17	10:15 a.m.	2:00 p.m.	225	1.80	3.5619	3.5960
E	22	10:15 a.m.	2:00 p.m.	225	1.83	3.8424	3.8761

Table B-3. Data Collected June 2-3, 1974

Equilibration Conditions: < 50% Relative Humidity/ 25°C ± 2°C

Sampler	Filter No.	Sampling Period			Elapsed Time (min)	Flow Rate (m ³ /min)	Weights (g)	
		Start	Stop				W _i	W _f
A	23	10:00 a.m.	10:00 a.m.		1440	1.83	3.6341	3.8490
F	24	10:00 a.m.	10:00 a.m.		1440	1.90	3.8228	4.0467
B	28	10:00 a.m.	1:45 p.m.		225	1.82	3.7533	3.7842
C	26	10:00 a.m.	1:45 p.m.		225	1.90	3.7858	3.7984
D	25	10:00 a.m.	1:45 p.m.		225	1.85	3.5885	3.6230
E	27	10:00 a.m.	1:45 p.m.		225	1.93	3.6124	3.6448
B	32	2:00 p.m.	5:45 p.m.		225	1.78	3.7650	3.8007
C	30	2:00 p.m.	5:45 p.m.		225	1.87	3.7330	3.7731
D	29	2:00 p.m.	5:45 p.m.		225	1.86	3.5905	3.6321
E	31	2:00 p.m.	5:45 p.m.		225	1.95	3.6214	3.6634
B	36	6:00 p.m.	11:45 p.m.		345	1.76	3.7517	3.8165
C	34	6:00 p.m.	11:45 p.m.		345	1.77	3.7411	3.8126
D	33	6:00 p.m.	11:45 p.m.		345	1.85	3.6248	3.6975
E	35	6:00 p.m.	11:45 p.m.		345	1.92	3.5956	3.6699
B	40	12:00 p.m.	6:00 a.m.		360	1.78	3.7682	3.8097
C	38	12:00 p.m.	6:00 a.m.		360	1.78	3.8069	3.8527
D	37	12:00 p.m.	6:00 a.m.		360	1.88	3.6113	3.6583
E	39	12:00 p.m.	6:00 a.m.		360	1.90	3.5841	3.6319
B	44	6:15 a.m.	10:00 a.m.		225	1.80	3.7521	3.7859
C	42	6:15 a.m.	10:00 a.m.		225	1.78	3.7644	3.8017
D	41	6:15 a.m.	10:00 a.m.		225	1.89	3.5815	3.6211
E	43	6:15 a.m.	10:00 a.m.		225	1.93	3.6037	3.6433

2.0 DATA COLLECTED FOR THE EQUILIBRATION STUDY

Table B-4. Sample weight as a function of equilibration time,
samples collected by Sampler B,
Environment 1

Equilibration Conditions: < 50% RH/ 25°C

Weight, $W_f(t_E)$, in grams.

t_E = Equilibration time, hours.

Filter No.	W_f (1)	W_f (2)	W_f (4)	W_f (24)	W_i
44	3.7860	3.7858	3.7849	3.7855	3.7521
40	3.8102	3.8093	3.8086	3.8088	3.7682
36	3.8175	3.8164	3.8157	3.8160	3.7517
3	3.6337	3.6335	3.6328	3.6331	3.6048
15	3.6054	3.6052	3.6045	3.6045	3.5838
18	3.8668	3.8666	3.8661	3.8664	3.8385
8	3.8972	3.8963	3.8956	3.8962	3.8342
12	3.8511	3.8502	3.8497	3.8503	3.8167
32	3.7999	3.7996	3.7992	3.7996	3.7650
28	3.7838	3.7835	3.7831	3.7833	3.7533
2 (Sampler F)	4.0289	4.0222	4.0179	4.0179	3.8249
47 (Blank)	3.6244	3.6245	3.6245	3.6250	
48 (Blank)	3.7737	3.7739	3.7740	3.7742	

Table B-5. Sample weight as a function of equilibration time,
samples collected by Sampler C,
Environment 2

Equilibration Conditions: < 10% RH/ 25°C
Weight, $W_f(t_E)$, in grams.
 t_E = Equilibration time, hours.

Filter No.	W_f (1)	W_f (2)	W_f (4)	W_f (24)	W_i
10	3.8866	3.8860	3.8856	3.8859	3.8183
21	3.6231	3.6224	3.6219	3.6222	3.5917
7	3.6542	3.6541	3.6536	3.6535	3.6187
20	3.8741	3.8736	3.8732	3.8730	3.8520
14	3.8948	3.8943	3.8938	3.8935	3.8562
42	3.8009	3.8006	3.8004	3.8001	3.7644
38	3.8522	3.8516	3.8513	3.8512	3.8069
34	3.8122	3.8110	3.8106	3.8112	3.7411
26	3.7969	3.7962	3.7960	3.7959	3.7658
30	3.7715	3.7710	3.7706	3.7706	3.7330
5 (Sampler A)	3.8322	3.8303	3.8295	3.8294	3.6460
49 (Blank)	3.6214	3.6217	3.6217	3.6220	
50 (Blank)	3.6457	3.6453	3.6456	3.6459	

Table B-6. Sample Weight as a function of equilibration time,
samples collected by Sampler D,
Environment 3

Equilibration Conditions: < 10% RH/ 50°C

Weight, $W_f(t_E)$, in grams.

t_E = Equilibration time, hours.

Filter No.	W_f (1)	W_f (2)	W_f (4)	W_f (24)	W_i
6	3.9029	3.9029	3.9019	3.9012	3.8382
17	3.5938	3.5929	3.5936	3.5920	3.5619
4	3.8416	3.8416	3.8412	3.8414	3.8082
11	3.6697	3.6693	3.6685	3.6679	3.6316
16	3.8520	3.8513	3.8500	3.8503	3.8292
41	3.6205	3.6202	3.6194	3.6198	3.5815
37	3.6570	3.6561	3.6551	3.6538	3.6113
33	3.6964	3.6957	3.6949	3.6949	3.6248
25	3.6215	3.6209	3.6211	3.6208	3.5885
29	3.6303	3.6300	3.6293	3.6285	3.5905
23 (Sampler A)	3.8462	3.8444	3.8424	3.8422	3.6341
51 (Blank)	3.7772	3.7772	3.7772	3.7774	
52 (Blank)	3.6086	3.6086	3.6087	3.6089	

Table B-7. Sample weight as a function of equilibration time,
samples collected by Sampler E,
Environment 4

Equilibration Conditions: < 50% RH/ 50°C

Weight, $W_f(t_E)$, in grams.

t_E = Equilibration time, hours.

Filter No.	W_f (1)	W_f (2)	W_f (4)	W_f (24)	W_i
13	3.6965	3.6968	3.6963	3.6961	3.6591
35	3.6678	3.6676	3.6667	3.6658	3.5956
9	3.7063	3.7058	3.7054	3.7050	3.6392
22	3.8747	3.8738	3.8738	3.8735	3.8424
27	3.6431	3.6422	3.6422	3.6428	3.6124
31	3.6614	3.6609	3.6605	3.6607	3.6214
19	3.5820	3.5815	3.5812	3.5816	3.5592
1	3.6699	3.6690	3.6684	3.6685	3.6358
43	3.6423	3.6420	3.6413	3.6417	3.6037
39	3.6298	3.6291	3.6278	3.6271	3.5841
24 (Sampler F)	4.0427	4.0410	4.0391	4.0376	3.8228
53 (Blank)	3.7737	3.7738	3.7735	3.7741	
54 (Blank)	3.6286	3.6283	3.6287	3.6388	

Table B-8. Values of $\bar{y}(t_E)$ and $s(y)$ for varying equilibration times

Environment	t_E	Actual $\bar{y}(t_E)$ (fig. 4)	Comparative $\bar{y}(t_E)$ (fig. 3)	$s(y)$
1	1	0.0200	0.0200	0.0145
	2	0.0145	0.0145	0.0100
	4	0.0077	0.0077	0.0061
	24	0.0000	0.0000	--
2	1	0.0226	0.0200	0.0118
	2	0.0136	0.0110	0.0082
	4	0.0049	0.0023	0.0037
	24	0.0000	-0.0026	--
3	1	0.0367	0.0200	0.0251
	2	0.0274	0.0107	0.0179
	4	0.0153	-0.0014	0.0152
	24	0.0000	-0.0167	--
4	1	0.0246	0.0200	0.0160
	2	0.0180	0.0134	0.0119
	4	0.0097	0.0051	0.0058
	24	0.0000	-0.0046	--

3.0 DATA COLLECTED FOR VALIDATION OF EQUILIBRATION STUDY RESULTS

Table B-9. Sample weight as a function of equilibration time

Weight, $W_f(t_E)$, in grams.
 t_E = Equilibration time, hours.

Environment	Filter No.	W_f (1)	W_f (2)	W_f (4)	W_f (24)	W_i
1	59	3.8787	3.8770	3.8759	3.8755	3.7650
	60	3.7102	3.7090	3.7067	3.7064	3.6032
	61	3.8777	3.8771	3.8748	3.8739	3.7316
	62	3.7447	3.7445	3.7422	3.7410	3.5972
	67	3.9715	3.9704	3.9671	3.9657	3.7810
	68	3.8040	3.8029	3.8000	3.7986	3.6113
2	57	3.8670	3.8657	3.8644	3.8641	3.7564
	58	3.7407	3.7390	3.7380	3.7380	3.6275
	63	3.9051	3.9048	3.9032	3.9030	3.7623
	64	3.7636	3.7636	3.7621	3.7620	3.6178
	73	4.2537	4.2466	4.2404	4.2353	3.7676
	74	4.0899	4.0846	4.0787	4.0743	3.5996
3	55	3.8680	3.8652	3.8634	3.8630	3.7523
	56	3.7098	3.7074	3.7057	3.7049	3.5992
	69	3.9629	3.9589	3.9554	3.9554	3.7693
	70	3.7999	3.7938	3.7907	3.7906	3.6032
	75	4.2754	4.2755	4.2719	4.2682	3.8121
	76	4.2239	4.2185	4.2116	4.2092	3.7606
4	65	3.9059	3.9057	3.9040	3.9022	3.7675
	66	3.7551	3.7549	3.7549	3.7506	3.6240
	71	3.9824	3.9801	3.9785	3.9767	3.7956
	72	3.7882	3.7870	3.7849	3.7820	3.6133
	77	4.2551	4.2491	4.2411	4.2382	3.7907

APPENDIX C

DETERMINATION OF PRECISION FOR SHORT-TERM SAMPLING PERIODS AND VARIOUS EQUILIBRATION CONDITIONS

1.0 INTRODUCTION

The material presented in this section will detail the construction of confidence limits for the coefficients of variation of the 4-hour and 6-hour sampling periods and will propose a technique by which, given a measured suspended particulate concentration determined from either 4- or 6-hour sampling and equilibrated in one of the four environments studied, one can determine with 90 percent confidence the interval in which the true concentration can be found.

2.0 SHORT-TERM SAMPLING STUDY

2.1 Estimation of CV

The sample coefficient of variation (relative standard deviation) is an estimate of the population coefficient, $CV = \sigma/\mu^*$.

This estimate is biased and ref. 1 suggests that following estimate of the population CV based on k samples of size n each:

$$\widehat{CV} = B_n \sum_{j=1}^k \frac{\widehat{CV}_j}{k} \quad (1)$$

$$\widehat{CV}_j = \frac{s'(x)}{\bar{x}} = \frac{\left(\sum_{i=1}^n \frac{(x_i - \bar{x})^2}{n} \right)^{1/2}}{\bar{x}} \quad (2)$$

where

$s'(x)$ = An estimator of the standard deviation of x

\bar{x} = Average of all x_i

B_n = The value such that $E\{B_n s'\}^\dagger = \sigma$ (see table 2 in ref. 1).

*It is assumed that the population of measurements is normally distributed with mean μ and standard deviation σ .

$^\dagger E\{x\}$ is read as average or expected value of x.

Since the usual estimator of the standard deviation (as defined in the short-term sampling study) is given in the form

$$s(x) = \left[\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1} \right]^{1/2} = s'(x) \times \left(\frac{n}{n-1} \right)^{1/2}. \quad (3)$$

The values of B_n listed in ref. 1 were corrected by

$$B_n^* = B_n \left(\frac{n-1}{n} \right)^{1/2}. \quad (4)$$

Table C-1 lists B_n and B_n^* for a few values of n .

Table C-1. Values of B_n and B_n^* such that $E(B_n s') = E(B_n^* s) = \sigma$

n	B_n	B_n^*
2	1.2533	0.8861
3	1.1284	0.9213
4	1.0854	0.9400
5	1.0638	0.9515
6	1.0509	0.9593
10	1.0281	0.9754
15	1.0180	0.9834
20	1.0132	0.9876

Table C-1 indicates that \hat{CV} based on

$$\hat{CV} = \sum_{j=1}^k \frac{CV_j}{k} \quad (5)$$

where

$$\hat{CV}_j = \frac{s_j}{SP_j} \quad (6)$$

will in fact yield a more conservative estimate of the true coefficient of variation than the suggested form of

$$\widehat{CV} = B_n^* \sum_{j=1}^k \frac{\widehat{CV}_j}{k} \quad (7)$$

Hence, equation (6) is recommended for determining the precision of short sampling periods.

2.2 Confidence Interval of CV

The construction of confidence intervals for the true coefficient of variation, CV, based on an estimate, \widehat{CV} , was determined by a simple and accurate approximation presented in ref. 2. For values of CV < 0.2 and assuming that CV is normally distributed, the approximation of the confidence interval for CV is given by the following.

$$\frac{\widehat{CV}}{(1 + r)} < CV < \frac{\widehat{CV}}{(1 - r)} \quad (8)$$

where

$$r = U_\gamma \frac{1}{\sqrt{2N}} \quad (9)$$

U_γ = The standard normal variable whose absolute value (two-tail value) is exceeded with probability $1 - \gamma$ where γ is the confidence level

N = Total number of measurements used in obtaining CV.

3.0 FILTER EQUILIBRATION STUDY

Measured suspended particulate concentrations are determined from samples that have been equilibrated for 24 hours by the following calculation:

$$SP_M = \frac{(W_f - W_i) \times 10^6}{\frac{Q_i + Q_f}{2} \times T} \quad (10)$$

where

SP_M = Measured average suspended particulate concentration, $\mu\text{g}/\text{m}^3$
 W_i = Tare weight of filter, g
 W_f = Weight of filter plus particulates after 24 hours of equilibration, g
 Q_i = Initial airflow rate, m^3/min
 Q_f = Final airflow rate, m^3/min
 T = Sampling time, min.

The equilibration study has indicated that the term W_f varies as the equilibration time, i.e., that W_f decreases exponentially from the beginning of equilibration to reach some equilibrium value as the equilibration time, t_E , approaches 24 hours. Writing W_f as a function of equilibration time, $W_f = W_f(t_E)$ with $W_f(24)$ as the equilibrium value, equation 10 becomes:

$$SP_M = \frac{[W_f(t_E) - W_i] \times 10^6}{\frac{Q_i + Q_f}{2} \times T} \quad (11)$$

with $W_f = W_f(24)$ in equation 10.

The net collected particulate weight at anytime t_E can then be written

$$W_{SP}(t_E) = W_f(t_E) - W_i \quad (12)$$

where $W_{SP}(t_E)$ = Net collected particulate weight at equilibration time, t_E , g.
 Since the reference method for high-volume sampling (ref. 1) indicates 24 hours as the optimum time to allow samples to reach an equilibrium weight, the relative difference between the particulate weight at $t_E < 24$ hours and the equilibrium weight at $t_E = 24$ hours can be given by

$$y(t_E) = \frac{W_{SP}(t_E) - W_{SP}(24)}{W_{SP}(24)} \quad (13)$$

where $y(t_E)$ = Error introduced into the measured particulate weight by equilibrating for $t_E < 24$ hours.

Hence, if a sample is equilibrated for less than 24 hours, the equilibrium particulate weight can be estimated by

$$W_{SP}(24) = \frac{W_{SP}(t_E)}{1 + y(t_E)} \quad (14)$$

Assuming that 24 hours of postsampling equilibration yields the best estimate of the true average suspended particulate concentration, the combination of equations (11), (12), and (14) allows an unbiased estimate of the true average concentration.

$$\hat{SP}_T = \frac{[W_f(t_E) - W_i] \times 10^6}{\frac{Q_i + Q_f}{2} \times T \times [1 + y(t_E)]} = \frac{SP_M}{1 + y(t_E)} \quad (15)$$

where \hat{SP}_T = Unbiased estimate of the true average suspended particulate concentration, $\mu\text{g}/\text{m}^3$.

The 90 percent confidence interval of the true average suspended particulate concentration based on the measured average concentration was derived by taking the natural log of equation (15) and differentiating the resulting expression.

$$\ln SP_T = \ln [W_f(t_E) - W_i] - \ln(Q_i + Q_f) - \ln T - \ln[1 + y(t_E)] \quad (16)$$

$$\frac{d SP_T}{SP_T} = \frac{d[W_f(t_E) - W_i]}{W_f(t_E) - W_i} - \frac{d(Q_i + Q_f)}{Q_i + Q_f} - \frac{dT}{T} - \frac{d y(t_E)}{1 + y(t_E)} \quad (17)$$

Since the estimated variance of dx/x is defined as $s^2(x)/\bar{x}^2 = \hat{CV}^2(x)$

$$\hat{CV}^2(SP_T) = \hat{CV}^2[W_f(t_E) - W_i] + \hat{CV}^2(Q_i + Q_f) + \hat{CV}^2(T) + \hat{CV}^2[1 + y(t_E)] \quad (18)$$

The quantities $\hat{CV}^2[W_f(t_E) - W_i]$
 $\hat{CV}^2(Q_i + Q_f)$, and
 $\hat{CV}^2(T)$

are discussed in reference 3 and will be combined as

$$\hat{CV}(\text{sampling time}) = \{\hat{CV}^2[W_f(t_E) - W_i] + \hat{CV}^2(Q_i + Q_f) + \hat{CV}^2(T)\}^{1/2} \quad (19)$$

CV(sampling time) is the estimated coefficient of variation which describes the variability of measured concentrations resulting from the various sampling period times, i.e., 4-hour, 6-hour, 24-hour sampling.

Therefore,

$$\widehat{CV}(SP_T) = \{\widehat{CV}^2(\text{sampling time}) + \widehat{CV}^2[1 + y(t_E)]\}^{1/2} \quad (20)$$

where

$$\widehat{CV}[1 + y(t_E)] = \frac{s(y)}{1 + y(t_E)} \quad (21)$$

4.0 COMBINED RESULTS

In order to be 90 percent confident that a measured value of the average suspended particulate concentration will be an estimate of a true average of suspended particulate concentration, confidence intervals for the true concentrations which need to be constructed take into account the error in the measured values caused when samples are equilibrated for less than 24 hours and variability which is a function of sampling time.

The bias, the difference between the measured average concentration, SP_M , and the estimated true average concentration, \widehat{SP}_T , is determined in the following manner:

Since

$$\hat{\tau} = SP_M - \widehat{SP}_T \quad (22)$$

and

$$\widehat{SP}_T = \frac{SP_M}{1 + y(t_E)} \quad (15)$$

it follows that

$$\hat{\tau} = SP_M \times \left[\frac{y(t_E)}{1 + y(t_E)} \right] \quad (23)$$

Hence, the confidence interval for the true average suspended particulate concentration based on a measured average concentration is calculated by

$$SP_T = SP_M - \hat{\tau} \pm U_Y \hat{\sigma} \quad (24)$$

where

$$\hat{\sigma} = SP_M \times \{\hat{CV}^2 + \hat{CV}^2[1 + y(t_E)]\}^{1/2}$$

and U_Y for 90 percent confidence is 1.645.

5.0 REFERENCES

1. R. K. Ziegler. "Estimators of Coefficients of Variation Using k Samples." Technometrics 15, No. 2 (May 1973).
2. B. Iglewicz and R. H. Myers. "Comparison of Approximations to the Percentage Points of the Sample Coefficients of Variation." Technometrics 12(1970):166-70.
3. U.S. Environmental Protection Agency. Guidelines for Development of a Quality Assurance Program: Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method). EPA-R4-73-028b, Washington, D.C., June 1973.