

FINAL REPORT

on

INTERLABORATORY COOPERATIVE STUDY OF THE PRECISION OF THE MEASUREMENT OF PARTICULATE MATTER

IN THE ATMOSPHERE (Optical Density of Filtered Deposit) **USING ASTM METHOD D1704**

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INTERLABORATORY COOPERATIVE STUDY OF THE PRECISION OF THE MEASUREMENT OF PARTICULATE MATTER IN THE ATMOSPHERE (OPTICAL DENSITY OF FILTERED DEPOSIT) USING ASTM METHOD D 1704

by

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

INTRODUCTION

This report presents the results obtained from an experimental study of the variability inherent in measurements of particulate matter in the atmo sphere using ASTM Method D 1704 $(1)^*$. This procedure measures the optical density of particulate deposits filtered from a measured quantity of ambient air. The report includes a description of the experimental program, together with tabulations of the data and the statistical interpretations of the results.

The evaluation of ASTM Method D 1704 was performed as part of the first phase of Project Threshold, a comprehensive program to validate ASTM methods of measuring atmospheric contaminants. In addition, methods for measuring the content of nitrogen dioxide (D 1607), sulfur dioxide (D 2914), lead (D 3112), dustfall (D 1739), and total sulfation (D 2010) in the atmosphere have also been evaluated during Phase 1.

SUMMARY OF RESULTS

This report presents information obtained from an interlaboratory evaluation of a reference method for measuring the particulate matter in the atmosphere by the tape sampler technique.

The testing program, identified as Project Threshold and sponsored by the American Society for Testing and Materials, was coordinated by Battelle-Columbus. The test method, designated as ASTM Standard D 1704-61, was conducted by a total of eight laboratories. The atmosphere was sampled at three different geographical locations for periods ranging from 30 minutes to 24 hours.

 $\overline{\mathbf{x}}$ References at end of report.

A statistical analysis of 806 determinations of particulate matter in the atmosphere at the three different sites provides the following results:

> • The average standard deviation, s_h , for variations among single measurements taken by different laboratories (reproducibility) is related to the mean soiling index, m, as follows:

$$
s_{b} = 0.193 + 0.367m,
$$

where, s_{h} , and, m, are expressed in Cohs per 1000 linear feet.

• The standard deviation of 86 duplicate measurements of the optical density of the same spot by one laboratory at one site (Manhattan), is 0.55 Cohs per 1000 linear feet.

In addition to the measure of reproducibility this report contains the statistical design of the experimental program, a complete tabulation of the experimental data and a comprehensive presentation of descriptive statistics.

EXPERIMENTAL PROGRAM

ASTM Method of Test

The ASTM method for measuring particulate matter in the atmosphere, D 1704-61, which was evaluated is given in the Appendix. In this method particulate matter in atmospheric air is collected on a defined area of the surface of a white filterpaper tape by drawing a known volume of air into the one end of a tube and through filter paper at the opposite end. The sample area is defined by the inner cross section of the tube. The tube edge is sealed by pressure against the paper by the mating end of a coaxial tube of the same diameter so that sample flow is directed through a circular area of the paper.

Sample is collected for a time period estimated to accumulate a deposited layer with an optical density of 0.05 to 0.30. The apparatus incorporates a roll of the filter paper tape, which is advanced to expose a clean area to the sample stream at the end of each period, so that a succession of spots of collected material represents consecutive exposure times.

 $\overline{2}$

Many apparatuses have timers and automatic tape-advance mechanisms, which permit them to draw consecutive samples while unattended.

Optical density of each deposit is measured by determining the attenuation of a light beam after transmission through the filtered sample and its supportive paper for comparison with the initial transmission through the same area before the sample was deposited. In some instruments the net optical density of the deposit alone is measured by manually setting the meter to indicate 100 percent transmission when the beam is applied to a virgin area of the filter contiguous to each spot, and then reading the percentage transmission through the spot. Both integral and separate spot evaluator units were used for the transmission measurements.

Instrumentation

Each cooperating laboratory supplied its own instrument for making the measurements. Six were A.I.S.I. Automatic Smoke Samplers, Model F-2, manufactured by Research Appliance Corporation which deposit the filtered particulate matter in a 1-inch-diameter spot. Two were Gelman Instrument Company's Sentinel, which produce a 1/2-inch-diameter spot. Data were reported in Cohs per 1000 linear feet, as specified by the method.

Data normalized to optical density per unit linear flow are completely independent of the type of sampler used, so that air may be sampled at any desired rate, using any convenient area of paper. Cooperators were instructed to adjust the flow rate on each sampler to the same linear velocity, equivalent to 0.25 cfm through a circular area 1 inch in diameter.

At the indoor installations at Bloomington and Manhattan each instrument was equipped with a short sampling probe of flexible tubing extending through a window and terminating near the outside wall below the sill in a flared end covered with 325-mesh metal screen to exclude large particles. The inlet was directed vertically downward to preclude intake of falling particles.

Calibration of Instruments

It was impractical to generate a standard sample of suspended particulate matter in the atmosphere from which filtered deposits of identical optical density could be collected by each instrument. In most cases, the photometer of each tape sampler was calibrated using an optical density standard. All photometers used wide-band monochromatic light (375-450 nm).

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Test Sites

Site No. 1, Los Angeles, California

Each instrument was placed on a raised support above the parapet level and near the corner of the roof top of the Hancock Foundation building on the campus of the University of Southern California. Figure ¹ shows a view of several installations on the roof top. Sampling was performed during the period of August 16 to August 21, 1971.

Site No. 2, Bloomington, Indiana

The test site was a vacant greenhouse of Indiana University Department of Botany located in an isolated experimental plot on the edge of the city. Tape samplers were placed on a long table along one side of the test area near the movable windows of the greenhouse wall. The flexible probes were extended through the slightly opened windows, and samples were taken near the outside wall. Figures ² and ³ are interior and exterior views of the installations. Sampling was performed during the period of October 24 to October 30, 1971.

Site No. 3, Manhattan, New York City

The tape samplers were placed at sill level next to a row of windows on the north side of the sixth floor of Cooper Union, 51 Astor Place, New York City. The probes extended through the windows and hung downward ^a short distance at the building wall which bordered Ninth Street. Sampling was performed during the period of January 9 to January 15, 1972.

Selection of Test Periods

The length of each test period was selected with the following objectives:

FIGURE 1. TAPE SAMPLER INSTALLATION ON THE ROOF TOP SITE AT LOS ANGELES

FIGURE 2. TAPE INSTALLATION AT THE BLOOMINGTON SITE

FIGURE 3. TAPE SAMPLER PROBE ARRANGEMENT AT THE BLOOMINGTON SITE

- (a) to produce all spots within the optical density range of 0.05 to 0.30 specified by Method D 1704
- (b) to complete the series of tests within the five consecutive 24-hour periods during which other methods were being tested simultaneously
- (c) to make synchronous changes of filter tape on each instrument, so that optical densities would be comparable from all instruments during each test period
- (d) to obtain an equal number of samples in each of two groups, representing optical densities near the upper and lower limits of the permitted optical density range
- (e) to minimize attention to the instruments at night and to use the automatic paper-change timer of each instrument, as much as possible.

The amount of particulate loading differed at each site, and with the time of day particularly at Site No. 3, Manhattan; it was therefore impossible to meet all the objectives listed above.

Table 1 shows the test schedule at Site 1, Los Angeles. Particulate loading was relatively low so the duration of the sampling periods were selected to be 8 hours, 12 hours, and 24 hours.

(a) Times varied slightly among laboratories, because tape changes were made within an interval between other tests.

In analysis of the Site ¹ data, the 8 and 12-hour tests and the 23 and 24-hour tests are designated short and long duration tests, respectively. In performing the tests, it was not possible to synchronize all sampling periods exactly. However, slight variations of a half hour or so in the length of simultaneous sampling periods should be immaterial since the sampling periods were long (8-24 hours) and comparable data, Cohs per 1000 linear feet, are obtained even though sampling duration and volumes are different.

Table 2 gives the test schedule at Bloomington, where particulate loading was so low that 24-hour samples were necessary to achieve measurable optical densities of the filtered deposits. The same considerations as to the exact synchronization of tape changes applied at Bloomington as at Los Angeles.

Test Number	Sampling Duration, hr ^(a)	Sampling Date-Time ^(a) Stop Start				
1	24.5	$10/24 - 1700$	$10/25 - 1730$			
$\overline{2}$	23.5	$10/25 - 1730$	$10/26 - 1700$			
3	23.5	$10/26 - 1700$	$10/27 - 1630$			
4	24.	$10/27 - 1630$	$10/28 - 1630$			
5	36.5	$10/28 - 1630$	$10/30 - 0500$			

TABLE 2. SCHEDULE OF TAPE SAMPLER TESTS AT BLOOMINGTON

(a) Times varied slightly among laboratories, because tape changes were made within an interval between other tests.

Table 3 gives the time schedule for 88 tests performed at Manhattan, where traffic patterns in the street below undoubtedly contribute to rapid variations and peak periods in the concentration of particulate matter in the atmosphere. Here, exact tape changes synchronization was attempted by specifying the exact sampling time for short periods during the day and longer periods by the automatic-change timers during unattended overnight periods. In general,

Test Number	Sampling Duration, hr (a)	Sampling Date -Time ^(a) Start Stop			
$\mathbf{1}$	15:00	-1700 1/9	$1/10 - 0800$		
$\overline{2}$	2:30	$1/10 - 0800$	$1/10 - 1030$		
$3 - 11$	0:40	$1/10 - 1100$	$1/10 - 1700$		
$12 - 194$	2:00	$1/10 - 1700$	$1/11 - 0900$		
$20 - 23$	0:30	$1/11 - 0900$	$1/11 - 1100$		
$24 - 32$	0:40	$1/11 - 1100$	$1/11 - 1700$		
$33 - 40$	2:00	$1/11 - 1700$	$1/12 - 0900$		
41	1:00	$1/12 - 0900$	$1/12 - 1000$		
$42 - 45$	0:40	$1/12 - 1000$	$1/12 - 1240$		
46,47	1:00	$1/12 - 1240$	$1/12 - 1440$		
$48 - 56$	2:00	$1/12 - 1440$	$1/13 - 0840$		
$57 - 70$	0:40	1/13 - 0840	$1/13 - 1800$		
$71 - 88$	2:00	$1/13 - 1800$	$1/15 - 0800$		

TABLE 3. SCHEDULE OF TAPE SAMPLER TESTS AT NEW YORK CITY

(a) Operators were instructed to use this pattern, but actual cycle lengths varied occasionally because of malfunctions. Each apparatus was readjusted into phase as soon as possible. Actual times were recorded and reported by each laboratory.

the long periods were two hours each, because this was the maximum change period setting on several timers. An approximately equal number of short and long test periods were specified. Short periods were varied to include sequences of 30 minutes, 40 minutes, or 60 minutes each in attempting to match, optical density of the collected sample with anticipated atmospheric variations at the test site. On ^a few occasions there were instrument or timer malfunctions, so that synchronization was incomplete. The data are therefore separated into 44 approximately isochronous groups for statistical analysis as described in detail in following sections.

Participating Laboratories

The participating laboratories were:

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

Throughout this report the identity of the participants is concealed by using a set of code letters. Each participant is supplied the key to the code letters for himself in all data tables, but no key for the other participants.

ANALYSIS OF PARTICULATE MATTER DETERMINATIONS

Tables 4, 5, and 6 show the results of the measurements of particulate matter by the tape sampler method at Los Angeles, Bloomington, and Manhattan, respectively. The formats of these three tables differ slightly. In the first column of each table appears a letter identification code for each laboratory, which was adopted to conceal the identity of the laboratory from which the associated data originated. The second column of each table gives the test number. The remaining columns of each table contain data for each laboratory. Laboratory E reported two readings for each spot. The readings are duplicate determinations for the same spot with the spot evaluator.

In Table 4, the third column indicates whether the nominal exposure time is 24 hours (L) or 8 hours (S). In Table 6, the third column indicates the day of the month on which the test was conducted, and the fourth column gives the starting time of each test run.

The test numbers in Table 6 should run from 1 to 88, however, some laboratories did not perform all 88 tests. In other cases, some laboratories used slightly different test designations which resulted in more than 88 measurements. In analysis of the data, measurements were grouped by time period and not necessarily by test number.

Table 7 shows the sampling pattern at Manhattan by laboratory and day. During this more comprehensive test program seven laboratories made a total of 697 measurements.

TABLE 4. DATA FROM MEASUREMENTS OF PARTICULATE MATTER AT LOS ANGELES, SITE 1, USING ASTM ^D 1704

(a) Data not reported.

Laboratory	Test Number	Sampling Duration	Sampling Time, hr	Sample Volume, cu ft	Coh/1000 Linear Feet		
${\bf E}$	$\begin{array}{c} 1 \\ 2 \\ 3 \end{array}$ $\mathbf{4}$ 5 6 $\overline{7}$	L S S S L $\frac{S}{S}$	16.9 7.7 7.6 8.4 23.8 10.4 13.7	(a) ditto † Ħ $\pmb{\mathsf{H}}$ H. \mathbf{H}	$\overline{\text{4D}}$ 0.548(c)0.558(c) 1.099 1.099 0.527 0.555 0.620 0.665 0.712 0.673 1.271 1.339 0.381 0.445		
$\mathbf F$	8 $\pmb{1}$ $\overline{\mathbf{c}}$ $\overline{\mathbf{3}}$ $\mathbf{t}_\mathbf{p}$ 5	L \mathbf{L} s s s	23.5 24. 8. 8. 8. 24.	$\pmb{\mathfrak{m}}$ (a) ditto Ħ \mathbf{H} $\pmb{\mathsf{H}}$	0.580 0.599 0.190 0.039 0.059 0.206 0.106		
${\bf G}$	6 7 $\bf{8}$ $\mathbf i$	L $\overline{\mathsf{s}}$ S \mathbf{L} L	12. 12. 24. 24.0	Ħ 11 Ħ 508.3	0.474 0.355 0.090 0.194 0.345		
	$\overline{\mathbf{c}}$ $\overline{\mathbf{3}}$ 4 5 6 $\overline{7}$ 8	s S S L $\overline{\mathsf{S}}$ s L	8.0 $8 - 0$ 7.9 24.0 12.0 12.0 24.0	170.4 169.5 167.8 598.8 255.3 253.1 508.1	0.147 0.213 0.208 0.344 0.120 0.186		
$\, {\rm H}$	$\mathbf 1$ $\frac{2}{3}$ $\mathbf{f}_\mathbf{+}$ 5 6 $\overline{\mathbf{r}}$ 8	L s s s L $\frac{S}{S}$ L	23.5 8. 8.5 8. 23.5 11.8 12.5 22.5	(a) ditto Ħ Ħ Ħ п \mathbf{H} 11	0.24 0.38 0.20 0.30 0.24 0.26 0.22 $0 - 20$		

TABLE 4. (Continued)

(a) Data not reported.
(b) Duplicate measurement of the same spot.

(c) Test 1 readings were not used in statistical analysis since sampling period was not concurrent with other laboratories.

TABLE 5. DATA FROM MEASUREMENTS OF PARTICULATE MATTER AT BLOOMINGTON, SITE 2, USING ASTM D 1704

(a) Data not reported.

 $\frac{1}{2}$, $\frac{1}{2}$

(b) Duplicate measurement of the same spot.

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TABLE 6. DATA FROM MEASUREMENTS OF PARTICULATE MATTER AT MANHATTAN, SITE 3, USING ASTM D 1704

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(a) Duplicate measurement of the same spot.

(a) Duplicate measurement of the same spot.

Laboratory	Test Number	Day	Start Time	hr	Sampling Time min	min	Sample Volume, cu ft	Coh/1000 Linear Feet
F	56	13	0840	0	40	40		4.71
F	57	13	0920	$\boldsymbol{0}$	40	40		2.96
F	58	13	1900	0	40	40		2.44
F	59	13	1040	0	40	40		2.96
F	60	13	1120	0	40	40		3.23
F	61	13	1200	O	40	40		3.50
F	62	13	1240	$\mathbf 0$	40	40		2.96
F	63	13	1320	O	40	40		2.70
F	64	13	1400	0	40	40		3.36
F	65	13	1440	0	40	40		4.48
F	66	13	1520	0	40	40		5.14
F	67	13	1600	0	40	40		4.48
F	68	13	1640	0	40	40		3.72
F	69	13	1720	0	40	40		2.70
F	70	13	1800	\mathbf{z}	0 ₀	120		1.31
F	71	13	2000	$\overline{\mathbf{c}}$	0 ₀	120		1.69
F	72	13	2200	2	0 ₀	120		1.50
F	73	14	0000		0 ₀	120		0.63
F	74	14	0200	2 2 2 2 2	0 ₀	120		0.42
F	75	14	0400		0 ₀	120		0.59
F	76	14	0600		0 ₀	120		0.93
F	77	14	0500		0 ₀	120		1.29
F	78	14	1000	$\begin{array}{c} 2 \\ 2 \\ 2 \end{array}$	0 ₀	120		0.99
F	79	14	1200		0 ₀	120		$0 - 86$
$\mathsf F$	80	14	1400	$\overline{\mathbf{c}}$	0 ₀	120		0.99
F	81	14	1600		0 ₀	120		1.04
F	82	14	1800	$\begin{array}{c} 2 \\ 2 \\ 2 \end{array}$	0 ₀	120		1.26
F	83	14	2000		0 ₀	120		1.40
F	84	14	2200		$0\hat{u}$	120		1.36
F	85	15	0000	$\begin{array}{c} 2 \\ 2 \\ 2 \end{array}$	0 ₀	120		1.04
F	86	15	0200		0 ₀	120		1.59
F	87	15	0400	\overline{c}	0 ₀	120		1.40
F	88	15	0600	$\mathbf{1}$	53	113		1.48

TABLE 6. (Continued)

L,

 $\hat{\boldsymbol{\gamma}}$

TABLE 7. NUMBER OF MEASUREMENTS AT MANHATTAN BY LABORATORY AND DAY

STATISTICAL MEASURES OF THE TEST METHOD

Reproducibility

In accordance with the experimental design for all tests, seven or eight laboratories simultaneously sampled and analyzed ambient atmospheres that should have contained the same concentration of particulate matter. Differences among determinations from simultaneous samples represent a measure variability between laboratories in application of the Test Method. The average standard deviation of all such samples by all laboratories is a measure of precision of the Test Method which in this report is called "reproducibility" and is denoted by the symbol, s_t .
Repeatability

In order to measure repeatability, i.e., a laboratory's ability to obtain the same result for duplicate samples, it would be necessary for a given laboratory to obtain duplicate pairs of samples by sampling simultaneous with at least two instruments. Experiments to determine repeatability, as defined here, were not included in the experimental design. However, data reported by one laboratory (E) provide a measure of precision of the optical density measurement through the use of duplicate readings of the same tape sampler spot.

Additional discussions of the concepts of reproducibility and repeatability are presented by Mandel⁽²⁾ and in ASTM publications^(3,4).

Analysis of Variance

The statistical analysis of the tape sampler determinations takes into account the variability of the data arising from several sources. The amount of particulate matter in the atmosphere varies from site to site, day to day, and even hour to hour. Even if the concentration of particulate matter remains constant, different laboratories would probably not find the same amount of particulate matter in their samples, nor would the same laboratory often find the same amount of particulate matter in two identical samples. All of these effects combine to produce the variability observable in the determinations reported by the test laboratories. The burden is on the statistical analysis to partition the total variability of the data into components associated with the primary sources of variability. The numerical procedure for this partitioning is called analysis of variance. This kind of analysis is adaptable to many situations, including the nested design with unequal subsamples encountered here. Although the assumptions implied by such an analysis are not completely satisfied by the tape sampler data, the conclusions from the results of the statistical analysis are not likely to be seriously affected by this shortcoming. For a good account of the underlying theory of nested designs, including formulas for computing the

coefficients of the components of variance in the expressions for the expected mean squares, the reader is referred to Kempthorne⁽⁵⁾ and Scheffe⁽⁶⁾.

Components of Variance

An analysis of variance was performed on the data for each site using the tape sampler results in Tables 4, 5, and 6.

Table 8 shows an analysis of variance for measurements of particulate matter at Los Angeles (Site l). The last row of the table shows that the sum of squared deviations (SSD) for the variation between measurements within laboratories is equal to 0.00671. This number is obtained from the ⁷ pairs of duplicate measurements representing ⁷ degrees of freedom (df) made by Laboratory E. If x_1 and x_2 denote a pair of duplicate measurements made by Laboratory E, then these two measurements contribute an amount equal to $(x_{2} - x_{1})^{2}/2$ to the SSD for the last row. If x_{1} and x_{2} are nearly equal, then this contribution to the SSD is small. The value 0.00671 thus represents the sum 65 $(x_2-x_1)^2/2$ for every duplicate pair of measurements made by Laboratory ^E at Los Angeles. The average SSD for the ⁷ pairs of measurements is given by the mean square (MS) shown in the table as 0.00096, the ratio of 0.00671 to 7. This mean square is denoted by $\frac{2}{w}$ and is called the within-laboratory variance. The precision of the measurements is then represented by $\sqrt{0.00096}$ = 0.031 Cohs per 1000 linear feet. This number serves as a statistical estimate of one standard deviation for these measurements. As noted earlier, this estimate does not represent repeatability, as ordinarily defined, but it does represent an measure of the precision of the optical density measurement.

The agreement between laboratories within a test period is associated in the table with an SSD equal to 4.12634. This number is obtained from the sum of squares given by

TABLE 8. ANALYSIS OF VARIANCE OF DETERMINATIONS OF PARTICULATE MATTER AT LOS ANGELES $(SITE 1)(a)$

(a) Column headings: SSD, sum of squared deviations from the mean; df, degrees of freedom; MS, mean square; s, standard deviation.

$$
\sum n_i (\overline{x}_i - \overline{x})^2,
$$

were, \bar{x}_i denotes the measurement value obtained by the ith laboratory, and x denotes the arithmetic mean of the measurements obtained by all laboratories for a given test period. This expression is also summed over test periods to obtain the number given in the table. For the laboratory making duplicate measurements, \overline{x}_i is taken to be the average of the two measurements, and the mean is given a weight of 2 so that $n_i = 2$. For the laboratories which made a single determination in a given test period, \bar{x}_i is equal to that determination and n_i is 1.

The agreement between laboratories within a test period is associated with a mean square equal to 0.07502. This mean square is algebraically represented by $s_{12}^2 + K s_{12}^2$, where s_{12}^2 denotes the within-laboratory variance, s_h^2 denotes the between-laboratory variance, and K denotes a weighted average

number of runs per lab⁽⁵⁾. An estimate of the variability (s_b²) among laboratories can be derived by taking the difference between these two mean squares, $(s_w^2 + K s_b^2)$ - (s_w^2) , and dividing by K. Application of this procedure to the results in Table 8 gives $(0.07502 - 0.00096)/K = 0.0676$ for the variance among laboratories, and $\sqrt{0.0676}$ = 0.260 Cohs per 1000 linear feet for the corresponding standard deviation (s_h) . This standard deviation represents the reproducibility of the pooled tape sampler determinations at Los Angeles.

 ϵ

Although large variations were expected to occur between tests, and were possibly expected between short and long time spans, these variations were not of primary interest in this program. They are included in the table simply to show the relationship of variations due to laboratories and to time differences between test periods.

Table 9 shows an analysis of variance for measurements of particulate matter at Bloomington (Site 2). This analysis is similar to the analysis for Los Angeles described above, with one exception. In that analysis, there was a component of variance between short and long duration tests which is absent in the analysis for Bloomington. The between-measurement variation in particulate matter is given by $\sqrt{0.00152}$ = 0.039 Cohs per 1000 linear feet. The betweenlaboratory variation in the measurement of particulate matter is given by $(0.02856 - 0.00152)/K = 0.0240$ for the variance among laboratories, and $\sqrt{0.0240}$ = 0.155 Cohs per 1000 linear feet for the corresponding standard deviation (s) of the pooled measurements.

Table 10 shows an analysis of variance for measurements of particulate matter at Manhattan (Site 3). The statistical treatment is similar to the analysis for the Los Angeles and Bloomington data described above. Only about half of the data from the Manhattan tests were used in the analysis which is summarized in Table 10. Data from the Manhattan tests were initially divided into 88 groups. In these groupings, not all laboratories started or terminated sampling at exactly the same time; therefore these data include changes in particulate concentration with time. To eliminate this shortcoming, the Manhattan data were selected and compiled into 44 tests, as shown in

TABLE 9. ANALYSIS OF VARIANCE OF DETERMINATIONS OF EXPARTICULATE MATTER AT BLOOMINGTON (SITE 2)^(a)

- (a) Column headings: SSD, sum of squared deviations from the mean; df, degrees of freedom; MS, mean square; s, standard deviation.
- (b) This variation could not be calculated because the averages for different spots were more nearly equal than the measurements by different laboratories. The model for computing "s" does not hold in this case.

TABLE 10. ANALYSIS OF VARIANCE OF DETERMINATIONS OF PARTICULATE MATTER AT MANHATTAN (SITE 3)^(a)

(a) Column headings: SSD, sum of squared deviations from the mean; df, degrees of freedom; MS, mean square; s, standard deviation. **Table 11, in which all laboratories started and terminated at the same time (within ten minutes) in each group.** It is these **44** tests which were used to **obtain the results presented in Table 10.**

							Sample			
Labora-	Test		Start		Sampling Time			Linearo ³)	Coh/1000	
tory	Number	Day	Time	hr	min	min	cu ft		Linear Feet	
A	$\mathbf{1}$	9	1700	15	10	910	173.55		0.937	
\pmb{B}		9	1720	14	40	880	59.0		1.598	
C		9	1700	15	0 ₀	900			1.15	
		9	1700	15	00	900			1.01	
$\frac{1}{2}$		9	1700	15	00	900			1.76	1.69
F		9	1700	14	20	860			0.58	
G		9	1705	14	55	895	312.982	57.428	0.65	
A	\overline{c}	10	0810	\mathbf{c}	20	140	33.79		3.36	
8		10	0800	2	30	150	10.1		5.541	
C		10	0800	\overline{c}	30	150			3.88	
D		10	0800	2	30	150			3.36	
E F		10	0800	$\overline{\mathbf{1}}$	53	113			4.11	5.10
		10	0800	2	45	165			0.29	
Ġ		10	0800	\overline{c}	30	150	52.590	9.650	2.37	
A	ϵ	10	1300	û	48	40	9.65		3.20	
\pmb{B}		10	1310	û	40	40	2.68		4.568	
$\mathbf c$		10	1300	û	40	40			6.56	
$\mathbf 0$		10	1300	Ø	40	40			$3 - 20$	
E		10	1300	0	40	40			7.54	7.86
F		10	1300	û	40	40			0.94	
G		10	1300	D	$7 - 0$	40	14.056	2.579	3.13	
A	\overline{r}	10	1340	O	40	40	9.65		2.86	
8		10	1350	Đ	40	40	2.68		6.823	
$\mathbf c$		10	1340	ū	40	40	\bullet		5.41	
$\mathbf 0$		10	1340	Û	48	40			2.64	
E		10	1340	Ũ	40	40			6.43	7.62
F G		10	1340	O	40	40			0.58	
		10	1340	Û	40	40	14.068	2.581	2.73	

TABLE **11.** MANHATTAN, SITE 3, DATA ARRANGED INTO **44 ISOCHRONOUS** TESTS GROUPS

								Sample				
Labora-	Test		Start	Sampling Time				Linear		Coh/1000		
tory	Number	Day	Time	hr	min	min	cu ft	$_{\text{Fect}}(10)$		Linear Feet		
A	8	10	1420	$\mathbf{0}$	40	40	9.65	\bullet	5.01			
8		10	1430	0	40	40	2.68	\bullet	5.648	\bullet		
$\ddot{\mathbf{c}}$		10	1420	O	40	40	\bullet	\bullet	7.65	\bullet		
$\ddot{\mathbf{0}}$		10	1420	O	40	40	٠	٠	3.78	٠		
$\pmb{\mathsf{E}}$		10	1420	0	40	40			7.07	8.49		
F		10	1420	a	48	40			0.70			
$\mathbf G$		10	1420	û	48	40	14.068	2.581	3.33			
$\pmb{\mathbb{A}}$	9	10	1500	$\mathbf{0}$	40	40	9.65	\bullet	4.13	\bullet		
8		10	1510	0	48	40	2,68	\bullet	6.763			
C		10	1500	O	48	40	\bullet	\bullet	7.40			
D		10	1500	0	40	40	\bullet	\bullet	2.92			
		10	1500	0	40	40			7.30	6.27		
EF		10	1500	0	40	40			0.58	\bullet		
G		10	1500	Ū	40	40	14.068	2.581	3.13			
A	10	10	1540	$\mathbf{0}$	40	40	9.65	\bullet	4.71			
8		10	1550	O	40	40	2.68	\bullet	6.585			
C		10	1540	0	40	40	\bullet		7.95			
D		10	1540	0	20	28	\bullet		4.15			
E		10	1540	O	40	40	\bullet		9.53	8.97		
F		10	1540	$\bf{0}$	40	40			0.94	۰		
$\ddot{\mathbf{G}}$		10	1540	o	40	40	14.064	2.581	3.75			
A	14	10	2100	\mathbf{z}	0 ₀	120	24.82	\bullet	4.11	٠		
8		10	2100	\overline{c}	D D	120	$8 - 04$	\bullet	6.170			
C		10	2050	\overline{c}	00	120	\bullet	\bullet	6.14	\bullet		
D		10	2110	1		37.5 97.5	\bullet		4.69			
E		10	2100	$\overline{\mathbf{c}}$	00	120	\bullet		7.12	6.75		
F		10	2100	$\overline{\mathbf{c}}$	00	120			1.08			
Ġ		10	2100	$\overline{2}$	0 ₀	120	42.192	7.742	2.95			
A	17	11	0300	2	00	120	24.74	\bullet	2.63			
\bf{B}		11	0300	$\overline{\mathbf{c}}$	0 ₀	120	8.04	\bullet	4.153			
C		11	8250	\overline{c}	0 O	120	\bullet	\bullet	3.90			
$\mathbf 0$		11	0257.5	$\mathbf{1}$	40	100	\bullet	\bullet	2.69			
ε		11	0300	\overline{c}	0 O	120	\bullet		6.88	6.96		
F		11	0300	\overline{c}	0 ₀	120			0.73	\bullet		
G		11	0300	\overline{c}	0 ₀	120	42.168	7.737	1.61			

TABLE 11. (Continued)

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TABLE 11. (Continued)

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							Sample			
Labora-	Test		Start		Sampling Time		Linear		Coh/1000	
tory	Number	Day	Time	hr	min	min	cu ft	Fect(10)	Linear Feet	
A	59	13	1040	0	40	40	9.66		4.42	٠
		13	1040	Ü	40	40	2.68	\bullet	4.153	٠
$\frac{\mathbf{B}}{\mathbf{C}}$		13	1040	IJ	40	40	\bullet		4.67	٠
$\pmb{0}$		13	1036	O	40	40			1.58	
E		13	1040	0	40	40			9.16	9.24
F		13	1040	0	40	40			2.96	
G		13	1040	0	40	40	13.964	2.562	2.95	\cdot \bullet
A	69	13	1120	0	40	40	9.66		4.29	
B		13	1120	0	40	40	2.68	٠	3.933	۰
$\mathbf c$		13	1120	0	40	40				٠
		13	1116	0	40	40	\bullet		5.81	\bullet
$\pmb{0}$ $\pmb{\mathsf{E}}$		13	1120	0	40	40			2.36	
				O	40	40			6.16	5.92
$\mathsf F$ G		13 13	112u 1120	0	40	40	13.980	2.565	3.23 2.95	
				Ĵ	40	40				
Α	61	13	1200	O	40	40	9.66	\bullet	4.42	
B		13	1200	0	40	40	2.68		4.153	
$\mathbf C$		13	1200	0	40	40	٠		5.14	٠
$\mathbf 0$		13	1156						2.61	
E		13	1200	0	40	40			5.97	7.54
F		13	1200	0	40	40			3.50	
G		13	1200	0	40	40	13.988	2.567	3.15	
A	62	13	1240	Û	40	40	9.66	٠	4.27	
8		13	1240	0	40	40	2.68		4.764	
$\mathbf C$		13	1240	0	40	40	٠		5.98	
$\boldsymbol{0}$		13	1236	0	40	40			2.61	
E		13	1240	0	40	40			5.92	7.78
F		13	1240	0	40	40			2.96	٠
G		13	1240	0	40	40	13.980	2.565	2.95	٠
Α	63	13	1320	0	40	40	9.66	\bullet	5.31	
8		13	1320	0	40	40	2.68	\bullet	5.832	
C		13	1320	O	40	40	٠		7.06	
$\pmb{0}$		13	1316	0	40	40			2.95	٠
E		13	1320	Û	40	40			11.10	8.02
		13	1320	Û	40	40			2.70	\bullet
$\frac{F}{G}$		13	1320	0	40	40	13.980	2.565	3.15	
A	64	13	1400	J	40	40	9.66		5.16	
8		13	1400	0	40	40	2.68		6.170	
$\mathbf c$		13	1400	Ū	40	40	\bullet		7.91	
$\pmb{\mathsf{D}}$		13	1356	Ü	44	44			2.63	
		13	1400	0	40	40			6.81	7.29
E F		13	1400	0	40	40			3.36	
Ġ		13	1400	0	40	$\boldsymbol{4}$ 0	13.992	2.567	3.90	

TABLE 11. (Continued)

Analysis of Tests

Tables 12, 13, and 14 show a detailed analysis of tape sampler determination for each test at each of the three test sites. Each row, corresponding to a given test at a given site, contains the mean value of particulate matter, the between-laboratory standard deviation, and the coefficient of variation relating these two statistics. In test 2 at Los Angeles, for example, the table shows that number of measurements (n) is equal to 9; the mean tape sampler determination (m) for these measurements is 0.639 Cohs per 1000 linear feet; the between-laboratory variation (reproducibility) is given by s_b = 0.401 Cohs per 1000 linear feet based on ⁷ degrees of freedom (df); and the associated coefficient of variation (CV), obtained from the ratio s_h/m , is 63 percent. The summary rows that appear at the bottom of each table give the associated totals for n and df, and the average values for m, s_{h} , and CV.

Relationship of Standard Deviation to Mean

The 57 paired values of mean concentration (m) and between-laboratory standard deviation (s_b) in Tables 12, 13, and 14 are plotted in Figure 4. This graph reveals a marked correlation between m and s, which is supported by the correlation coefficient (r) of 0.80. The regression line shown in the figure, which was computed by the method of least squares, has the equation,

 $s_L = 0.193 + 0.367$ m.

Analysis of Duplicate Measurements

Duplicate readings of the same spot $(R_1$ and $R_2)$ obtained at all sites by Laboratory ^E by the spot evaluator are plotted in Figure 5. The line in the figure labeled $R_1 = R_2$ represents perfect agreement between duplicate measurements. The overall standard deviation of the 86 duplicate optical density measurements by Laboratory E at the Manhattan site is 0.55 Coh per 1000 linear feet.

Test	Test			Between-Lab Variation			
Duration	Number	$\mathbf n$	m	df	$s_{\mathbf{b}}$	(%) CV	
Short	$\overline{2}$	9	0.639	7	0.401	63	
	3	9	0.268		0.171	64	
	4	9	0.395	7	0.167	42	
	6	9	0.712		0.439	62	
	7	9	0.286	7	0.134	47	
	A11	45	0.460	35	0.293	64	
Long	$1^{(b)}$	7	0.284	6	0.129	45	
		9	0,360		0.212	59	
	8	9	0.336		0.194	58	
	$_{A11}$ ^(b)	25	0.330	20	0.185	56	

TABLE 12. BETWEEN-LABORATORY VARIABILITY (REPRODUCIBILITY) OF DETERMINATIONS OF PARTICULATE MATTER AT LOS ANGELES (SITE 1) ACCORDING TO TEST DURATION AND TEST(a)

(a) Column headings: n, number of measurements; m, mean concentration of particulate matter; df, degrees of freedom; s_b , between-lab standard deviation (reproducibility); CV, coefficient of variation.

(b) Laboratory E was excluded from the statistical analysis because its sampling period for test number ¹ did not correspond with the other laboratories.

(a) Column headings: n, number of measurements; m, mean concentration of particulate matter; df, degrees of freedom; s_h, between-laboratory standard deviation (reproducibility); CV, coefficient of variation.

(b) Laboratory G was excluded from the statistical analysis for test number 3.

Test				Variation Between-Lab				
Number	n	m	đf	ŝЪ	(%) CV			
1	7	1.098	6	0.446	41			
$\overline{\mathbf{2}}$	7	3.273	6	1.630	50			
6	7	4.163	6	2.259	54			
7	7	3.925	6	2.320	59			
8	7	4.741	6	2.381	50			
9	7	4,603	6	2.620	57			
10	7	5,374	6	2.876	53			
14	$\overline{\mathbf{z}}$	4,609	6	2.103	46			
17	7	3.228	6	2.006	62			
28	$\overline{\mathbf{z}}$	2.636	6	1.126	43			
29	7	2.743	6	1.264	46			
30	7	2.230	6	1.216	55			
32	$\overline{\mathbf{z}}$	2,826	6	1.022	36			
33	7	3,660	6	1.053	29			
34	7	3.122	6	1.255	40			
41	7	3,095	6	1.739	56			
42	7	1.805	6	0.400	22			
43	7	2,069	6	1,024	50			
44	7	1.952	6	0.918	47			
45	7	1.545	6	0.392	25			
46	$\overline{\mathbf{z}}$	2.043	6	0.877	43			
47	$\overline{\mathbf{z}}$	2.482	6	0.991	40			
48	7	2.878	6	1.130	39			
49	7	3.253	6	1.090	34			
50	7	2.911	6	1.017	35			
51	$\overline{7}$	2,621	6	1.638	62			
52	7	2.226	6	0.892	40			
53	7	2.680	6	0.973	36			
54	7	4.124	6	1.246	30			
55	7	4.062	6	1.316	32			
56	$\overline{7}$	6.728	6	1.954	29			
57	7	4.113	6	1.674	41			
58	7	3.827	6	1.543	40			
59	7	4.270	6	2.408	56			
60	7	4.105	6	1.434	35			
61	7	4.278	6	1.454	34			
62	7	4,208	6	1.419	34			
63	7	5.443	6	2.994	55			
64	7	5.134	6	1.938	38			
65	7	6.715	6	1.819	27			
66	7	7.184	6	2.729	38			
67	7	7.100	6	2.795	39			
68	7	4,834	6	1.650	34			
69	7	3.170	6	1.362	43			
A11	308	3.706	264	1.60	43			

TABLE 14. BETWEEN-LABORATORY VARIABILITY (REPRODUCIBILITY) OF DETERMINATIONS OF PARTICULATE MATTER AT MANHATTAN
(SITE 3) ACCORDING TO TEST^(a)

(a) Column headings: n , number of measurements; m , mean concentration of particulate matter; df, degrees of freedom; s_b , between-laboratory standard deviation (reproducibility); CV, coefficient of variation.

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Mean Concentration (m), Cohs per 1000 linear feet

FIGURE 4. RELATIONSHIP OF BETWEEN-LABORATORY STANDARD DEVIATION (REPRODUCIBILITY) TO MEAN CONCENTRATION OF PARTICULATE MATTER

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FIGURE 5. COMPARISON OF DUPLICATE READINGS (LAB E)

DISCUSSION AND CONCLUSIONS

The reproducibility (between-laboratory variability) of ASTM Method D 1704 for determining the soiling index of particulate matter in the atmosphere can be characterized by the equation,

$s_h = 0.193 + 0.367m,$

where, s_{h} , and, m, are the reproducibility and mean soiling index, respectively, in Cohs per 1,000 linear feet. The observed coefficient of variation (100 s_b/m) of between-laboratory measurements over a soiling index range of 0.27 to ⁷ Cohs per 1,000 feet varied from about 64 to 22 percent. These statistical measures indicate that Method D 1704, as tested, does not yield highly reproducible between-laboratory measurements of particulate matter in the atmosphere.

The duplicate optical density measurements of the same spot by Laboratory E show a coefficient of variation on the order of 10 to 15 percent and suggest that the major source of the lack of reproducibility of the Test Method is not due to the spot evaluation step.

The factors which may have a significant affect on the precision of the measurements are (1) the selection of the sampling probe materials and design of the probe, (2) the location of the sampling probe inlet, and (3) the measurement of sample flow. Some laboratories used rubber or Tygon connections in their sampling probes which undoubtedly contributed to significant variations due to removal of particulates on the inside surface of the probe.

A significant variation in results was also noted by one laboratory when a slight restriction, causing particle impingement, occurred in the sampling probe. The location of the sampling probe inlet is another possible source of variation in the measurement. The collection of particulate material is likely to be highly dependent on the micrometeorology in the vicinity of the probe inlet.

The measurement of sample volume is typically obtained from the sampling time and the average of the flow rate readings at the start and the end of the

sampling period. Due to the characteristics of the filter media and variations in particulate concentration with time, the flow rate probably does not vary linearly with time as assumed. Consequently, errors can occur in the flow measurements which contribute to the lack of reproducibility.

In addition to the foregoing considerations, the reproducibility of measurements with D 1704 is affected by the particle size, shape, refractive index, and color of the particulate material. A discussion of these factors is included in the description of the Test Method. The determination of the variability introduced by the specific characteristics of the collected particulate matter was not included in the scope of this study.

These study data show that concurrent soiling index measurements by different laboratories using different tape samples systems yield rather widely scattered results even when sampling is performed at the same general location. The between-laboratory differences result from biases introduced by the sample collection and measurement systems, and by the application and performance of the Test Method. The soiling index measurements of a single laboratory using the same sampling and measurement equipment at the same sampling site should be subject to nearly the same bias. Therefore, within-laboratory precision might be expected to be much better than between-laboratory precision.

The Test Method describes a procedure to establish an empirical relationship between the soiling index and particulate mass concentration. If this procedure is used, the effect of laboratory bias should be decreased. As a result, between-laboratory measurements of particulate mass concentration should be more precise than the soiling index measurements.

Additional study is necessary to obtain a measure of within-laboratory precision and to validate the assumption that particulate mass concentration measurements can be performed with higher precision than the soil index determination.

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RECOMMENDATIONS

It is recommended that the statistical measures of between-laboratory precision of D 1704 and within-laboratory precision of the optical density measurement which were obtained in this study be incorporated into the description of the method. In addition, two modifications of the Test Method are suggested.

- (1) A continuous sampling probe line of Teflon, glass, or other inert material with a smooth inner surface should be specified to eliminate retention of incoming particulates at connections.
- (2) The sampling probe should be free of sharp bends, connections, or any restrictions which might trap particulates.

Additional study of Method D 1704 is recommended to evaluate its characteristics for determination of particulate mass concentration. Such ^a study should be designed to provide a measure of the accuracy and precision of the method when applied to the particulate mass measurements instead of Coh units.

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APPENDIX

REPRINT OF ASTM

STANDARD METHOD OF TEST FOR PARTICULATE MATTER IN THE ATMOSPHERE OPTICAL DENSITY OF FILTERED DEPOSIT

ASTM Designation: D 1704-61

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Standard Method of Test for PARTICULATE MATTER IN THE ATMOSPHERE (OPTICAL DENSITY OF FILTERED DEPOSIT)¹

This Standard is issued under the fixed designation D 1704: the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope and Application

1.1 This method² covers the measurement of the extent of soiling or darkening of clean filter paper or other white fibrous media by filtration of particulate matter in the atmosphere. Measurement is based on the light transmission or reflectance properties of the deposited solid or liquid particles that originally were dispersed in a gaseous medium.

1.2 The maximum amount of deposited matter evaluated accurately by this method is that corresponding to 50 percent attenuation of incident light or a maximum optical density of about 0.30. For testing under heavily contaminated atmospheric conditions, leading to the deposition of closely packed particles that may give rise to higher optical densities than the maximum range, the sampling cycle is shortened to ¹ h or less by suitable adjustment of the instrument. Conversely, in relatively clean atmospheres, the sampling cycle may be increased to 2, 3, 4, or 6-h periods of the day. The most useful range for measurement of the light attenuation of the circular deposits is between optical densities of 0.05 and 0.30.

1.3 In an aerosol, the optical density is proportional to the mass concentration only when the particle size, shape, refractive index, color, etc., remain constant. For the filtered layer, Beer's law does not apply because of the interference in the light scattering from closely packed particles. However, various units of measurement may be employed to characterize such deposits if the volume of air filtered, the area of the deposit, and its optical density are accurately known. For information relative to meteorological and topographical factors affecting the application of this method, refer to ASTM Recommended Practice D 1357, Planning the Sampling of the Atmosphere.³

2. Summary of Method

2.1 The atmosphere under test is screened to remove particles greater than about 40 μ m in diameter. The screened air is then passed through a definite circular area of filter paper at a measured sampling rate for a 1-h period or longer, as required. This operation is repeated automatically on fresh areas of paper at equal time periods and constant sampling rate. Simultaneously, over a 24-h or other period, a parallel sample of the atmosphere may be filtered through a specially prepared asbestos pad or other suitable filter at a sampling rate sufficient to collect enough particulate matter for the determination of mass concentration by weight or for carbon analysis.

2.2 The optical density of the circular spots o. stains is measured by reflectance or transmittance in comparison with that of the clean paper in a spectrophotometer or colorimeter using white light or preferably light of wavelength of approximately 400 nm.

2.3 For comparison purposes the optical density readings may be converted into a concentration scale relating the optical density of the deposit to the volume of the air filtered

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^{&#}x27;This method is under the jurisdiction of ASTM Com-mittee D-22 on Sampling and Analysis of Atmospheres. Current edition effective Sept. 18, 1961. Originally is-sued 1959. Replaces D 1704 - 59 T.

² For further information on this method, see the refer-

ences at the end of this method. *'Annual Book of ASTM Standards,* Part 23.

and the area of the circular spot or to the size of the air sample in linear units. Such a scale serves to describe the quantity of aerosols in a linear unit of air in terms of its staining or soiling properties. It is related only indirectly to the mass of deposit, however, the recommended simultaneous collection, using a high volume sampler, of a weighable sample of the aerosol, permits a direct conversion of the optical densities to mass concentration units.

3. Definitions

3.1 For definitions of terms used in this method, refer to ASTM Definitions D 1356, Terms Relating to Atmospheric Sampling and Analysis.³

4. Apparatus⁴

4.1 *General Description*—The instrument consists of an assembly containing a sampling probe with filter screen for removing coarse material, clamping device or head to hold the inlet plug securely to the paper, paper holder to accommodate a roll of filter paper, interval timer actuated by a clock, calibrated flowmeter, electrically driven air pump, and timer control device for adjustment of the sampling cycle (see Figs. ¹ and 2). The optical density of the deposit or circular stain on the filter paper is determined by measurement of light transmittance or reflectance in a laboratory optical instrument of conventional design, such as a spectrophotometer or photoelectric colorimeter.

NOTE 1—In order to characterize the deposits more definitely, with every set of paper spot samples, a parallel sample of air should be filtered through a fibrous filter at a measured flow rate, over the same period. The mass of the filtered material shall be determined by weighing on a laboratory type analytical balance. This collected material may be analyzed for carbon content, or for metallic and non-metallic constituents by spectrographic and microchemical methods.

4.2 *Filter Paper, Fibrous*—Any suitable type of filter paper of relatively low resistance to air flow and good filtering efficiency. It is essential to specify the type of paper used in sampling, for example soft, open-texture, rapid filtering filter paper.

4.3 *Filter, Fibrous, for Weight Determination and Analysis*—Suitable types for this purpose are purified asbestos and prepared fiberglass of high filtration efficiency and low resistance to air flow.⁵

4.4 *Flow Meters*—Gas meters of any suitable type, such as calibrated orifice or capillary flow meters; one to measure air flow in the range of 0.10 to 0.50 ft³ (0.003 to 0.014 m 3) min for stain or spot samples; one to measure air flow of about 10 to 50 ft³ (0.28 to 1.40 m 3)/min for collection of particulate matter for weight determination and analysis.

4.5 *Pumps*—For the spot samples, a reciprocating diaphragm pump, or one of the constant displacement vacuum type, with an initial capacity of about 2.0 ft³ (0.056 m³)/min is employed. Mass samples are collected by means of a relatively large capacity pump of the multivane fan or compressor type, with initial delivery of about 10 to 50 ft³ (0.28 to $1.40 \, \text{m}^3$)/min.

4.6 *Clamping Device and Interval Timer*— The inlet head shall be equipped with a clamping device to fasten securely over a constant exposed area of filter paper. This area is exposed for 1, 2, 3 h or more for a given spot sample, depending upon atmospheric and meteorological conditions. The timing device at the end of this period releases the paper, which is moved to expose a fresh area and the cycle of operations is repeated. The timing cycle must be capable of adjustment in order to avoid sample spots of excessive optical density. Parts that come in contact with the filter paper shall be of stainless steel, plastic, or other corrosion-resistant noncontaminating materials. Filter holder shall be adequate to provide area and flow rate for spot samples .
0.25 to 0.40 ft³ (0.007 to 0.011 m³)/min through a circle of paper ¹ in. in diameter or, alternatively, through an area of 1 in.^2 (6.4) cm²).

4.7 *Spot Sampling Probe*—A small cyclone chamber gravity dust trap or funnel covered with a 325-mesh screen and connected with a suitable length of glass tubing, the other end of which is attached to the sample inlet head by short rubber connections. This is designed to exclude coarse particles of dust larger than about 40 μ m in diameter.

^{&#}x27;The AISI Automatic Smoke Sampler designed by Hemeon *el al* of the Mellon Institute and manufactured by Research Appliance Co.. Pittsburgh, Pa. is a typical example of equipment that has been found to be satisfactory for this purpose. A number of other satisfactory instruments are also available commercially.

⁵ A 1106 Fiberglass flash-Tired web (Mine Safety Appliances Co.. Penn and Braddock Aves., Pittsburgh, Pa. 1520&) with a DOP efficiency of 99.97 percent at 28 fpm has been found satisfactory.

4.8 *Transmission or Reflectance Meter*— Any conventional laboratory instrument is suitable if equipped with a stable light source, preferably having an adjustment for wave length to yield substantially monochromatic light, and photoelectric optical system suitable for determining incident, transmitted, or reflected light from clean paper in comparison with spot samples. For convenience, the instrument may be provided with an optical density scale. The monochromatic light source shall provide light of wavelength about 400 nm. If monochromatic light is not available, white light may be employed or a set of suitable filters may be used to pass a band of light in the region of 375 to 450 nm.

5. Sampling

5.1 For information on sampling, refer to ASTM Recommended Practice D 1357, Planning the Sampling of the Atmosphere.³

6. Procedure for Spot Samples

6.1 After assembling the apparatus described in Section 4, place a roll of clean filter paper tape in the holder and pass the atmosphere under test through the sampling probe at 0.25 ft³ (0.007 m³)/min if the exposed circular area of the paper under the inlet head is equivalent to a 1-in. (25-mm) diameter circle. For larger exposed areas the flow rates are proportionately greater. The time cycle, on which the sampler is operated, is set to avoid stains or spots of optical density exceeding 0.30. This specification is met usually by setting the time rotor to yield a spot sample every 2 h, although in summer weather under normal meteorological conditions it can be lengthened to ³ h. Under winter conditions where consumption of coal or other fuel is high and smoke conditions may be dense, the time cycle can be reduced accordingly.

6.2 Measure the air flow frequently enough with the gas flow meter to establish the average air sampling flow rate. Check the gas flow meter periodically by calibration with a standard wet test gas meter.

6.3 At convenient intervals remove the exposed paper tape from the rewind roller and measure each spot for optical density by transmittance or reflectance. Adjust the spectrophotometer or colorimeter scale to read 100 percent reflectance or transmittance of an

equivalent area of clean filter paper. Then determine the corresponding value for the spot sample. Record the readings in terms of the optical density scale of the spectrophotometer.

6.4 Calculate the optical density and optical reflectance, as follows:

Optical density = $log (I_0/I)$

where:

- I_0 = the intensity of transmitted light through the clean paper, and
- $I =$ the intensity of transmitted light through the sample.

Log refers to the logarithm to base 10.

Optical reflectance = $\log (R_0/R)$

where:

- R_0 = the intensity of the light reflected from the clean paper, and
- *R =* the intensity of the light reflected from the sample.

NOTE 2—The reflectance may be determined in a spectrophotometer, preferably at a constant wave-length of 400 nm with the light reflected at angles between 35 and 55 deg, and the readings taken on the density scale. It has been shown that there is an approximately linear relationship between optical density and optical reflectance.

7. **Procedure for Determination of** Mass **Concentration**

7.1 For collection of samples for mass concentration⁶ and analysis, pass the atmosphere under test through the high volume filtration apparatus, using an asbestos or mineral fiber paper or fiberglass filter previously dried and weighed. The sampling period is usually 24 h or a sufficient period of time to collect from 50 to 250 mg of paniculate matter.

7.2 Read the flowmeter of the high volume sampler at the start and at the end of each sampling period. It is also advisable to take readings at intervals during each test period if there is an appreciable drop in flow rate with increasing resistance of the filter. Record the average flow rate under the test conditions as the flow rate.

7.3 For flow rates of about 10 to 50 ft³ $(0.28 \text{ to } 1.40 \text{ m}^3)/\text{min}$ the filter is usually re-

⁶ The types of high-volume samplers employed by the U. S. Public Health Service, Robert A. Taft Sanitary En-gineering Center, Cincinnati, Ohio; the U. S. Atomic Energy Commission, or the International Joint Commission, Windsor-Detroit area, have been found to be satisfactory for this purpose.

placed every 24 h. Dry the test filter in an oven at 105 C for several hours to constant weight, and determine the weight by means of a laboratory analytical balance.

7.4 Record the increase in weight of the filter in terms of micrograms per cubic meter of air.

7.5 If desired, analyze the deposit for carbon, heavy metals, etc.

NOTE 3—For those samples which are collected in the atmosphere of industrial areas where carbon and dark tarry materials represent a considerable portion of the aerosol contaminants, the carbon content of the individual samples may be estimated by calibration of the optical density values with the carbon content of the deposit as determined by a representative number of chemical analyses. Where carbon is the principal coloring material, the color of the spot will vary with a given weight of deposit in direct ratio to the proportion of carbon. The carbon values estimated in this manner would be valid only for the particular industrial area in which the calibration was carried out.

8. Calculation

8.1 For comparison purposes with similar samples collected in other sampling areas and under sampling conditions where the area of paper exposed and the volume flow rate may be different, the optical density values for transmission are converted to a unit scale called the Coh unit. Similarly, the optical reflectance values are expressed in K_m or Ruds units. The Coh unit is defined as 100 times the optical density of the deposit, so that an optical density of 0.301 is 30.1 Coh units. Furthermore, since the intensity of the filter paper stain is determined by the total volume of air aspirated through the filter and the area of the exposed filter, the size of the air sample is properly expressed in linear units of air, that is, the volume of air aspirated divided by the area of the filter. For convenience, the results are reduced to multiples of 1000 linear ft (305 linear m) of air sample, so that the soiling for any time period is described in terms of Coh units/1000 linear ft of air.

8.2 If the quantity of air sampled during each spot sample is equal to L , in thousands of linear feet, then,

$$
L = \frac{\text{flow (ft}^3/\text{min}) \times \text{sampling time in min}}{1000 \times \text{circular area of spot (ft}^3)}
$$

Cohs/1000 ft =
$$
\frac{\text{optical density} \times 100}{L}
$$

NOTE 4: *Example*—Suppose measurements with the gas flow meter have established the average flow rate through each spot area of paper as $0.\overline{2}2$ ft³ (0.006 m³)/min, the area exposed is a sampling
circle 1 in. (25 mm) in diameter or 5.45 \times 10⁻³ ft³, and the timing spindles of the instrument are set for 2-h samples, then,

 $L = (0.22 \times 120)/(1000 \times 5.45 \times 10^{-3})$

= 4.85 (thousands of feet)

If a given spot shows a light transmission value of 50 percent, then,
Ontical density \sim (100/50) = log 2 = 0.301

plical density =
$$
\log (100/50) = \log 2 = 0.30
$$

Cohs/1000 ft = $(0.301 \times 100)/4.85 = 6.2$

8.3 The K_m unit is defined as the amount of deposit which produces an optical reflectance of 0.10 on an area of 1 cm² through which 1 m^3 (35.4 ft³) of air has been passed. This air sample represents 33,000 linear ft (10,058 linear in). Optical reflectance, *R,* of 0.1 is equivalent to 91 percent reflectance:

$$
R = \log (100/91) = \log 1.1 = 0.1
$$

$$
K_m = (0.1 \times 100)/33 = 0.3 \text{ Cohs}/1000 \text{ ft}
$$

8.4 The third unit, Ruds, "reflectance unit of dirt shade," is defined as a deposit which produces an optical reflectance of 0.01 due to 10,000 linear ft (3,050 linear m), of air:

 $R = \log(100/99) = \log 1.01 = 0.01$

 $Ruds = (0.01 \times 100)/10 = 0.1 \text{ Cohs}/1000 \text{ ft}$

9. Report

9.1 Report the results of the optical tests and observations described in Section 6 and the calculations given in Section 7 as follows:

9.1.1 Date of test,

9.1.2 Air sampling volume and area of stain or deposit. Specify type of paper filter employed,

9.1.3 Size of air sample in linear feet (linear meters), expressed in multiples of 1000 linear ft (305 linear m),

9.1.4 Type of optical measurement, that is, transmission or reflectance at specified wavelength of light in millimicrons,

9.1.5 Values in Coh units/1000 ft of air sample (or other units) for 1, 2-h, or other time cycle,

9.1.6 Average Coh units for each 24-h period,

9.1.7 Monthly average Coh units for each hour of the day, or for each sampling cycle of the day,

9.1.8 Monthly minimum, maximum, and average Coh units for each month of the year,

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9.1.9 Report the weight collected by filtration on a fibrous filter in a high-volume sampler or other paper filtration unit as mass concentration in micrograms per cubic meter of air and record the time and date of the sampling period, and

9.1.10 Relate the mass concentration values to the corresponding Coh or other units over the same sampling period.

10. Limitations

10.1 The size of the air sample when described in linear units is by specification completely independent of the type of filter paper sampler employed. Thus air may be sampled at any desired rate using any convenient area of paper.

10.2 In the evaluation of the spot sample the magnitude of the result is dependent on the characteristics of the filter paper, and on the particular method of optical measurement employed, that is, light transmission, light reflectance, and wavelength of light, whether monochromatic or polychromatic. The relation between transmittance and reflectance measurements of spot samples is only approximately linear and depends upon the nature of the deposit. The ratio of optical densities by reflectance and transmittance may vary in progressing from light to heavy deposits. This ratio also varies with the wavelength of light employed so that it is advisable to use a substantially monochromatic light source. Transmittance is more sensitive, especially for light deposits. However, variations in filter paper transmittance as a source of error may be avoided by use of reflectance. The use of a white porcelain backing plate for the spot is also helpful in eliminating variations in reflectance due to the paper itself.

10.3 Normal filter paper deposits are essentially various shades of black due primarily to carbon. They may be tinted brown or reddish in areas where iron oxides or other material are discharged into the air. A few locations may show a light gray deposit, but such colors are not the rule and should be regarded as a local source of contamination or local problem only.

10.4 The values based on optical density of the deposit are indicative of the soiling characteristics of particles of less than about 10 μ/m to below 0.1 μ/m in size and, therefore, describe the smoke or haze content of the atmosphere. There is no direct relation between such values and mass concentration of particulates per unit volume of air, although empirical relations may be calculated for a specific case if the particle size, shape, refractive index, etc., and other factors are reasonably constant. These empirical relations should be useful in comparing deposits from different types of sources and in different locations. In order to have the results of different determinations at different locations under different conditions comparable with each other, every effort shall be exerted to have the independent variables as consistently uniform as possible.

11. Precision and Accuracy

11.1 The precision and accuracy of this method depend upon the accuracy of calibration of the gas flow meter, extent of variation of aspiration rate through the paper during each sampling cycle, and the filtration efficiency of the paper. All these factors should be controlled and the extent of variation kept within reasonably narrow limits. The optical measurements can be made with a high degree of precision if a steady source of monochromatic light is used, or light from a stable source is passed through neutral filters whose transmission remains unchanged indefinitely. Periodic checks of the sampling instrument and photoelectric colorimeter or spectrophotometer should be carried out for satisfactory operation.

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FIG. 1 AISI Antomatic Smoke Sampler,

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FIG. 2 Diagrammatic Representation of the AISI Automatic Smoke Sampler.

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