Interlaboratory Cooperative Study of the Precision and Accuracy of the Measurement

of

TOTAL SULFATION
IN THE ATMOSPHERE
using
ASTM Method D 2010

DS 55-S2

ASTM AMERICAN SOCIETY FOR TESTING AND MATERIALS

THRESHOLD

FINAL REPORT

on

INTERLABORATORY COOPERATIVE STUDY OF THE PRECISION AND ACCURACY OF THE MEASUREMENT OF TOTAL SULFATION IN THE ATMOSPHERE USING ASTM METHOD D 2010

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INTERLABORATORY COOPERATIVE STUDY OF THE
PRECISION AND ACCURACY OF THE MEASUREMENT OF TOTAL SULFATION
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by

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INTRODUCTION

This report presents the results obtained from an experimental
study of the variability inherent in measurements of total sulfation,
using ASTM Method D 2010[1]*. The evaluation of Method D 2010 was per-
formed as part of the first phase of Project Threshold, a comprehensive
program to validate ASTM methods for measuring various atmospheric contam-
inants. In addition, methods for measuring the content of nitrogen
dioxide (D 1607), sulfur dioxide (D 2914), lead (D 3112), dustfall (D 1739),
and particulate matter (D 1704) in the atmosphere have also been evaluated
during Phase 1.

Project Threshold is a multiphase program sponsored by American
Society for Testing and Materials to provide tested methods for measuring
contaminants in both ambient air and in source emissions. Tests of the
methods are performed by groups of competent laboratories who are brought
together at field locations for concurrent analysis of actual ambient and
source atmospheres. Coordination of the Threshold program has been performed
by Battelle's Columbus Laboratories.

The following section provides a brief summary of the results of
the study of Method D 2010. Subsequent sections include detailed descriptions
of the test method, test procedure, test sites, and the statistical analysis
of the experimental data.

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* References at end of report.

SUMMARY OF RESULTS

A statistical analysis of 79 total sulfation determinations performed in accordance with ASTM Method D 2010 produced the following results:

- The standard deviation, s_b, for variations among single sulfation rate measurements by different laboratories (reproducibility) is related to the mean sulfation rate, m, as follows:

$$s_b = 0.0136 \sqrt{m}$$

  where, s_b, and, m, are given in mg/cm^2-day. This relationship is based on measurements at three sulfation rates over the range of 0.00178 to 0.01371 mg/cm^2-day.

- The mean of the combined measurements between laboratories at all sites is 0.00630 mg/cm^2-day and the overall standard deviation is 0.00135 mg/cm^2-day.

- The standard deviation, s_w, for variations among repeated sulfation rate measurements within laboratories (repeatability) is related to the mean sulfation rate, m, as follows:

$$s_w = 0.00504 \sqrt{m}$$

  where, s_w, and, m, are given in mg/cm^2-day. The relationship is based on duplicate determinations at three sulfation rates over the range of 0.00178 to 0.01371 mg/cm^2-day.

- The overall standard deviation of combined duplicate determinations within laboratories, at all sites is 0.00034 mg/cm^2-day and is associated with a mean sulfation rate of 0.00630 mg/cm^2-day.

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- Sulfate spikes were added to some candles following exposure and prior to the sulfate analysis. The average recovery of the spikes is 98 percent based on measurements by all laboratories at all sites.
- The overall standard deviation of the recovery of the sulfation spikes within laboratories is 21 percent.
- The overall standard deviation of the recovery of the sulfation spikes between laboratories is 10 percent.

EXPERIMENTAL PROGRAM

Characteristics of ASTM Method D 2010

The measurement of total sulfation in the atmosphere is a passive test in which sulfur compounds from the atmosphere are reacted with a lead peroxide surface of known area for a specified time period. The reactive surface is a layer of dried paste of lead peroxide in a binder applied to a cylindrical support or "candle". The candle is exposed in a shelter with a roof and louvered sides that permit free access of the atmosphere but protects the absorbent surface from the weather. Following exposure, sulfate in the candle formed from oxidation of ambient sulfur compounds is determined by ASTM Method D 516 (Referee Method)[1]. The sulfation rate is reported in units of milligrams of SO_2 per square centimeter of candle per day of exposure (mg/cm^2-day).

Test Procedure

Each of the seven participating laboratory performed sulfation measurements at three test sites in accordance with ASTM Methods D 2010 and D 516 as reproduced in the Appendix. The laboratories prepared their own candles prior to the tests as prescribed by the Test Method using lead peroxide obtained from Research Appliance Company. Sampling stations were supplied by the participating laboratories. Following the tests, the candles

were sealed in jars under Battelle supervision and returned to the respective laboratories for sulfate analysis by Method D 516 (Referee Method).

Test Pattern

Table 1 shows the statistical design of the tests for all three sites with random distribution of total-sulfation candles on the four racks. At all sites, seven laboratories participated in the test. Figure 1 shows diagrammatically the placement of containers according to the design of Table 1.

Spiking Procedures

Known quantities of solid potassium sulfate were provided to the collaborators to be added to selected samples according to the patterns given in Table 1. These spikes were packaged in gelatin capsules, and were added during the digestion step prior to sulfate analysis by ASTM Method D 516. The spikes contained from about 17 to 280 milligrams of potassium sulfate or an equivalent of 6 to 105 milligrams of SO_2. The equivalent sulfation rate of the spikes ranged from about 0.002 to 0.035 mg/cm^2-day.

Test Sites

Site No. 1, Los Angeles, California

At Site 1 the total-sulfation candles in their louvered shelters were mounted on four wooden racks placed on a rooftop at the Hancock Foundation building on the campus of the University of Southern California in Los Angeles. Each laboratory placed its own candles in their shelters and monitored them during the first five days of the test period. The tests were continued for a total of 30 days between August 15 and September 14, 1971 during which the candle: were inspected about two times per week. At the end of the test period the candles were sealed in containers and shipped to the participating laboratories under direction of Battelle personnel.

TABLE 1. STATISTICAL DESIGN OF SULFATION EXPERIMENTS

Sampling Site	Rack	Candle Position on Rack[a]							
		1	2	3	4	5	6	7	8
Los Angeles	E	L_1	O_1	P_1	(Q_1)	-	(K_1)	(L_1)	(P_1)
	F	(J_1)	(O_1)	N_1	-	Q_1	K_1	(N_1)	J_1
	G	L_1	K_1	J_1	(Q_1)	-	(J_1)	(L_1)	O_1
	H	(N_1)	(P_1)	P_1	-	Q_1	(N_1)	(O_1)	(K_1)
Bloomington	E	(L_2)	O_2	-	(P_2)	(K_2)	-	-	K_2
	F	-	(N_2)	(M_2)	M_2	O_2	(P_2)	O_2	(L_2)
	G	(K_2)	(N_2)	(J_2)	(O_2)	L_2	J_2	(J_2)	N_2
	H	L_2	(M_2)	P_2	P_2	J_2	K_2	N_2	M_2
Manhattan	E	K_3	(K_3)	P_3	-	-	(P_3)	O_3	(O_3)
	F	(L_3)	(M_3)	J_3	N_3	(J_3)	M_3	L_3	(N_3)
	G	M_3	(M_3)	(O_3)	(P_3)	L_3	O_3	P_3	(L_3)
	H	J_3	(K_3)	K_3	(J_3)	-	N_3	(N_3)	-

(a) Entries are laboratory code letters. Parentheses designate samples which were spiked following exposure.

RACK E

```
S-E1            U-E2          (NONE)
     +---------------+---------------+
     |               |               |
     |     S-E4      |     S-E5      |
     |               |               |
     +---------------+---------------+
(NONE)          (NONE)         U-E8
```

RACK F

```
(NONE)          S-F2          S-F3
     +---------------+---------------+
     |               |               |
     |     U-F4      |     S-F5      |
     |               |               |
     +---------------+---------------+
S-F6            U-F7          S-F8
```

RACK G

```
S-G1            S-G2          S-G3
     +---------------+---------------+
     |               |               |
     |     S-G4      |     U-G5      |
     |               |               |
     +---------------+---------------+
U-G6            S-G7          U-G8
```

RACK H

```
U-H1            S-H2          U-H3
     +---------------+---------------+
     |               |               |
     |     U-H4      |     U-H5      |
     |               |               |
     +---------------+---------------+
U-H6            U-H7          U-H8
```

```
1       2       3
+-------+-------+      Rack
|   4   |   6   |      Position
+-------+-------+      Designations
6       7       8
```

S = Spiked
U = Unspiked

Code: S-E1

Rack   Position
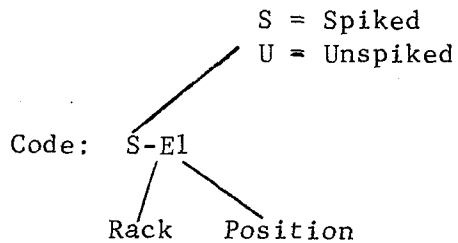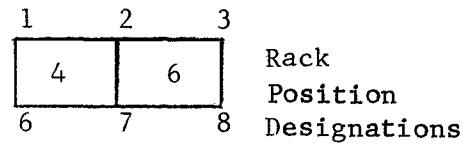
FIGURE 1.   DIAGRAM OF PLACEMENT OF THE SULFATION STATIONS (D 2010)

The racks were placed on the roof as shown in the foreground and far background of Figure 2. The locations of the individual containers were randomized on the racks. The exposure area also included sampling stations for measurement of dustfall. These sampling stations, which also appear in the photograph, were placed so that no direct interaction would be expected between the two tests.

Site No. 2, Bloomington, Indiana

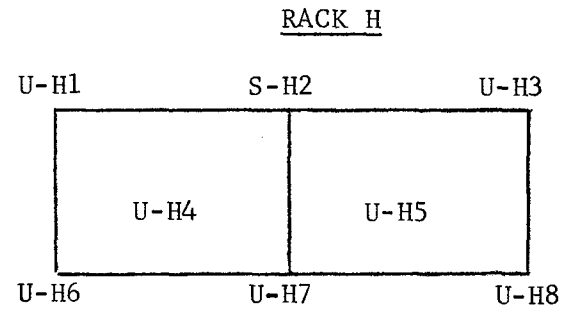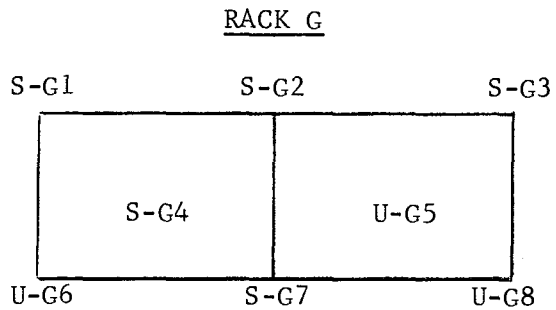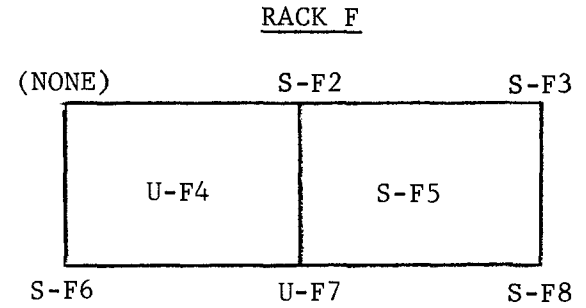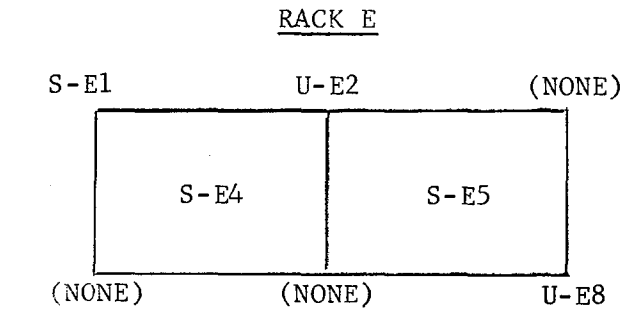The total-sulfation candles at Site 2 were mounted on wooden racks placed on the ground, as shown in the foreground of Figure 3.

After nine days exposure at Bloomington, some of the neighboring dustfall racks were tipped over by trespassers but the total-sulfation racks were not disturbed. The candles were then placed in sealed shipping containers and the experiment was moved to suburban Columbus, Ohio. At Columbus, exposure of the same candles was continued from November 4 - December 6, 1971, at Battelle's industrial research location inside a fenced area as shown in the foreground of Figure 2. For simplicity, the combined test at two locations is designated in this report at the Bloomington test of the Phase 1 program.

Site No. 3, Manhattan, New York City

The total-sulfation candles in their shelters were mounted on racks in the same manner as shown in Figure 2 and exposed on a rooftop of Cooper Union, 51 Astor Place, in lower Manhattan, with an arrangement similar to exposures at the other two sites. The tests were made from January 9 through February 8, 1972.

Participating Laboratories

The participating laboratories are listed below in alphabetical order:

George D. Clayton and Associates

Arthur D. Little, Inc.
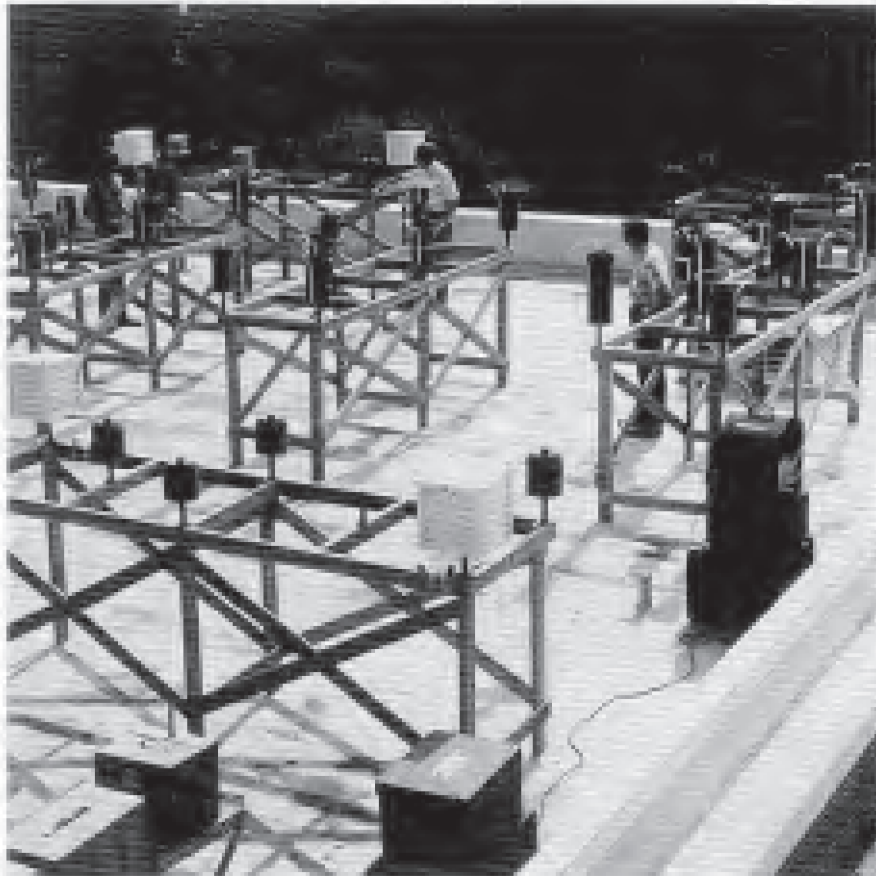
Midwest Research Institute

FIGURE 2. ARRAYS OF DUSTFALL COLLECTORS (D 1739) AND
TOTAL SULFATION DETECTORS (D 2010) ON ROOF-
TOP RACKS AT LOS ANGELES
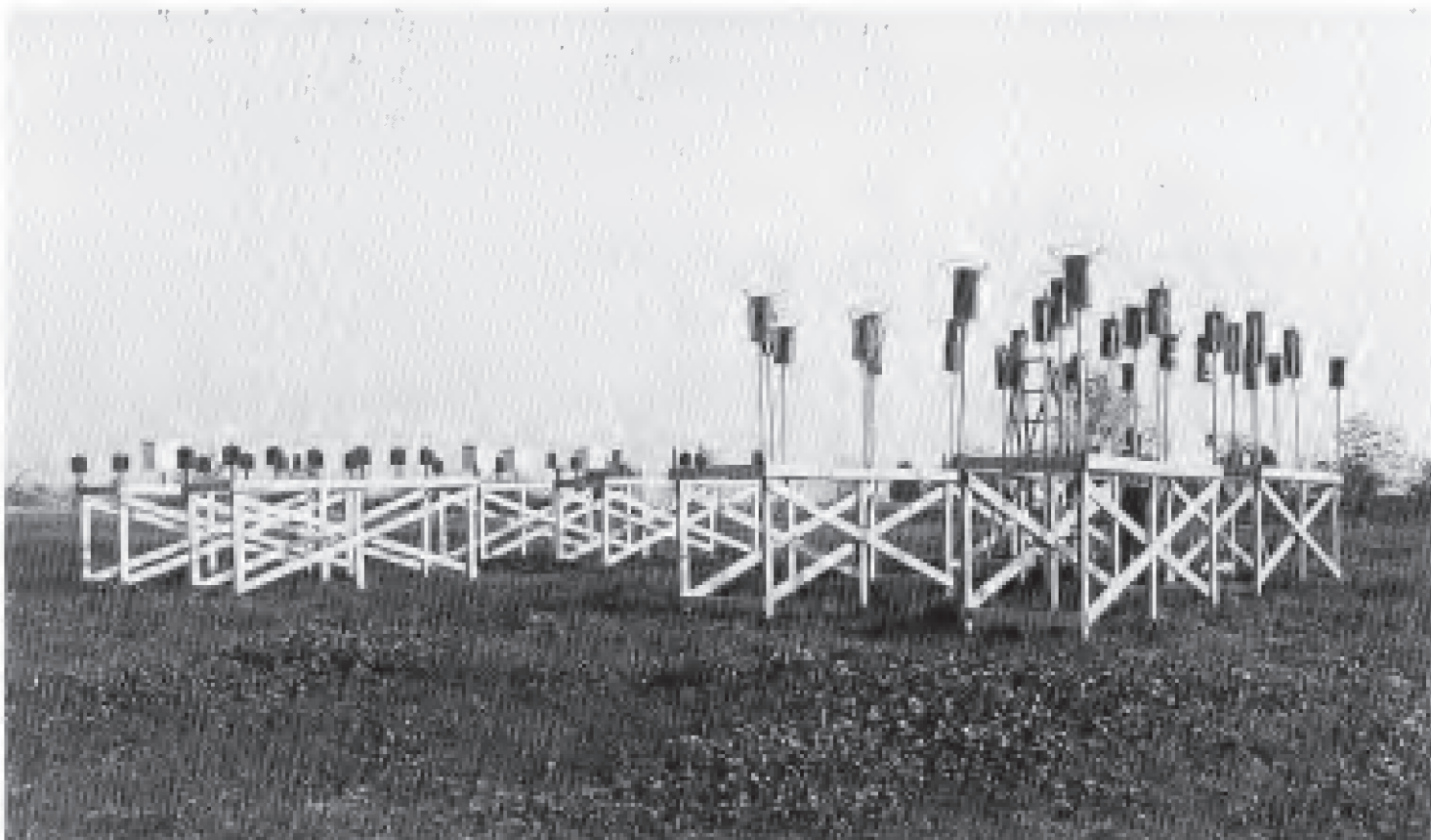
FIGURE 3.   THE DUSTFALL (D 1739) AND TOTAL SULFATION RATE (D 2010) TESTS STARTED AT
BLOOMINGTON, INDIANA (COMPLETED AT COLUMBUS, OHIO TEST SITE)

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. Numerical subscripts with the code letters designate the site at which samples were collected. In general, any particular letter designates a different laboratory at each site. Each participant is supplied the key to the code letters for himself in all data tables, but no key for the other participants.

STATISTICAL ANALYSIS OF SULFATION MEASUREMENTS

Statistical Measures

The experimental test program was designed and conducted so that statistical analysis of the results would provide measures of the following characteristics of ASTM Method D 2010.

Reproducibility

The participating laboratories performed concurrent measurements of sulfation rate. Differences among the sulfation rates found in the simultaneous measurements represent a measure of variability between laboratories. The standard deviation of all such measurements by all laboratories is a measure of precision of the Test Method which in this report is called "between-laboratory variability" or "reproducibility" and is represented by the symbol, s_b.

Repeatability

Each laboratory performed duplicate measurements which, ideally, should have produced identical sulfation rate values. Thus, a difference between a pair of determinations is a measure of another type of variability. The standard deviation of all such differences by all laboratories is a measure of precision of the Test Method which in this report is called "within-laboratory variability" or "repeatability" and is denoted by the symbol, s_w.

Accuracy

Sulfation measurements were performed by each laboratory in which the sulfate content in an exposed candle and a duplicate exposed candle spiked with a known quantity of potassium sulfate prior to the digestion step were determined. The difference between the determinations for such pairs is a measure of the equivalent sulfation rate of the spike. Differences between the experimentally determined and the "true" equivalent sulfation rate of the spike is a measure of accuracy of the sulfate analysis procedure. The data are presented as the percentage of the spike which was recovered in the analysis.

Additional discussions of the preceding statistical measures have been presented by Mandel[2] and in ASTM publications[3,4].

Experimental Results

The results of the sulfation measurements at Los Angeles, Bloomington, and Manhattan are presented in Tables 2, 3, and 4, respectively. The first column of each table contains a laboratory identification code, which was adopted to conceal the identity of the laboratory from which the associated data originated. In the second column is shown the candle location for each unspiked sample; the letter specifies the rack, and the number specifies the position of the candle on the rack. The next two columns show the area of the reactive surface of the sulfation candle, in units of square centimeters, and the exposure time in days, respectively. This is followed by the sulfation

TABLE 2. DATA FROM SULFATION EXPERIMENTS AT LOS ANGELES

Lab	Unspiked Samples Candle Location	Exposed Area, cm^2	Exposure Time, days	Sulfation, mg/cm^2-day (U)	Spiked Samples Candle Location	Exposed Area, cm^2	Exposure Time, days	Sulfation, mg/cm^2-day (S)	Estimated Spiking Rate, mg/cm^2-day (S-U)	Spike Added Code Number	Weight, mg SO_2	Sulfation mg/cm^2-day (S')	Spike Recovery (E), percent of (S')
J_1	F8	106	30	0.00162	F1	106	30	0.00433	0.00271	11	7.90	0.00248	109
	G3	108	30	0.00176	G6	105	30	0.00379	0.00203	15	6.36	0.00202	100
K_1	F6	100	30	0.00200	E6	100	30	0.00512	0.00312	12	8.38	0.00279	112
	G2	100	30	0.00226	H8	100	30	0.00558	0.00332	16	8.46	0.00282	118
L_1	E1	100	30	0.00165	E7	100	30	0.00522	0.00357	1	10.20	0.00340	105
	G1	100	30	0.00166	G7	100	30	0.00429	0.00263	9	8.79	0.00293	90
N_1	F3	103.8	30	0.00167	F7	105.2	30	0.00385	0.00218	3	6.18	0.00196	111
	H6	105.3	30	0.00178	H1	103.2	30	0.00487	0.00309	8	8.49	0.00274	113
O_1	E2	100	30	0.00174	F2	100	30	0.00374	0.00200	2	6.91	0.00230	87
	G8	100	30	0.00247	H7	100	30	(a)	–	10	9.52	0.00317	–
P_1(b)	E3	100	30	0.00064	E8	100	30	0.00171	0.00107	4	6.47	0.00215	50
	H3	100	30	0.00174	H2	100	30	0	-0.00174	6	8.53	0.00284	-61
Q_1	F5	98.7	30	0.00116	E4	98.7	30	0.00431	0.00315	5	9.38	0.00317	99
	H5	98.7	30	0.00164	G4	98.7	30	0.00545	0.00381	7	9.12	0.00308	124

(a) Part of sample lost during analysis.

(b) Data from Laboratory P_1 were excluded from the statistical analyses.

TABLE 3. DATA FROM SULFATION EXPERIMENTS AT BLOOMINGTON

Lab	Candle Location	Unspiked Samples Exposed Area, cm^2	Exposure Time, days	Sulfation, mg/cm^2-day (U)	Candle Location	Spiked Samples Exposed Area, cm^2	Exposure Time, days	Sulfation, mg/cm^2-day (S)	Estimated Spiking Rate mg/cm^2-day (S-U)	Code Number	Spike Added Weight, mg SO_2	Sulfation mg/cm^2-day (S')	Spike Recovery (E), percent of (S')
J_2	G3	106	42	0.00227	G6	107	42	0.00507	0.00280	20	12.2	0.00271	103
	H5	107	42	0.00243	G7	106	42	0.00454	0.00211	27	10.0	0.00225	94
K_2	E8	100	42	0.00271	E5	100	42	0.00488	0.00217	24	9.5	0.00226	96
	H6	100	42	0.00283	G1	100	42	0.00433	0.00150	17	6.5	0.00155	97
L_2	H1	100	42	0.00289	E1	100	42	0.00533	0.00244	28	9.4	0.00223	109
	G5	100	42	0.00259	F8	100	42	0.00438	0.00179	21	6.7	0.00160	112
M_2	F4	100	42	0.00272	F3	100	42	0.00514	0.00242	25	9.4	0.00224	108
	H8	100	42	0.00313	H2	100	42	0.00444	0.001313	18	6.5	0.00155	85
N_2	H7	105.4	42	0.0026	F2	102.9	42	0.0040	0.0014	26	11.9	0.00275	51
	G8	105.2	42	0.0027	G2	103.6	42	0.0044	0.0017	19	9.9	0.00227	75
O_2	E2	100	42	0.00100	F5	100	42	0.00371	0.00271	29	10.3	0.00245	111
	F7	100	42	0.00165	G4	100	42	0.00166	0.00001	31	9.5	0.00226	0
P_2	H3	100	42	0.0048	E4	100	42	0.0075	0.0027	23	9.1	0.00217	124
	H4	100	42	0.0042	F6	100	42	0.0078	0.0036	30	9.8	0.00233	155

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TABLE 4. DATA FROM SULFATION EXPERIMENTS AT MANHATTAN

Lab	Candle Location	Unspiked Samples Exposed Area, cm²	Exposure Time, days	Sulfation, mg/cm²-day (U)	Candle Location	Spiked Samples Exposed Area, cm²	Exposure Time, days	Sulfation, mg/cm²-day (S)	Estimated Spiking Rate mg/cm²-day (S-U)	Code Number	Spike Added Weight, mg SO₂	Sulfation mg/cm²-day (S´)	Spike Recovery (E), percent of (S´)
J_3	F3	100	30	0.0122	F5	100	30	0.0435	0.0313	36	98.1	0.0327	96
	H1	100	30	0.0124	H4	100	30	0.0417	0.0293	44	98.5	0.0328	89
K_3	E1	100	30	0.018	E2	100	30	0.048	0.030	43	97.3	0.0324	93
	H3	100	30	0.017	H2	100	30	0.050	0.033	50	99.5	0.0332	99
L_3	F7	100	30	0.0131	F1	100	30	0.0443	0.0312	48	93.4	0.0311	100
	G5	100	30	0.0128	G8	100	30	0.0470	0.0342	40	103.5	0.0345	99
M_3	F6	108	30	0.0125	F2	107	30	0.0414	0.0289	47	93.3	0.0291	99
	G1	108	30	0.0124	G2	108	30	0.0423	0.0299	39	98.8	0.0305	98
N_3	F4	104.6	30	0.0114	F8	102.6	30	0.0401	0.0287	38	103.3	0.0336	85
	H6	102.3	30	0.0113	H7	104.7	30	0.0410	0.0297	46	101.2	0.0322	92
O_3	E7	100	30	0.0150	E8	100	30	0.0439	0.0289	37	104.0	0.0347	83
	G6	100	30	0.0138	G3	100	30	0.0449	0.0311	45	100.7	0.0336	93
P_3	E3	100	30	0.0152	E6	100	30	0.0450	0.0298	49	97.9	0.0326	91
	G7	100	30	0.0148	G4	100	30	0.0553	0.0405	41	94.0	0.0313	129

rate determination of unspiked samples (U) in units of milligrams per square centimeter per day. The next four columns present similar data for the spiked samples (S). The column headed S-U contains the difference between corresponding spiked and unspiked determinations. The next three columns contain the spike code number, the amount by which the sulfation rate of the unspiked samples was increased by the addition of known quantities of potassium sulfate, and the equivalent spiking rate (S') in units of milligrams per square centimeter per day, respectively. The last column of each table shows the percent recovery (E) of the sulfation spike computed from the formula $100(S-U)/S'$.

All laboratory P_1 data from Los Angeles (Table 2) were excluded from the statistical analysis on the following basis. The determination for unspiked sample E3, reported by Laboratory P_1 as 0.00064 mg/cm^2-day, is considered questionable on the basis of statistical significance at the 95 percent level of the T-statistic[5] computed from the 14 determinations in the column headed U. Both the determination for spiked sample E8 and the determination for spiked sample H2, reported by Laboratory P_1 as 0.00171/cm^2-day and 0 mg/cm^2-day, respectively, appear unreasonably low compared with the other values in column (S) of Table 2. A statistical test of homogeneity could not be applied to the spiked sample determinations because of lack of uniformity in spiking levels. However, a test[5] for two outliers in a single sample was applied to the recoveries 49 and 0 percent computed from the data reported by Laboratory P_1. Using the 13 values of spike recovery in the last column of Table 2, this test produced a value for the ratio $S_{1,2}^2/S^2$ as defined in Reference (5) which was statistically significant at the 99 percent level, therefore the data were rejected.

Analysis of Reproducibility

The analysis of between-laboratory variability (reproducibility) was performed using the sulfation rate measurements for unspiked samples in Tables 2, 3, and 4. A summary of the results of the analysis is presented in Table 5. The table shows, for each site, the number (n) of sulfation rate measurements performed, the mean (m) of the sulfation rate of all laboratories,

the number of degrees of freedom (df) associated with the statistical analysis, the mean square (MS) of the sulfation rate measurements, the between-laboratory standard deviation (s_b), and the coefficient of variation (CV).

TABLE 5. SUMMARY OF BETWEEN-LABORATORY VARIABILITY (REPRODUCIBILITY) OF SULFATION RATE MEASUREMENTS[a]

| | | | | Between-Laboratory Variation | | |
| | | m, | | $MS^{[b]}$ | s_b, | |
Site	n	mg/cm^2-day	df	$(mg/cm^2$-day$)^2$	mg/cm^2-day	CV(%)
Los Angeles[c]	12	0.00178	5	0.158	0.00021	12
Bloomington	14	0.00275	6	1.765	0.00092	33
Manhattan	14	0.01371	6	8.742	0.00207	15
All Sites[c]	40	0.00630	17	3.755	0.00135	21

(a) Column heading: n, number of sulfation rate measurements; m, mean sulfation rate; df, degrees of freedom; MS, mean square; s_b, reproducibility; CV, coefficient of variation.

(b) Mean square values are multiplied by 10^6.

(c) Data from Laboratory P_1 were excluded from the statistical analysis.

The mean square of sulfation rate measurements at each site in Table 5 is obtained by the equation

$$MS = \frac{\Sigma\ n_i(\bar{x}_i - \bar{x})^2}{df} \qquad \text{Equation (1)}$$

where, $\bar{x}_i$ denotes the measurement value obtained by the ith laboratory, $\bar{x}$ denotes the arithmetic mean of the measurements obtained by all laboratories at the site, and df is the degrees of freedom. For those laboratories making duplicate measurements, $\bar{x}_i$ is taken to be the average of the two measurements, and the mean is given a weight of 2 so that $n_i = 2$. If a laboratory made a single determination, then $\bar{x}_i$ is equal to that determination and n_i is 1.

The mean square calculated from Equation (1) includes both the within- and between-laboratory variance. The relationship is described by the equation

$$MS = s_w^2 + Ks_b^2 \qquad \text{Equation (2)}$$

where, s_w^2 denotes the within-laboratory variance, s_b^2 denotes the between-laboratory variance, and K is the number of replicate measurements by each laboratory[6]. The between-laboratory variance (s_b^2) is determined by substitution of values for MS, s_w, and K in Equation (2). Duplicate determinations were performed by each laboratory at each site, therefore K = 2.

The reproducibility of the Test Method, defined in this report as the standard deviation (s_b) of the sulfation rate measurements between laboratories, is computed by extracting the square root of the between-laboratory variance. Another measure of reproducibility is provided by the coefficient of variation (CV) computed from the following equation

$$CV = 100 \, s_b/m.$$

The coefficient of variation, as formulated here, measures reproducibility as a percentage of the mean sulfation rate.

The statistical analysis of the sulfation rate measurements at the three different sites provides a limited quantity of data with which an estimate of the relationship of m and s_b can be made. Figure 4 shows a plot of the reproducibility, s_b, versus the mean, m, of the Los Angeles, Bloomington, and Manhattan data. A curve of the form $\hat{s} = b\sqrt{m}$ was fitted to the data points in Figure 4 by the method of weighted least squares. Weights were assigned to the data points in order to compensate for the fact that two assumptions of the statistical method were being violated:

(1) the coordinates of the data points are averages which are not computed from the same number of measurements, and

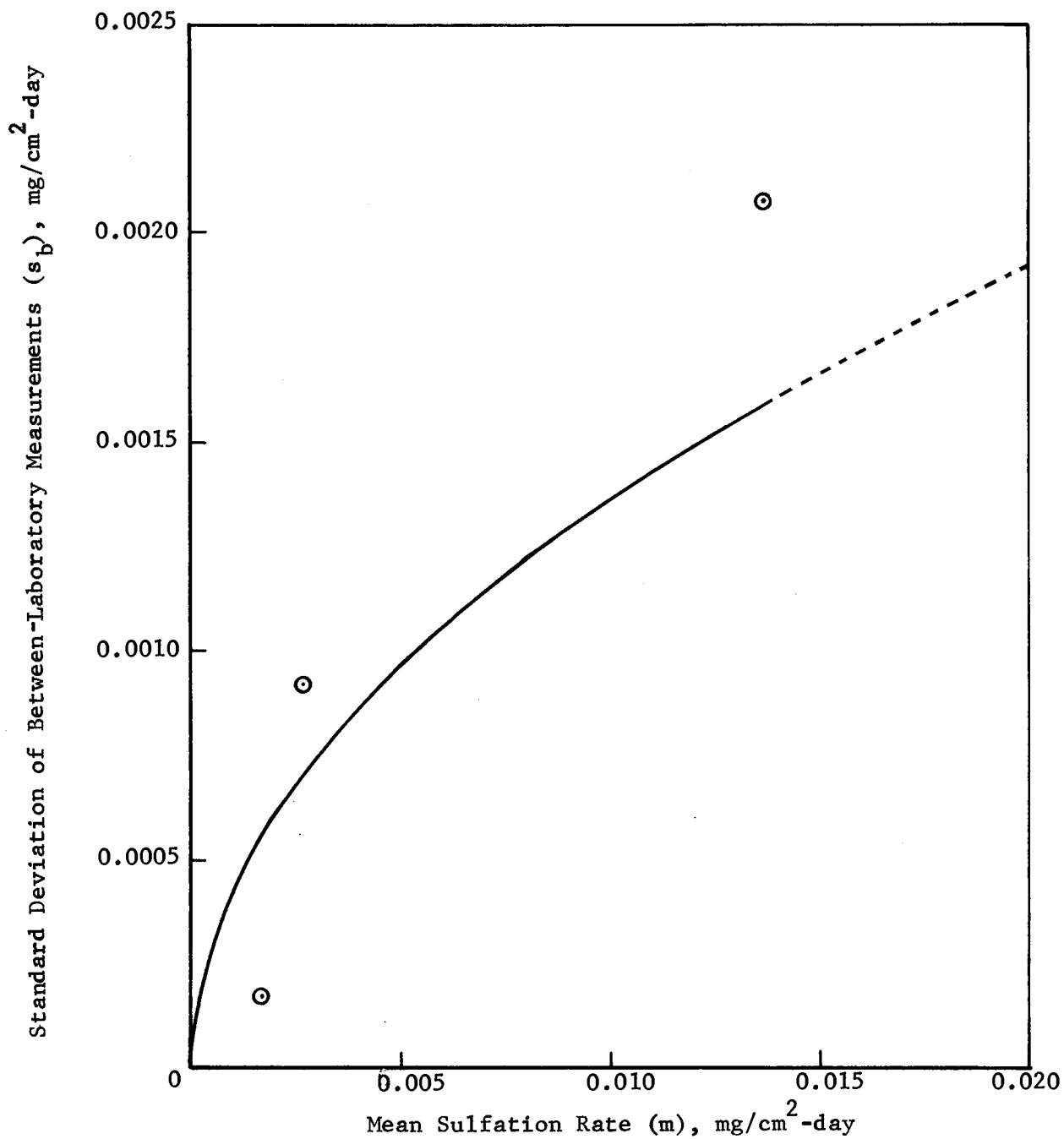(2) the variances along the regression curve are not equal.

FIGURE 4. LEAST-SQUARES CURVE SHOWING THE RELATIONSHIP
BETWEEN REPRODUCIBILITY AND SULFATION RATE

The appropriate weighting formula is $W = f/m$ where, W represents the weight, f denotes the degrees of freedom associated with the computed standard deviation $\hat{s}$, and m is the mean sulfation rate. The weighted least-squares procedure yields a curve with the equation $\hat{s} = 0.0136\sqrt{m}$ as an estimate of the true regression curve $s = \beta\sqrt{m}$. The standard deviation of residuals about the calculated regression curve is 0.00034 mg/cm^2-day.

The bottom line of Table 5 lists the mean of the pooled data for all three sites. The mean sulfation rate for all sites is 0.0063 mg/cm^2-day and the overall reproducibility is 0.00135 mg/cm^2-day. The coefficient of variation based on the mean sulfation rate and average reproducibility is 21 percent.

Analysis of Repeatability

The pairs of duplicate unspiked sulfation rate determinations were used to obtain a measure of within-laboratory variability (repeatability) of the Test Method. Table 6 presents the results of the analysis of repeatability. The mean square or variance of the measurements at each site was determined by the equation

$$MS = \frac{\sum \frac{(x_i - y_i)^2}{2}}{df}$$

where, x_i and y_i denote the pairs of duplicate measurements made by the ith laboratory.

The repeatability of the Test Method is obtained by taking the square root of the mean square of the within-laboratory measurements.

The coefficient of variation, CV, is calculated from the mean sulfation rate, m, and the repeatability, s_w, as follows

$$CV = 100 \, s_w/m.$$

TABLE 6.   SUMMARY OF WITHIN-LABORATORY VARIABILITY (REPEATABILITY)
OF SULFATION RATE MEASUREMENTS[a]

				Within-Laboratory Variation		
Site	n	m, mg/cm^2-day	df	MS[b], (mg/cm^2-day)^2	s_W, mg/cm^2-day	CV(%)
Los Angeles[c]	12	0.00178	6	0.072	0.00027	15
Bloomington	14	0.00275	7	0.078	0.00028	10
Manhattan	14	0.01371	7	0.196	0.00044	3
All Sites[c]	40	0.00630	20	0.118	0.00034	5

(a) Column headings: n, number of measurement of sulfation rate;
m, mean sulfation rate; df, degrees of freedom; MS, mean square;
s_W, within-laboratory standard deviation (repeatability); CV,
coefficient of variation.

(b) Mean square values are multiplied by 10^6.

(c) Data from Laboratory P_1 were excluded from the statistical analysis.

Table 6 shows, for each site, the number (n) of sulfation rate measurements
performed, the mean (m) of the sulfation rate of all laboratories, the number
of degrees of freedom (df) associated with the statistical analysis, the mean
square (MS) of the sulfation rate measurements, the repeatability (s_w), and
the coefficient of variation (CV).

The site values for repeatability are plotted versus the mean
sulfation rate in Figure 5. A curve of the form $\hat{s} = b\sqrt{m}$ was fitted to the
data points by the method of weighted least squares using the weighting formula,
$W = f/m$. The resultant curve is characterized by the equation $\hat{s} = 0.00504\sqrt{m}$.
The standard deviation of the residuals is 0.000056 mg/cm^2-day. The curve
summarizes the relationship between repeatability and sulfation rate based on
the limited number of observations which were made.

The last line of Table 6 summarizes the pooled data from the three
test sites. The mean sulfation rate is 0.00630 mg/cm^2-day and the over-all
repeatability is 0.00034 mg/cm^2-day. The repeatability expressed as a per-
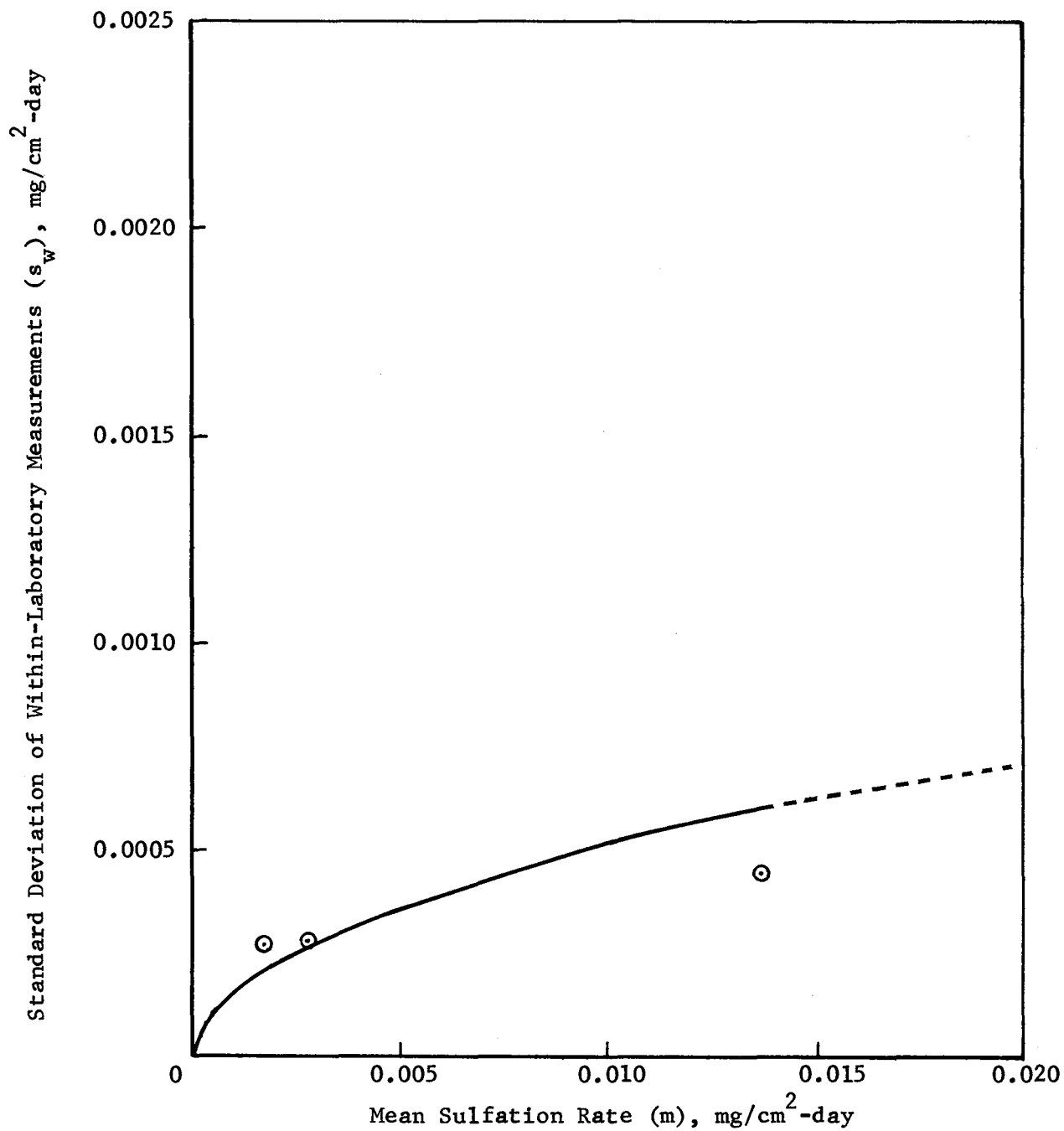centage of the mean value is five percent.

FIGURE 5. LEAST-SQUARES CURVE SHOWING THE RELATIONSHIP
BETWEEN REPEATABILITY AND SULFATION RATE

Analysis of Accuracy

A measure of the accuracy of the analytical steps of the sulfation measurement is provided by the results of corresponding spiked and unspiked determinations. The difference (S-U) between the spiked determination (S) and the unspiked determination (U) is a measure of the known quantity of potassium sulfate added prior to the sulfate analysis. The spike recoveries are listed by site and laboratory in the last columns of Tables 2, 3, and 4.

Table 7 summarizes the sulfate spike recovery data for each site and for all sites combined. The statistics in this table represent average results for all laboratories. The mean spike recoveries ranged from 94 percent at Bloomington to 106 percent at Los Angeles with a pooled average for all sites of 98 percent. The standard deviations of the between- and within-laboratory recovery measurements over all sites are 10 and 21 percent, respectively.

The accuracy of the sulfate determinations of the spiked samples by individual laboratories at the three test sites are shown in Figures 6, 7, and 8. Each figure presents the relationship of the estimated spiking rate to the actual spiking rate for each laboratory at a given site. Lines of constant recovery are included for comparative purposes. In addition, a dashed line representing the mean recovery for all laboratories is included in each graph.

From the Los Angeles data (Figure 6) it appears that all of the laboratories, except for Laboratory P_1, constitute a homogeneous group. On the average (excluding Laboratory P_1) they overestimated the spiking rate by 6 percent, as shown by the dashed line in the figure.

The Bloomington results (Figure 7) show more scatter in the recovery values. Laboratories J_2, K_2, L_2, and M_2 seem to form a homogeneous group, but whether Laboratories N_2, O_2, and P_2 belong to this group is not obvious. On the basis of statistical tests, however, none of the Bloomington data could be rejected. The dashed line in Figure 7 represents the mean recovery for all laboratories which shows that on the average, they underestimated the spiking rate by 6 percent.

TABLE 7. SUMMARY OF SULFATE SPIKE RECOVERY DATA[a]

| | Mean Recovery (m), % | Between-Laboratory Variation | | | Within-Laboratory Variation | | |
		df	MS, $(\%)^{2}$ [b]	σ_b, %	CV, %	df	MS, $(\%)^{2}$	σ_w, %	CV, %
Los Angeles [c]	11	106	5	163	6	6	5	100	10	9
Bloomington	14	94	6	1606	17	18	7	1034	32	34
Manhattan	14	96	6	116	(d)	(d)	7	120	11	11
All Sites [c]	39	98	17	655	10	10	19	451	21	21

(a) Column headings: n, number of measurements; m, mean spike recovery; df, degrees of freedom; MS, mean square; σ_b, between-laboratory standard deviation of recovery; σ_w, within-laboratory standard deviation of recovery; CV, coefficient of variation.

(b) Mean square contains both within- and between-laboratory variations and is related to these variations by the equation MS = σ_w^{2} + Kσ_b^{2} where K=2.

(c) Data from Laboratory P_1 at Los Angeles were excluded.

(d) These variations could not be calculated because the mean square of between-laboratory measurements is less than the mean square of within-laboratory measurements. The model for computing σ_b does not hold in this case.
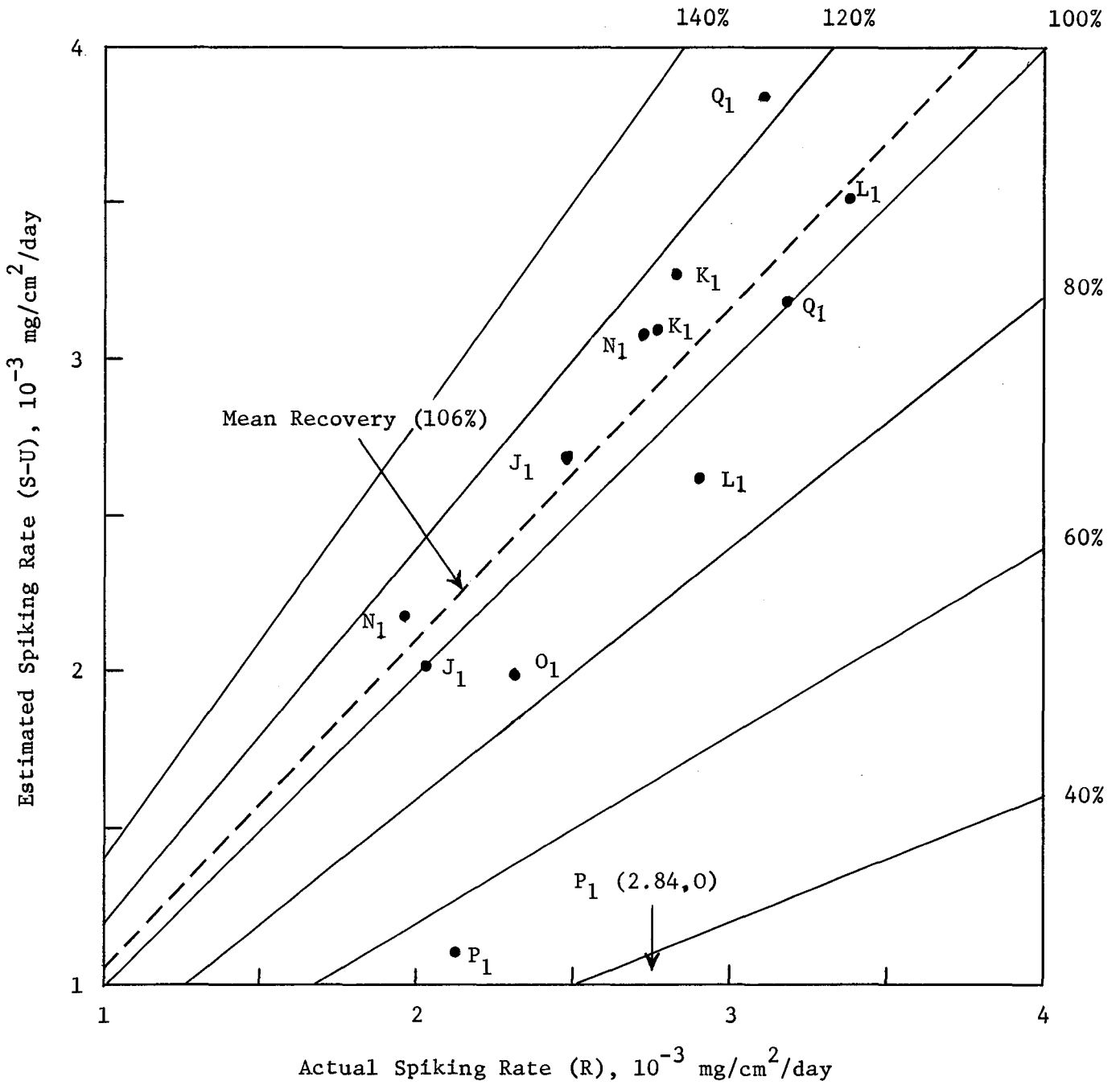
FIGURE 6. RELATIONSHIP OF ESTIMATED SPIKING RATE TO ACTUAL SPIKING RATE AT LOS ANGELES

Rays fanning outward are lines of constant recovery.

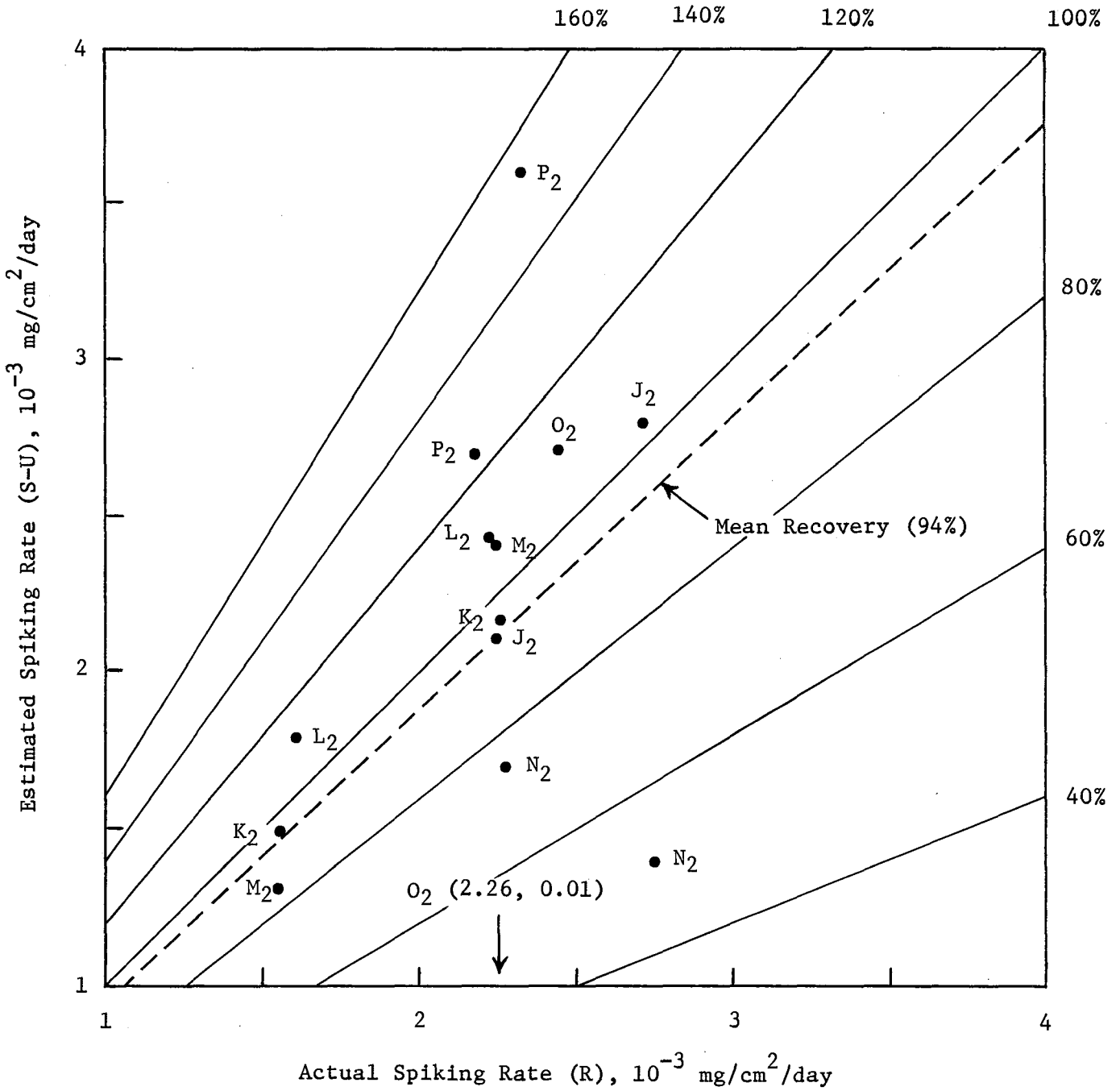In computing mean recovery, Laboratory P_1 was excluded.

FIGURE 7. RELATIONSHIP OF ESTIMATED SPIKING RATE TO ACTUAL SPIKING RATE AT BLOOMINGTON

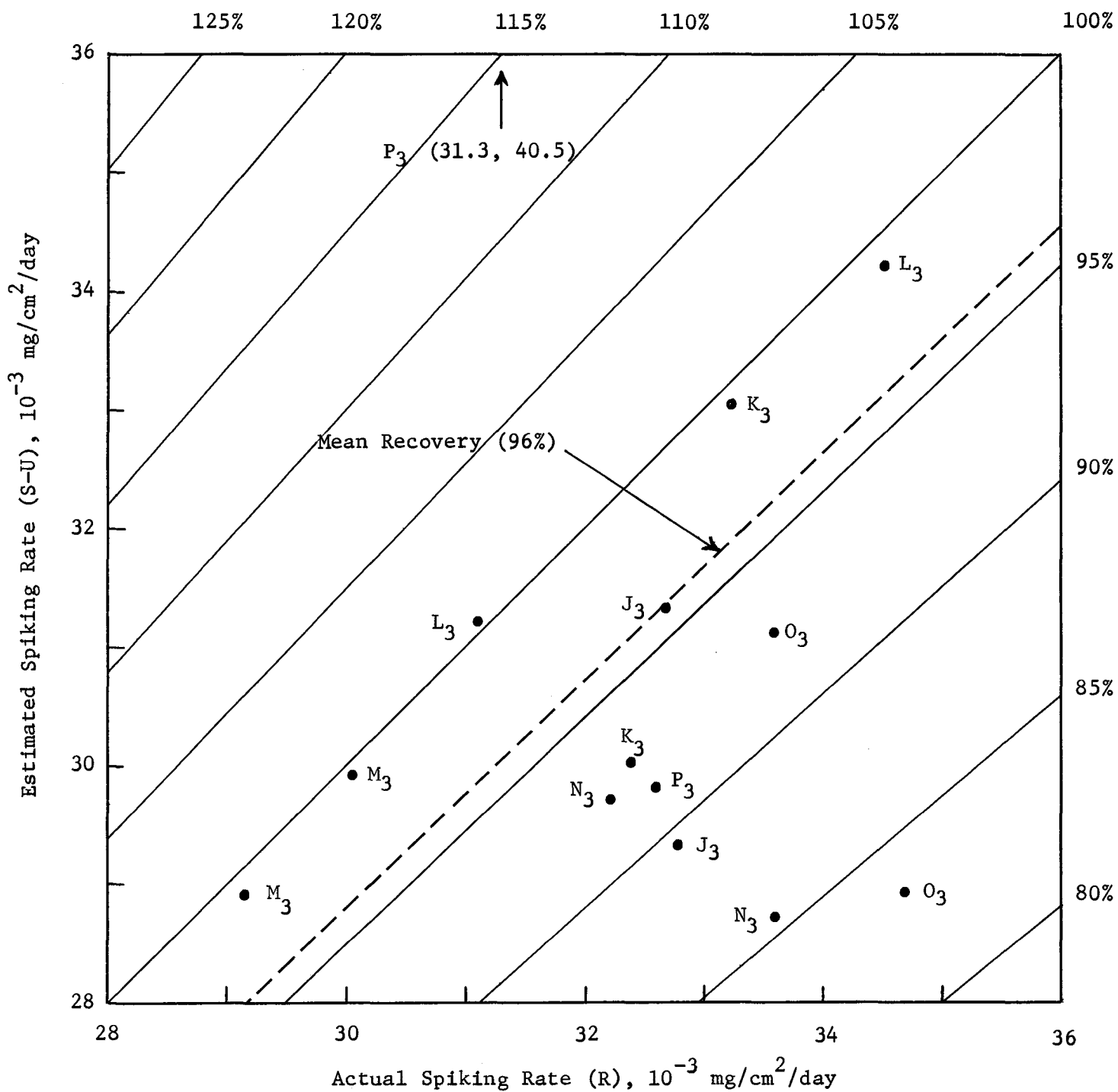Rays fanning outward are lines of constant recovery.

FIGURE 8. RELATIONSHIP OF ESTIMATED SPIKING RATE TO ACTUAL SPIKING
RATE AT MANHATTAN

Rays fanning outward are lines of constant recovery.

The Manhattan data (Figure 8) also exhibits more scatter than the Los Angeles results. However, on the basis of statistical tests none of the Manhattan data could be rejected. The dashed line in Figure 8 represents the mean recovery for all laboratories, and shows that, on the average, the laboratories underestimated the spiking rate by 4 percent.

Analysis of Between-Rack and Within-Rack Variability

The statistical design in Table 1 does not provide for evaluating the effect of location of sampling stations. The number of determinations allotted to the sulfation test method is insufficient to support any analysis capable of isolating the separate effects of laboratory, geographical site, rack location, and location of sampling stations within racks. Out of physical considerations, the last two variables, between-rack and within-rack variability, are not expected to contribute significantly to the observed measurements of reproducibility, repeatability, and recovery.

DISCUSSION AND CONCLUSIONS

The interlaboratory study provides the following conclusions regarding the accuracy and precision of ASTM Method D 2010 for determining total sulfation in the atmosphere.

(1) The standard deviation, s_b, for the reproducibility of sulfation rate measurements by different laboratories over the range of 0.00178 to 0.01371 mg/cm^2-day may be expressed by the equation:

$$s_b = 0.0136\sqrt{m}$$

where, s_b, and, m, the mean sulfation rate are given in mg/cm^2-day.

(2) The standard deviation, s_w, for replicate measurements of sulfation rate over the range of 0.00178 to 0.01371 mg/cm^2-day by the same laboratory (repeatability) may be expressed by the equation:

$$s_w = 0.00504 \sqrt{m}$$

where, s_w, and, m, the mean sulfation rate are given in mg/cm^2-day.

(3) The average results of the analysis of spiked samples indicates that the determination of sulfate in an exposed candle by ASTM Method D 516 can be performed with an accuracy which is two percentage points less than the true value.

(4) The standard deviation of the percentage of sulfate spike recovery of the sulfate analysis step is 10 percent for between-laboratory measurements and 21 percent for within-laboratory measurements.

The determination of reactive sulfur compounds by the sulfation candle technique is generally considered to be a rather unrefined, qualitative method. However, results of this study demonstrate that total sulfation measurements made in accordance with ASTM Method D 2010 can be performed quantitatively and that the Method can yield accurate and precise results.

RECOMMENDATIONS

The results of this study demonstrate that no changes are required in ASTM Method D 2010 to obtain sulfation measurements of satisfactory accuracy and precision. Results with comparable statistical characteristics to those reported here can be achieved with the Test Method as it is presently written and performed.

It is recommended that the accuracy and precision data obtained in this study be incorporated into the description of the Test Method.

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(3) "Tentative Recommended Practice for Statements on Precision and Accuracy", ASTM Method D 2906.

(4) "Use of the Terms Precision and Accuracy as Applied to Measurement of a Property of a Material", ASTM Method E 177.

(5) "Standard Recommended Practice for Dealing with Outlying Observations", ASTM Method E 178.

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APPENDIX

REPRINT OF ASTM

STANDARD METHOD FOR EVALUATION OF TOTAL SULFATION IN ATMOSPHERE
BY LEAD PEROXIDE CANDLE

ASTM Designation: D 2010-65

and

STANDARD METHODS OF TEST FOR SULFATE ION IN WATER AND WASTE WATER

ASTM Designation: D 516-68

Standard Method for
EVALUATION OF TOTAL SULFATION IN ATMOSPHERE BY THE LEAD PEROXIDE CANDLE[1]

This Standard is issued under the fixed designation D 2010; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 This method covers the evaluation of the total sulfation in atmosphere. It provides a means for determining the amount of sulfur dioxide attacking a specific area during a definitely decided period of time where this gas is known to be the only sulfur compound present. Because of its oxidizing power, lead peroxide converts other compounds, such as mercaptans and hydrogen sulfide, into sulfate. It fixes sulfur trioxide (Note) and sulfuric acid mist present in the atmosphere. It converts the oxides of nitrogen into nitrate. The method is based on the following reaction:

$$PbO_2 + SO_2 \rightarrow PbSO_4$$

NOTE—It has been shown that the rate of sulfation per unit area of lead peroxide exposed surface is independent of the concentration of sulfur dioxide up to levels of 1000 ppm, if 15 percent or less of the lead peroxide has been reduced (1).[2] Fifteen percent of the lead peroxide is equivalent to 13 mg of sulfur trioxide per square centimeter per day for 30 days when a candle having 8 g of lead peroxide/100 cm² is used.

2. Definitions

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

3. Reagents and Materials

3.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Low sulfate re-

agents should be used. The sulfate content of the lead peroxide used should be the lowest possible obtainable.

3.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to ASTM Specifications D 1193, Reagent Water.[3]

3.3 *Barium Chloride (50 g/liter)*—Dissolve 50 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in water and dilute to 1 liter.

3.4 *Ethyl Alcohol (95 percent)*.

3.5 *Gum Tragacanth*, powdered.

3.6 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

3.7 *Hydrochloric Acid (0.05 N)*—Prepare and standardize a 0.05 N solution of HCl.

3.8 *Lead Peroxide*—Powdered lead peroxide (PbO_2) of the highest purity.[5]

3.9 *Sodium Carbonate* (Na_2CO_3), anhydrous powder.

4. Sampling

4.1 The sampling period may be 1 month of 30 days or any period long enough to provide a convenient minimum of total sulfate for analysis. The work of Keagy and Associates (5) which is used as the criterion for the sampling procedure indicates a range from 5 to 2000 mg of barium sulfate per

[1] This method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres.
Current edition effective Aug. 31, 1965. Originally issued 1962. Replaces D 2010 – 62 T.
[2] Boldface numbers in parentheses refer to the list of references appended to this method.
[3] *Annual Book of ASTM Standards*, Part 23
[4] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N.Y., and the "United States Pharmacopeia."
[5] "Pregel" grade lead peroxide has been found satisfactory for this purpose.

candle. The sampling frequency should be uniform and may be determined by the requirements of the survey. Monthly, bimonthly, and seasonal sampling periods have been shown to provide consistent and reliable data (5).

4.2 *Sampling Station*—The sampling station may be a louvered box as described in Fig. 1 (1). The dimensions of the louvered area on each side should be not less than 203 mm (8 in.) and the louvers should be placed at an angle of 45 deg to provide maximum shelter from rainfall. The box may be made of metal or wood. If it is of metal it should be of material that will have a low order of reactivity with sulfuric acid and sulfur dioxide. When wood is used it may be shellacked or varnished for protection. The use of a lead base paint is not advised. The center of the louvered box should be fitted with a suitable holder for the sampling device.

4.2.1 Sampling stations should be selected at random on a uniform network grid over the area to be studied and the density of the sampling stations should be not less than two per square mile. Spacing of sampling stations should be uniform.

4.3 *Location of Sampling Device*—The box should be located in a manner that will assure protection from tampering, and it should be secured from falling. The height of the box from ground level should be the same at all stations.

5. Preparation of Lead Peroxide Candle

5.1 *Support of Reactive Surface*—A suitable support for the reactive surface may be a glass jar, test tube, plastic container, or any inert, impervious cylinder that conveniently provides the desirable area.

5.2 *Reactive Surface*—There shall be a minimum reactive surface of 100 cm^2 containing not less than 8 g of lead peroxide. The weight of lead peroxide per candle in any batch should not vary more than 10 percent.

5.3 *Bonding Paste*—Gum tragacanth glue has been found satisfactory (1–5) and may be prepared as follows: Disperse a sufficient weight of good grade powdered gum tragacanth in five times its weight of ethyl alcohol (95 percent) and add hot water carefully, with stirring, until a 2 to 3 percent' mixture is formed. The concentration of the glue shall

not exceed 3 percent gum tragacanth. Warm the mixture gently on a low-temperature hot plate until a clear, uniform gel has been obtained. *Take care not to overheat the gum.*

5.3.1 Prepare batch quantities of paste (3) by adding the desired weight of lead peroxide to the glue, in small portions, with continuous stirring to make the paste entirely free from lumps. The paste then may be applied to the support to provide the minimum reactive surface.

5.3.1.1 When large quantities of paste are made care must be taken to maintain an even dispersion of the lead peroxide reagent and excessive heating of the mixture avoided. The viscosity of the paste can be controlled by using an adequate water bath (6). When single lead peroxide candles are prepared (1) 8 g of the lead peroxide shall be triturated in sufficient glue to make paste of desirable working consistency. This may be done conveniently with a spatula on a glass plate. The same spatula, or a stiff bristled brush 1 in. (25 mm) wide can be used to spread the paste on the support.

5.3.1.2 When quantity batches of candles are prepared a small, hand-operated centrifuge may be adapted to facilitate the task. This is done by removing the tube holders and fastening to the rotating shaft an appropriate device for securing the candle (6).

6. Procedure

6.1 Apply the lead peroxide paste to a fabric binder on the support (1). Wash a fabric subsurface, such as tapestry cloth (1), or stockinette (5) in boiling water and dry in a sulfur dioxide-free atmosphere. Secure an adequate area of fabric to the support by means of cotton thread (1) or rubber bands (3) and then apply the peroxide paste to the fabric.

6.2 Drying of the coating must be accomplished in a sulfur dioxide-free atmosphere. Retain a blank, unexposed candle from every batch of candles prepared. Keep candles in sealed containers, away from exposure to sulfur dioxide or other gases that would contaminate the reactive surface, until used. At the end of the exposure period return the candles to containers that can be sealed against further contamination.

6.3 *Treatment of Exposed Candles*—

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Measure the surface area at this time. Separate the impregnated cloth surface from the support, using a spatula or knife point, if necessary. The fabric may be cut into smaller pieces. Transfer the lead peroxide-covered fabric to a 250-ml beaker containing 5 g of Na_2CO_3 dissolved in 60 ml of water. Allow the immersed pieces to soak for 3 h, with occasional stirring. Then simmer the mixture gently on a thermostatically controlled hot plate for 30 min. With reasonable care this operation can be conducted with minimum evaporation of water when properly covered beakers are used. However, care should be taken to maintain an approximately constant volume. Filter the beaker contents through a fast filter paper, with appropriate washings, and neutralize the filtrate with $2N$ HCl to a pH range from 3.0 to 4.0 with methyl orange. Care should be taken to prevent loss of sample by foaming, particularly when the point of neutralization is approached.

6.4 *Determination of Sulfate as Barium Sulfate*—Determine the sulfate ion in accord-ance with the referee method of ASTM Methods D 516, Test for Sulfate Ion in Industrial Water and Industrial Waste Water.[3] Barium sulfate precipitates are slightly soluble in dilute HCl (7). The precipitation with $BaCl_2$, therefore, must be performed in a dilute acid solution of 0.05 N HCl for optimum results. It should be borne in mind during this phase of the analysis that the rapid addition of a hot (if possible, boiling) solution of $BaCl_2$ to a gently boiling solution of the sulfate in dilute acid will yield a granular and easily filterable barium sulfate precipitate.

7. Precision

7.1 The standard deviation from the mean of data using this method has been found to be 7 percent (8).

8. Report

8.1 Report the results as milligrams of sulfur dioxide per square centimeter per day, taking into consideration the possibility of the interferences described in Section 1.

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Annual Meeting, May 22-26, 1960.
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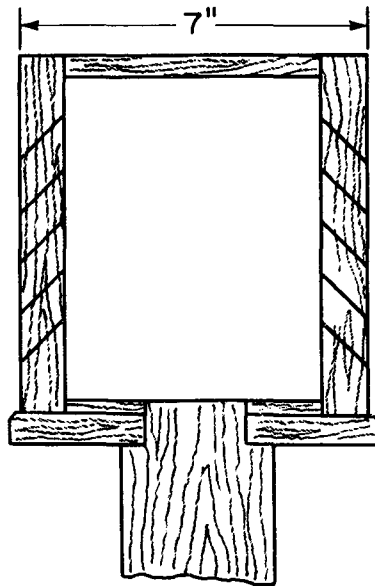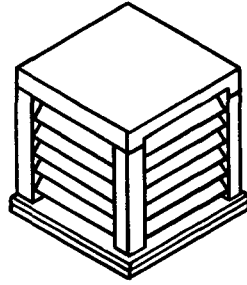
FIG. 1 Sampling Station.

Standard Methods of Test for
SULFATE ION IN WATER AND WASTE WATER[1]

This Standard is issued under the fixed designation D 516; 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.

ᵉ Note 1—Editorial changes were made throughout in April 1973.
ᵉ Note 2—Editorial changes were made deleting the word "industrial" in the title and text where appropriate in May 1973.

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1. Scope

1.1 These methods cover the determination of sulfate ion in water and waste water. Three methods are given as follows:

	Sections
Method A (Gravimetric Method)	5 to 11
Method B (Turbidimetric Method)	12 to 20
Method C (Volumetric Method)	21 to 31

1.2 Method A is a primary measure of sulfate ion in all water. Methods B and C are less time-consuming but often more liable to interference than Method A. They are particularly useful in the lower sulfate range, below 20 mg/liter ppm) SO₄

2. Definitions

2.1 For definitions of terms used in these methods, refer to ASTM Definitions D 1129, Terms Relating to Water.[2]

3. Purity of Reagents

3.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

3.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to ASTM Specifications D 1193, for Reagent Water.[2] In addition, reagent water used for these methods shall be sulfate-free.

4. Sampling

4.1 Collect the sample in accordance with the applicable ASTM method as follows:

D 510—Sampling Water,[2]
D 860—Sampling Water from Boilers,[2]
D 1066—Sampling Steam,[2]
D 1192—Equipment for Sampling Water and Steam,[2] and
D 1496—Sampling Homogeneous Industrial Waste Water.[2]

METHOD A—GRAVIMETRIC METHOD

5. Application

5.1 This method is applicable to all types of water and waste water. It is directly applicable to samples containing approximately 20 to 100 mg/liter (ppm) of sulfate ion (SO₄⁻⁻). It can be extended to higher or lower ranges by adjusting the sample size.

6. Summary of Method

6.1 Sulfate ion is precipitated and weighed as barium sulfate after removal of silica and other insoluble matter.

7. Interferences

7.1 Sulfites and sulfides may oxidize and precipitate with the sulfate. Turbidity caused by silica or other insoluble material would interfere if allowed to be present, but removal of such interference is provided in this method.

7.2 Other substances tend to be occluded or adsorbed on the barium sulfate, but these do not significantly affect the precision and accuracy of the method.

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[1] These methods are under the jurisdiction of ASTM Committee D-19 on Water.
  Current edition effective Sept. 13, 1968. Originally issued 1938. Replaces D 516 – 63 T.
[2] Annual Book of ASTM Standards, Part 23.
[3] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N.Y., and the "United States Pharmacopeia."

8. Reagents

8.1 *Ammonium Hydroxide* (*sp gr 0.90*)—Concentrated ammonium hydroxide (NH_4OH).

8.2 *Barium Chloride Solution* (*118 g/liter*)—Dissolve 118 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in water and dilute to 1 liter.

8.3 *Hydrochloric Acid* (*1+9*)—Mix 1 volume of hydrochloric acid (HCl, sp gr 1.19) with 9 volumes of water.

8.4 *Hydrofluoric Acid* (*48 to 51 percent*)—Concentrated hydrofluoric acid (HF).

8.5 *Methyl Orange Indicator Solution* (*0.5 g/liter*)—Dissolve 0.05 g of methyl orange in water and dilute to 100 ml.

8.6 *Nitric Acid* (*sp gr 1.42*)—Concentrated nitric acid (HNO_3).

8.7 *Picric Acid* (*saturated aqueous solution*).

8.8 *Silver Nitrate Solution* (*100 g/liter*)—Dissolve 10 g of silver nitrate ($AgNO_3$) in water and dilute to 100 ml.

8.9 *Sulfuric Acid* (*sp gr 1.84*)—Concentrated sulfuric acid (H_2SO_4).

9. Procedure

9.1 Filter the sample if it is turbid, using a fine, ashless paper (Note 1). Wash the beaker and the filter thoroughly with hot water.

NOTE 1—Silica may be removed before applying this method by dehydration with HCl or perchloric acid ($HClO_4$) in accordance with the respective procedures in ASTM Methods D 859, Test for Silica in Water and Waste Water.[2] In this case, the ignition described in 9.5 need not be done in a platinum crucible.

9.2 Measure into the beaker a quantity of the clear sample containing sulfate ion equivalent to 10 to 50 mg of barium sulfate ($BaSO_4$). Adjust the volume by evaporation or dilution with water to approximately 200 ml. Adjust the acidity of the sample to the methyl orange end point and add 10 ml excess of HCl (1+9).

9.3 Heat the acidified solution to boiling and slowly add to it 5 ml of hot $BaCl_2$ solution (Note 2). Stir the sample vigorously while adding the $BaCl_2$ solution. Keep the temperature just below boiling until the liquid has become clear and the precipitate has settled out completely. In no case shall this settling period be less than 2 h.

NOTE 2—Faster precipitation and a coarser precipitate can be obtained by adding 10 ml of saturated picric acid solution and boiling the sample 5 min before adding $BaCl_2$.

9.4 Filter the suspension of $BaSO_4$ on a fine, ashless filter paper, and wash the precipitate with hot water until the washings are substantially free of chlorides, as indicated by testing the last portion of the washings with $AgNO_3$ solution (Note 3). Avoid excessive washing. If any $BaSO_4$ passes through the filter, pour the filtrate through the paper a second time (Note 4).

NOTE 3—Do not attempt to obtain a completely negative test for chloride. Discontinue washing when no more than a faint opalescence is produced in the test.

NOTE 4—If the filtrate is poured through the paper a second time, $AgNO_3$ must not be present in the filtrate.

9.5 Place the filter paper and contents in a weighed platinum crucible (Note 1), and char and consume the paper slowly without flaming. Ignite the residue at approximately 800 C for 1 h, or until it is apparent that all carbon has been consumed.

9.6 Add a drop of H_2SO_4 and a few drops of HF, and evaporate under a hood to expel silica as silicon tetrafluoride (SiF_4). Reignite at about 800 C, cool in a desiccator, and weigh the $BaSO_4$.

10. Calculation

10.1 Calculate the concentration of sulfate ion (SO_4^{--}) in milligrams per liter, as follows:

$$\text{Sulfate, mg/liter (ppm)} = (W \times 411{,}500)/S$$

where:
W = grams of $BaSO_4$, and
S = milliliters of sample.

11. Precision

11.1 Results by this method are precise to 1.0 percent of the amount of sulfate ion present.

METHOD B—TURBIDIMETRIC METHOD

12. Application

12.1 This method is intended for rapid routine or control tests for sulfate ion in industrial water where extreme accuracy and precision are not required. It is directly appli-

cable over the range of 10 to 100 mg/liter (ppm) of sulfate ion (SO_4^{--}).

13. Summary of Method

13.1 Sulfate ion is converted to a barium sulfate suspension under controlled conditions. Glycerin solution and a sodium chloride solution are added to stabilize the suspension and minimize interferences. The resulting turbidity is determined by a photoelectric colorimeter or spectrophotometer and compared to a curve prepared from standard sulfate solutions.

14. Interferences

14.1 Insoluble suspended matter in the sample must be removed. Dark colors that can not be compensated for in the procedure interfere with the measurement of suspended barium sulfate ($BaSO_4$).

14.2 Although other ions normally found in water do not appear to interfere, the formation of the barium sulfate suspension is very critical. This method is more suitable as a control procedure where concentration and type of impurities present in the water are relatively constant. Determinations that are in doubt should be checked by the Method A in some cases, or by the procedure suggested in Note 7.

15. Apparatus

15.1 *Photometer*—A filter photometer or spectrophotometer suitable for measurements between 350 and 425 nm, the preferable wavelength range being 380 to 400 nm. The cell for the instrument should have a light path through the sample of approximately 40 mm, and should hold about 50 ml of sample. Filter photometers and photometric practices prescribed in this method shall conform to ASTM Recommended Practice E 60, Photometric Methods for the Chemical Analysis of Metals[4]; spectrophotometers shall conform to ASTM Recommended Practice E 275, for Describing and Measuring Performance of Spectrophotometers.[5]

16. Reagents

16.1 *Barium Chloride*—Crystals of barium chloride ($BaCl_2 \cdot 2H_2O$) screened to 20 to 30-mesh.

16.2 *Glycerin Solution (1+1)*—Mix 1 volume of glycerin with 1 volume of water.

NOTE 5—A stabilizing solution containing sodium carboxymethylcellulose (10 g/liter) may be used instead of the glycerol solution.[6]

16.3 *Sodium Chloride Solution (240 g/liter)*—Dissolve 240 g of sodium chloride (NaCl) in water containing 20 ml of concentrated hydrochloric acid (HCl, sp gr 1.19), and dilute to 1 liter with water. Filter the solution if turbid.

16.4 *Sulfate, Standard Solution (1 ml = 0.100 mg SO_4^{--})*—Dissolve 0.1479 g of anhydrous sodium sulfate (Na_2SO_4) in water, and dilute with water to 1 liter in a volumetric flask. Standardize by the procedure prescribed in Section 9.

17. Calibration

17.1 Follow the procedure given in Section 18, using appropriate amounts of the standard sulfate solution prepared in accordance with 16.4, and prepare a calibration curve showing sulfate ion content in milligrams per liter plotted against the corresponding photometer readings (Note 6). Prepare standards by diluting with water 0.0, 2.0, 5.0, 10.0, 15.0, 20.0, 30.0, 40.0, and 50.0 ml of standard sulfate solution to 50-ml volumes in volumetric flasks. These solutions will have sulfate ion concentrations of 0.0, 4.0, 10.0, 20.0, 30.0, 40.0, 60.0, 80.0 and 100.0 mg/liter (ppm), respectively.

NOTE 6—A separate calibration curve must be prepared for each photometer and a new curve must be prepared if it is necessary to change the cell, lamp, or filter, or if any other alterations of instrument or reagents are made. Check the curve with each series of tests by running two or more solutions of known sulfate concentrations.

18. Procedure

18.1 Filter the sample if it is turbid, and adjust the temperature to between 15 and 30 C.

18.2 Pipet into a 200-ml beaker 50 ml or less of the clear sample containing between 0.5 and 5 mg of sulfate ion (Note 7). Dilute to 50 ml with water if required, and add 10.0

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ml of glycerol solution (Note 5) and 5.0 ml of NaCl solution.

Note 7—The solubility of $BaSO_4$ is such that difficulty may be experienced in the determination of sulfate concentrations below about 10 mg/liter (ppm). This can be overcome by concentrating the sample or by adding 5 ml of standard sulfate solution (1 ml = 0.100 mg SO_4^{--}) to the sample before diluting to 50 ml. This will add 0.5 mg SO_4 to the sample, which must be subtracted from the final result.

18.3 Fill a 40-mm sample cell with sample solution, wipe it with a clean, dry cloth, and place it in the cell compartment. Set the colorimeter to zero absorbance (100 percent transmission) for a blank. This compensates for any acid-insoluble matter that has not been filtered out, or for color present, or for both.

18.4 Pour the sample solution from the cell back into the beaker and add, with stirring, 0.3 g of $BaCl_2 \cdot 2H_2O$ crystals (Note 8). Continue gently stirring the solution for 1 min. Let it stand for 4 min, and stir again for 15 s. Fill the sample cell as before, and immediately make a reading with the photometer.

Note 8—The stirring should be at a constant rate in all determinations. The use of a magnetic stirrer has been found satisfactory for this purpose.

18.5 If interferences are suspected, dilute the sample with an equal volume of water, and determine the sulfate concentration again. If the value so determined is one-half that in the undiluted sample, interferences may be assumed to be absent.

19. Calculation

19.1 Convert the photometer readings obtained with the sample to mg/liter sulfate ion (SO_4^{--}) by use of the calibration curve described in Section 17.

20. Precision

20.1 The precision of this method depends on the interferences present, and the skill of the analyst. When no interfering substances are present, a careful analyst can obtain a precision of 5 percent of the SO_4^{--} or 2 mg/liter, whichever is greater.

METHOD C⁷—VOLUMETRIC METHOD

21. Application

21.1 This method is intended for the rapid

volumetric determination of a wide range of sulfate ion concentrations in industrial water. It can be used directly for routine or control tests for sulfate ion (SO_4^{--}) in certain industrial waters and, when extended by the use of ion-exchange and micro technique, for the accurate determination of SO_4^{--} over the range 5 to 1000 mg/liter (ppm).

22. Summary of Method

22.1 Sulfate ion is titrated in an alcoholic solution under controlled acid conditions with a standard barium chloride solution using thorin as the indicator. Under controlled conditions of titration, the end point is relatively sharp, the indicator changing from a yellow to a stable pink color.

23. Interferences

23.1 Both cations and anions may cause coprecipitation errors with barium sulfate precipitate. Potassium, iron, aluminum, phosphate, fluoride, and nitrate are the worst offenders. Most metallic ions also interfere seriously by forming colored complexes with the thorin indicator, especially in alcohol - water mixtures.

23.2 Interference by cations is eliminated by removal by ion exchange. However, chromium and zirconium may form varying quantities of anion complexes with sulfate ion under certain conditions.

23.3 Fluorides and nitrates cause no serious interference up to concentrations of 2 and 50 mg/liter respectively.

23.4 Ortho and metaphosphates interfere when present in excess of about 2 mg/liter. In industrial water, such as boiler water, the orthophosphate is removed by precipitation with magnesium carbonate and filtration in the cold.

23.5 Sulfite interference is eliminated by determining the sulfate equivalent of the sulfite and subtraction of this sulfate from the determined sulfate content. Sulfides also interfere but can usually be removed by precipitation as zinc sulfide.

23.6 Chlorides obscure the pink end point if present in concentrations greater than 1000

⁷ For additional information on this method, see Fritz, James S., and Yamamura, Stanley S. "Rapid Microtitration of Sulfate," *Analytical Chemistry*, ANCHA, Vol 27, No. 9, September 1955, p. 1461.

mg/liter when the sulfate present is low (about 5 mg/liter). The noninterfering concentration of chloride increases with increasing sulfate content.

23.7 Chromium present as chromates and dichromates is converted by treatment with hydrogen peroxide to the cation, Cr^{+++}, which is then removed by ion exchange.

24. Apparatus

24.1 *Titration Assembly*—For high accuracy and determination of low SO_4^{--} concentration, a microburet reading to 0.01 ml is necessary. Efficient magnetic stirring improves the speed and convenience of titration.

24.2 *Ion Exchange Column*—A suitable continuous flow column may be prepared by pouring 30 cm of a washed, wet resin, 20 to 25-mesh size into a glass column of 9 to 10-mm inside diameter and 500 ± 5 mm in length, the top of which widens to a reservoir of 50 to 55-mm inside diameter and 100 ± 5 mm in length.

24.2.1 The resin is held on a suitable screen or filter plug and the flow is controlled by a length of 2-mm bore capillary tubing joined to the bottom of the column. This tubing is bent into a U shape and rises to about 13 mm above the resin bed and then makes a U bend downward for about 50 to 70 mm.

24.2.2 Other designs of exchange columns are suitable such as a small glass column, using only 25 mm of washed resin, 100 to 200-mesh size, 65 to 70-mm total length and 15-mm inside diameter widening to a reservoir cup 50 to 55 mm in length and 30 to 35-mm inside diameter. This column is useful for very small samples which must be washed through the bed with water. Correction must be made for the amount of wash water used.

24.3 The exchange columns shall be regenerated when about two thirds exhausted. Regeneration shall be carried out by passing HCl (1+4) through the resin column and thorough washing with water. If the resin column shows no visual change as exhaustion proceeds, it is advisable to regenerate after one or two samples have passed through it.

25. Reagents

25.1 *Alcohol*[8]—Ethyl alcohol (95 percent), isopropyl alcohol, or methyl alcohol.

25.2 *Ammonium Hydroxide (1+99)*—Mix 1 volume of ammonium hydroxide (NH_4OH, sp gr 0.90) with 99 volumes of water.

25.3 *Barium Chloride, Standard Solution (1 ml = 0.500 mg SO_4^{--})*—Dissolve 1.221 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in 1 liter of water that has been adjusted to pH 3.8 to 4.0 with dilute HCl. Standardize in accordance with 26.1 and 26.2, against standard sodium sulfate solutions that have been passed through the ion-exchange resin.

25.4 *Hydrochloric Acid (1+4)*—Mix 1 volume of concentrated hydrochloric acid HCl, (sp gr 1.19) with 4 volumes of water.

25.5 *Hydrochloric Acid (1+99)*—Mix 1 volume of HCl (sp gr 1.19) with 99 volumes of water.

25.6 *Hydrogen Peroxide (30 percent)*—Concentrated hydrogen peroxide (H_2O_2).

25.7 *Iodine, Standard Solution (1 ml = 0.480 mg SO_4^{--})*—Dissolve 10 g of potassium iodide (KI) in 100 ml of water, add 1.27 g of iodine crystals, and stir until solution is complete. Dilute to 1 liter with water and store in a dark bottle. Standardize against 0.01 N $Na_2S_2O_3$ solution.

25.8 *Ion-Exchange Resin*[9]—A cationic exchange resin, 20- to 25-mesh or 100 to 200-mesh.

25.9 *Magnesium Carbonate* ($MgCO_3$).

25.10 *Phenolphthalein Indicator Solution (5.0 g/liter)*—Dissolve 0.5 g of phenolphthalein in 50 ml of 95 percent ethyl alcohol.[8] Dilute to 100 ml with water.

25.11 *Potassium Dichromate*[10]—Heat potassium dichromate ($K_2Cr_2O_7$) in a platinum crucible to a temperature just above its fusion point (396 C), taking care to exclude all dust and organic matter. After cooling, crush the fused salt to a powder in an agate mortar and preserve in a glass-stoppered bottle.

25.12 *Potassium Iodide*[10]—This should not yield a blue color when 1 g is dissolved in freshly boiled reagent-grade deaerated water treated with 5 drops (0.25 ml) of 1 N sulfuric acid (H_2SO_4) and 1 ml of freshly prepared starch solution.

25.13 *Sodium Bicarbonate*[10] ($NaHCO_3$).

25.14 *Sodium Carbonate*,[10] anhydrous

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[8] Specially denatured ethyl alcohol conforming to Formula No. 3A or 30 of the U. S. Bureau of Internal Revenue may be substituted for 95 percent ethyl alcohol.
[9] Commercial resins Dowex 50 × 8 and Amberlite IR-120 have been found satisfactory for this purpose.
[10] Reagent used for standardization only.

(Na$_2$CO$_3$).

25.15 *Sodium Thiosulfate, Standard Solution (0.01 N)*[10]—Using a 1000-ml volumetric flask, dissolve 2.482 g of sodium thiosulfate (Na$_2$S$_2$O$_3$·5H$_2$O) in approximately 800 ml of water that has just been boiled and cooled and invert the flask at regular short intervals until the solid is dissolved. Stabilize the solution by dissolving in it in the same manner 1 g of Na$_2$CO$_3$ and dilute to 1 liter with the boiled water. Standardize against K$_2$Cr$_2$O$_7$ as follows:

25.15.1 Dissolve 2 g of KI and 2 g of NaHCO$_3$ in 300 ml of water in a 500-ml Erlenmeyer flask and add concentrated HCl (sp gr 1.19) slowly, while swirling the flask, until carbon dioxide gas evolution ceases. Add 10 ml excess of HCl, mix, and then dissolve 0.010 g of dried K$_2$Cr$_2$O$_7$ in the solution. Wash down the inside of the flask with a small amount of water without agitating the flask, and allow to stand for 10 min. Titrate with the Na$_2$S$_2$O$_3$ solution, using starch solution as the indicator, until the color just changes from blue to the green color of the chromic salt.

25.15.2 Calculate as follows:

Normality of thiosulfate

$$= \frac{\text{g of K}_2\text{Cr}_2\text{O}_7 \times 1000}{\text{equiv. wt of K}_2\text{Cr}_2\text{O}_7 \ (49.04) \times S}$$

where S = milliliters of Na$_2$S$_2$O$_3$ required.

25.16 *Starch Indicator*[10]—Make a paste of 1 g of arrowroot starch or soluble iodometric starch with cold water. Pour the paste into 100 ml of boiling water and boil for several minutes. Store in a glass-stoppered bottle in a cool place. Starch solution prepared in this manner will remain chemically stable for two or three days.

25.17 *Sulfate, Standard Solution (1 ml = 0.100 mg SO$_4^{--}$).*—See 16.4.

25.18 *Sulfuric Acid (sp gr 1.84)*[10]—Concentrated sulfuric acid (H$_2$SO$_4$).

25.19 *Thorin Solution (20 g/liter)*—Dissolve 0.2 g of thorin (2(2-hydroxy-3,6-disulfo-1-naphthylazo) benzene arsonic acid) in 100 ml of water.

26. Standardization of Barium Chloride Solution

26.1 Prepare a series of standard sulfate solutions by diluting with water 0.0, 2.0, 5.0, 10.0, 15.0, 25.0, 35.0, and 50.0 ml of the standard sulfate solution (1 ml = 0.100 mg SO$_4^{--}$) to 50 ml in volumetric flasks. These solutions will have sulfate ion concentrations of 0.0, 4.0, 10.0, 20.0, 30.0, 50.0, 70.0, and 100.0 mg/liter (ppm) respectively.

26.2 Determine the blank and sulfate equivalent of the barium chloride solution (Note 9) in accordance with 27.3, 27.4, and 27.5.

NOTE 9—A solution of known sulfate concentration should be run with each series of tests or new reagents to check the standardization curve. The blank used to determine sulfate content is preferably that determined from the standardization curve extrapolated to zero.

27. Procedure in the Presence of Sulfite, Phosphate, and Chromium

27.1 In the presence of sulfite and phosphate interference, as in boiler water, pipet 25.0 ml of filtered sample containing 10 to 500 mg/liter (ppm) SO$_4^{--}$ into a 100-ml beaker. Add 0.5 ml of starch indicator and titrate the sulfite with iodine solution (1 ml = 0.480 mg SO$_4^{--}$) (Note 10). Record the volume of standard iodine solution required to obtain a blue color.

NOTE 10—A separate sample may be used to determine the sulfite by ASTM Method D 1339, Test for Sulfite Ion in Water.[2]

27.2 Add 2 to 3 drops of phenolphthalein indicator solution and adjust pH to about 8.3 with HCl (1+99) or NH$_4$OH (1+99). Add 0.3 to 0.5 g MgCO$_3$ and boil gently for 5 min, using a cover glass to minimize evaporation loss. Cool to 10 C (Note 11). Filter through acid-washed, open-texture, rapid filter paper into a 50-ml volumetric flask. Wash the precipitate with three 5-ml portions of water at 10 C. If chromium is present or suspected, add, with shaking, a few drops of H$_2$O$_2$. Adjust the volume to 50 ml with water.

NOTE 11—Phosphate ion is almost completely precipitated at or below 10 C, but solubility increases with increasing temperature.

27.3 Pass the solution through the ion-exchange column and discard the first 25 to 30 ml of effluent. Pipet 10.0 ml of the next effluent into a small white porcelain dish (100 to 125-ml capacity).

NOTE 12—When the amount of sample is limited, the sample may be passed through the small ion exchange column described in 24.2 and rinsed through with four or five times its volume of water, so that the final elutriate is 50.0 ml. Concentrate this elutriate to 10.0 ml, or take a 10.0-ml aliquot.

27.4 Add 40 ml of alcohol and 2 drops of thorin indicator. Adjust the pH to 3.8 to 4.0 by carefully adding dropwise NH_4OH (1+99) until the solution just turns pink (Note 13). Then add HCl (1+99) dropwise until the pink color disappears.

NOTE 13—If the NH_4OH is added too fast, it is possible to overrun the color change from yellow to pink and the sample continues to be yellow. It is then impossible to develop the pink color by addition of NH_4OH.

27.5 Prepare a blank using water and reagents described in 27.1 to 27.4, and record the iodine solution used for the sulfite correction of the blank. Titrate the sample with $BaCl_2$ solution (1 ml = 0.500 mg SO_4^{--}), using the untitrated yellow blank as a color reference, to a stable pink color which deepens to a reddish pink on overtitration. Then titrate the blank to the same color reached in the sample. Allow a time lapse of 3 to 5 s between additions of the last few increments of $BaCl_2$ solution.

NOTE 14—The color change may best be seen with constant stirring and a daylight fluorescent light. If such a light is not available, the use of blue tinted glasses, such as American Optical No. F-9247, is helpful.

NOTE 15—For very low sulfate concentrations a less concentrated $BaCl_2$ solution (1 ml = 0.200 mg SO_4^{--}) is advised. A standard sodium sulfate solution may be added to the sample to raise the total sulfate concentration to 10 to 15 mg/liter (ppm) SO_4^{--}. This added sulfate must be subtracted from the final result.

28. Procedure in the Absence of Sulfite, Phosphate, and Chromium

28.1 Pass 50 ml of the filtered sample directly through the ion exchange column (Note 11). Collect 10.0 ml of effluent and proceed in accordance with 27.3, 27.4, and 27.5, using the extrapolated blank.

29. Procedure in the Presence of Negligible Interferences

29.1 If interfering cations are low and high accuracy is not required, as in certain control tests, directly titrate 10.0 ml of the filtered sample in accordance with the procedure described in 27.4 and 27.5.

30. Calculation

30.1 Calculate the sulfate ion (SO_4^{--}) concentration in the original sample, in milligrams per liter, as follows:

Sulfate, mg/liter (ppm)
$$= [(V_1 - B_1) \times 500]/S_1$$
$$- [(V_2 - B_2) \times 480]/S_2$$

where:

V_1 = milliliters of $BaCl_2$ solution required for titration of the sample,

V_2 = milliliters of iodine solution required for titration of the sample for sulfite correction,

B_1 = milliliters of $BaCl_2$ solution required for titration of the blank,

B_2 = milliliters of iodine solution required for titration of the blank for sulfite correction,

S_1 = milliliters of original sample titrated, consideration being given to any dilution when passing through the ion exchange column, and

S_2 = milliliters of original sample titrated for the sulfite correction.

31. Precision[11]

31.1 Titration of SO_4^{--} in the range 5 to 100 mg/liter, after ion-exchange treatment, is accurate to 1.5 mg/liter. The precision of this method up to 100 mg/liter (excluding laboratory differences) is 0.7 mg/liter. Single operator precision may be expected to be 0.5 mg/liter.

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[11] Supporting data giving results of cooperative tests have been filed at ASTM Headquarters as RR: D-19-145.