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Environmental Monitoring Systems
Laboratory
Research Triangle Park NC 27711

Research and Development

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Quality Assurance Handbook for Air Pollution Measurement Systems: Volume II. Ambient Air Specific Methods

Sections 2.1, 2.2, 2.6, and 2.9

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Test Method

Section 2.1
Reference Method for the Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method)

Outline

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Summary

When sulfur dioxide (SO_2) is absorbed from ambient air into a solution of potassium tetrachloromercurate (TCM), a monochlorosulfonatomercurate complex (MSM) is formed that resists oxidation by oxygen in the air. This complex can be considered stable at 15°±10°C only during sampling. The sample then must be stored at 5°C until analysis to prevent any further degradation. (Thermally controlled sampling equipment is commercially available.) The MSM is reacted with pararosaniline (PRA) and formaldehyde to form an intensely colored dye (pararosaniline methyl sulfonic acid), and the absorbance of the dye is measured spectrophotometrically.

This method can be used to determine SO_2 levels in ambient air during sampling periods ranging from 30 min to 24 h. The detection limit for the method is 25 $\mu g\ SO_2/m^3$ (0.01 ppm) in an air sample of 30 standard liters (short-term sampling) and 13$\mu g\ SO_2/m^3$ (0 005 ppm) in an air sample of 288 standard liters (long-term sampling)

Based on extensive review and on experience gained in audits and in collaborative tests,[1,2] the PRA method description and the recommended limits for quality checks and audits presented herein sometimes differ from and supersede those in the guideline document.[3] On the other hand, that document contains functional and error analyses that are not included in this Handbook

A copy of the Reference Method is in Section 2.1.11 Blank data forms in Section 2.1.13 are for the convenience of the Handbook user

Recommended equivalent methods are published in the Federal Register and quarterly in the Quality Assurance Newsletter issued by the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268. See Section 2.0.4 of this volume of the Handbook for a discussion of equivalency concepts.

Method Highlights

In this quality assurance document for the SO_2 Reference Method, the procedures are designed to serve as guidelines for the development of agency quality assurance programs. Because recordkeeping is a critical part of quality assurance activities, several data forms are included to aid in the documentation of necessary data. The blank data forms (Section 2.1.13) may be used as they are, or they may serve as guidelines for preparing forms more appropriate to the individual agency; partially filled-in forms are interspersed throughout the text of the method description to illustrate their uses. Activity matrices at the end of pertinent sections can be used for quick review of the material covered in the text sections Following is a brief summary of the material covered in this SO_2 method description

1. *Procurement of Equipment* Section 2.1.1 describes the selection of equipment and the performance of procurement and calibration checks of the equipment; all are prerequisites for a quality assurance program. Section 2.1.1 conveniently identifies the sections/subsections of this part of the Handbook that pertain to specific equipment and supplies, and Figure 1.1 provides an example of a permanent procurement record.

2. *Calibration of Equipment* Section 2 1 2 provides detailed calibration procedures for flow measurement equipment, analytical balance, timer, and elapsed-time meter This section can be removed, along with the corresponding sections of the other methods of this volume, to serve as a calibration handbook. Table 2.4 at the end of Section 2.1.2 provides a summary of the acceptance limits for calibration This section is unique in that it contains detailed calibration procedures for almost all flow measurement equipment used in ambient air sampling and analysis.

3. *Preparation of Reagents* Section 2.1 3 describes the preparation and handling of reagents Reagents must be carefully prepared, stored, and maintained fresh (i.e., within the acceptable limits of shelf life). Table 3 1 at the end of this section summarizes the important activities for their preparation and storage.

4. *Sampling Procedure* Section 2.1.4 provides a detailed description of the selection and assembly of the apparatus and the checkout of the performance. The operator must perform the initial and final flow measurements and should perform the operational checks listed in Subsection 4.3 1 before collection of the sample and the postsampling checks listed in Subsection 4.3.2 after the sample collection The data record form (Figure 4.10 of Section 2.1.4) summarizes the information required to ensure the availability of good quality data and background information Because the SO_2-TCM complex is thermally unstable, the SO_2 concentration depends greatly on the temperature history of the TCM absorbing solution. The user of this method should also refer to Reference 8 in Section 2 1.12.

5. *Analysis of Samples* Section 2.1.5 contains a step-by-step procedure for colorimetric analysis, acceptance limits for the calibration curve, traceability check, and laboratory data log. The appropriate limits are given in Table 5.2 at the end of Section 2.1.5.

6. *Data Reduction, Validation, and Reporting* Section 2.1.6 describes those activities pertaining to data calculations and reporting. An important part of a quality assurance program is the final data review, the data edit or validation, and the use of standardized reporting procedures. Independent checks of the data and calculations are recommended to ensure that the reported data are both accurate and precise.

7. *Maintenance* Section 2.1.7 recommends periodic maintenance schedules to ensure that the equipment is capable of performing in accordance with specifications.

8. *Assessment of Data for Accuracy and Precision* Section 2.1.8 and 2.1.9 describe the assessment of the data for accuracy and precision, respectively. Independent audit activities provide accuracy checks of the flow rate measurements, the analysis process with the use of reference samples (EPA audit samples), and the data processing The precision check is performed by using a collocated sampler as a reference. The expected agreement between two collocated sampling trains is given in Table 9.1 and Figure 9 1 of Section 2.1.9.

9. *Reference Information* Section 2.1.10 discusses the traceability of measurements to established standards of higher accuracy, a necessary prerequisite for obtaining accurate data.

Sections 2.1.11 and 2.1.12 contain the Reference Method and pertinent references.

Section 2.1.13 contains blank data forms for the convenience of the user.

Method Description

1.0 Procurement of Equipment and Supplies

Specifications for the sampling equipment and for the analytical and the support supplies for monitoring sulfur dioxide (SO_2) in ambient air are described in Section 2.1.11. The list below references the sections/subsections of this Handbook to help the user find specific information needed for procuring the equipment and supplies.

Item	*Section*	*Subsection*
Calibration Information		
Wet test meter	*2.1.2*	*2.1.1*
Soap bubble meter	*2.1.2*	*2.1.2*
Mass flow meter	*2.1.2*	*2.1.3*
Rotameter	*2.1.2*	*2.1.4*
Flow-control devices	*2.1.2*	*2.2*
Analytical balance	*2.1.2*	*2.3*
Elapsed-time meter	*2.1.2*	*2.4*
Timer	*2.1.2*	*2.5*
Preparation of Reagents	*2.1.3*	*3.1-3.14*
Sampling Procedure		
Absorber	*2.1.4*	*4.2.1-4.2.3, 4.2.5-4.2.7*
A 24-h bubbler train	*2.1.4*	*4.2.6*
Temperature-controlled shelter	*2.1.4*	*4.2.6*
Critical orifice	*2.1.4*	*4.2.7*
Vacuum pump	*2.1.4*	*4.3.1, 4.3.2*
Moisture trap	*2.1.4*	*4.3.2*
Timer	*2.1.4*	*4.3.1, 4.3.2*
Membrane particulate filter	*2.1.4*	*4.3.2*
Analysis of Samples		
Spectrophotometer	*2.1.5*	*5.2, 5.3*
Maintenance		
A 24-h bubbler train	*2.1.7*	*7.1*
Short-term sampling train	*2.1.7*	*7.2*

The quality assurance functions are summarized in Table 1.1. Upon receipt of the sampling equipment, apparatus, and supplies, the procurement checks described in Table 1.1 should be performed. All pertinent procurement, disposition, and check information should be recorded in a log such as the one shown in Figure 1.1. This log will serve as a permanent record for future procurement needs, provide continuity among users of equipment and supplies, and provide a basis for fiscal projections.

Item description	Quantity	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ordered	Received			
Vacuum pump Model 107 CA20	4	01579	Thomas Industries	3/27/79	5/13/79	$52	OK	

Figure 1.1 Example of procurement log.

Table 1.1 Activity Matrix for Procurement of Equipment and Supplies

Equipment	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Absorber	Reference Method, Sec 2.1.11	Upon receipt, check performance.	Return to supplier.
Vacuum pump	Capable of maintaining an air pressure differential >0.7 atmosphere at desired flow rate	Upon receipt, check performance.	Return to supplier.
Air flow control device	Capable of controlling air flow within 5% over the length of the sampling period	Check upon receipt; Sec. 2.2.	Adjust using manufacturer's instructions, or return to supplier.
Spectrophotometer	Suitable for measuring absorbance at 548 ±5 nm with an effective spectral band width <15 nm	Verify wavelength calibration upon receipt and after every 160 h of use or every 6 months, whichever comes first, using NBS traceable standard wavelength filter.	Request calibration check by manufacturer/supplier.
Flow measurement devices (wet-test meter, soap-bubble meter, mass-flow meter, rotameter, flow-control devices, analytical balance, elapsed-time meter, timers)	For acceptance limits relative to calibration checks, see Table 2.4	Upon receipt, conduct calibration check.	See Table 2.4.

2.0 Calibration of Equipment

Before beginning the SO_2 sampling and analysis, be sure to calibrate the sampling and analysis equipment. The calibration activities are summarized in Table 2.4 at the end of this section. Many of these calibration checks should also be used for the initial procurement activities.

All data and calculations in the calibration activities should be recorded in a separate calibration log; that is, the log should be arranged so that a separate section is designated for each calibrated apparatus and sampler

2.1 Calibration of Flow Measurement Equipment

The sampling procedure for determination of SO_2 in ambient air can be implemented by use of one of two basic sampling trains. The differences between the two sampling trains are the flow rate, absorber design, and flow control system. The short-term sampling train consists of all glass midget impingers and utilizes either a needle valve or critical orifice to control the flow. Short-term sampling periods range between 30 minutes and 3 hours and utilize flow rates of 900 to 1100 cm^3/min for 30-minute samples to 450 to 550 cm^3/min for 1- to 3-hour samples.

The long-term sampling train consists of a polypropylene absorber tube with a glass impinger stem and utilizes a critical orifice to control the flow. The sampling period is 24 hours, and the flow is between 180 to 220 cm^3/min

Although both trains have a flow-controlling device that must be calibrated to obtain the appropriate range for the sampling rate, these devices cannot be used to measure the actual sampling flow rate. The actual sampling flow rate is determined on site before and after each sampling period by use of an appropriate flow-measuring device that is not part of the sampling train. Typical flow measuring devices are wet-test meters, soap-bubble meters, mass-flow meters, and rotameters—all of which require calibration.

2.1.1 *Wet-Test Meters — Calibration Check* - Wet-test meters are calibrated by the manufacturer to an accuracy of ±0.5 percent; the calibration must be checked initially (upon receipt) and quarterly thereafter at standard temperature and pressure and at the flow rates at which the meter will be used. The following liquid positive-displacement technique can be used to verify and make any adjustments to the accuracy of the wet-test meter to ±1 percent.

1. Level the wet-test meter by adjusting the legs until the bubble on the top of the meter is centered.
2. Adjust the water volume in the meter until the pointer in the water level gauge just touches the meniscus. Refer to manufacturer's instructions because some types of meters may require additional adjustments.
3. Adjust the water manometer in the meter to zero by moving the scale or by adding water to the manometer.
4. Set up the calibration apparatus as shown in Figure 2.1. Do not attach the saturator at this time.

   a. Fill the 5-gal jug (the reservoir) with distilled water almost up to the air inlet tube, and allow it to equilibrate to room temperature (about 24 h) before use.

   b. Start water siphoning through the system at a flow rate of approximately 200 ml/min, and collect the water in a 1-gal container located in place of the volumetric flask (Figure 2.1).
5. Check the physical operation of the meter. If the manometer reading is <10 mm (<0.4 in.) H_2O, the meter is in proper working condition. Continue to Step 6. If it is >10 mm (0.4 in.) H_2O, the wet-test meter is defective. Return it to the manufacturer for repair if the defect(s) (e.g., bad connections or joints) cannot be found and corrected.
6. Attach the saturator and continue the operation until the 1-gal container is almost full, and then use a pinch clamp to turn the siphoning system off.
7. Read the initial volume (V_i) from the wet-test meter dial, and record it on the wet-test calibration log (Figure 2.2).
8. Place a clean, dry, 2000-ml volumetric flask (Class A) under the siphon tube; open the pinch clamp; and fill the flask to the 2000-ml mark.

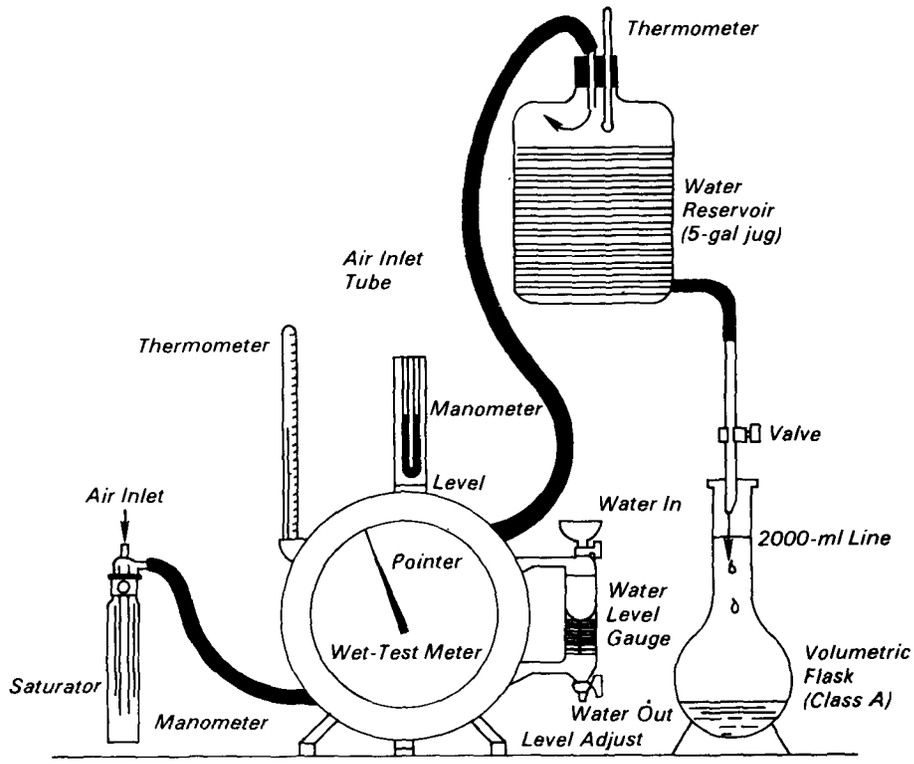


Figure 2.1 *Calibration check apparatus for wet-test meter.*

Wet test meter: Manufacturer ACME Calibrated by E.W. KING

Model 120 Date 6-13-82

SN 12-210 Test flask volume (V_t) 2000 ml

Test Number	Barometric pressure (P_b), mm Hg	Water reservoir data: Temperature (T_r), °C	Water reservoir data: Temperature (T_r), K	Wet test meter data: Temperature (T_m), °C	Wet test meter data: Temperature (T_m), K	Wet test meter data: Manometer reading (ΔP_m), mm H_2O	Wet test meter data: Manometer reading (ΔP_m), mm Hg	Wet test meter data: Meter reading: Final (V_f), liters	Wet test meter data: Meter reading: initial (V_i), liters	Wet test meter data: Meter reading: V_m^{ind}, liters	V_m^{act} actual volume of meter, liters	Percent error, %
1	742.2	23.0	296.2	22.5	295.7	35	2.6	2.020	0.005	2.015	1.9966	0.92

Calculations:

T_r = 23.0 °C + 273.2 = 296.2 K

T_m = 22.5 °C + 273.2 = 295.7 K

ΔP_m = 35 mm × H_2O x 0.0738 = 2.6 mm Hg

$V_m^{act} = \frac{T_m}{T_r} V_t$ = 1.9966 Note: If air is pushed through calibration system, ΔP_m is to be added to P_b.

Percent error = $\frac{V_m^{ind} - V_m^{act}}{V_m^{act}} \times 100 = 0.92$

Average percent error not to exceed ±1%.

Figure 2.2 Wet test meter calibration log.

9. Record the manometer reading while the water is flowing. Also record the following data:

a. Meter and reservoir air temperatures, °C (°F), and

b. Barometric pressure, mm (in.) Hg.

10. When the volumetric flask reaches its calibrated capacity, read the final volume (V_f) from the wet-test meter dial and record. Calculate the indicated volume measured by the wet-test meter ($V_m^{ind} = V_f - V_i$).

11. Repeat steps 7 through 10 twice.

12. Calculate the volume passing through the meter (V_m^{act}), using Equation 2-1, for each test.

$$V_m^{act} = \left(\frac{P_b - \Delta P_m}{P_b - \Delta P_m}\right)\left(\frac{T_m}{T_r}\right)V_t = \left(\frac{T_m}{T_r}\right)V_t$$

Equation 2-1

where

P_b = barometric pressure, mm Hg

ΔP_m = wet-test meter manometer reading, mm Hg

T_r = temperature of reservoir, K = °C + 273.2

T_m = temperature at wet-test meter, K = °C + 273.2

V_t = volume measured by volumetric flask, liters.

An example of this calculation is:

Barometric pressure, P_b = 742.2 mm Hg

Reservoir temperature, T_r = 23.0°C + 273.2 = 296.2 K

Meter temperature, T_m = 22.5°C + 273.2 = 295.7K

Meter manometer reading = 35 mm H_2O

ΔP_m = 35 mm H_2O x 0.074 mm Hg/mm H_2O = 2.6 mm Hg;

Volume measured by wet test meter

V_m^{ind} = 2.020 - 0.005 = 2.015 liters.

Volume measured by volumetric flask, V_t = 2.0000 liters

Corrected volume at meter conditions:

$$V_m^{act} = \left(\frac{295.7}{296.2}\right)2.000 = 1.9966 \text{ liters.}$$

13. Calculate the relative percent error as follows:

$$\% \text{ error} = \left(\frac{V_m^{ind} - V_m^{act}}{V_m^{act}}\right)100 =$$

$$\left(\frac{2.015 - 1.9966}{1.9966}\right)100 = 0.92\%.$$

Equation 2-2

The error should not exceed ±1 percent. If it does, check all connections within the test apparatus for leaks; gravimetrically check the volume of the standard flask; and repeat the calibration procedure. If the tolerance level is still not met, adjust the liquid level within the meter until the specifications in the manufacturer's manual are met or return the meter to the manufacturer.

Use of the wet-test meter for the calibration of flow rate devices such as rotameters and mass-flow meters requires corrections for temperature, barometric pressure, and possibly the vapor pressure of the water. If the device to be calibrated is placed after the wet-test meters (as shown later in Figure 2.5), no correction for the vapor pressure of water is required. Equation 2-3 is presented to assist the user with these corrections to the standard conditions of 760 mm (29.92 in.) Hg, 25°C (77°F), and 0 percent water vapor.

Flow rate at standard conditions

$$= \frac{\text{vol (ml)}}{\text{time (min)}} \times \frac{P - P_v}{760} \times \frac{298}{273 + T}$$

Equation 2-3

where

P = atmospheric pressure, mm Hg,

P_v = vapor pressure of water (see Table 2.1 on next page) mm Hg, and

T = temperature of gas, °C

Example: Assume the temperature to be 20°C and the atmospheric pressure to be 710 mm Hg.

Flow rate at standard conditions

$$= \frac{\text{vol (ml)}}{\text{time (min)}} \times \frac{710 - 17.54}{760} \times \frac{298}{273 + 20}$$

$$= \frac{\text{vol (ml)}}{\text{time (min)}} \times 0.927 = \text{ml/min.}$$

2.1.2 *Soap-Bubble Meter - Calibration checks* - Soap-bubble meters calibrated by the manufacturer to an accuracy of ±0.25 percent are commercially available; the volume of each of these soap-bubble meter tubes is traceable to a National Bureau of Standards (NBS) displacement volume. Frequently, however, soap-bubble meters are constructed in the laboratory by use of a burette of appropriate volume.

Two calibration methods are commonly used for soap-bubble meters: (1) the volume-displacement method described for the wet-test meter, and (2) the volume-displacement method measured gravimetrically. The gravimetric-displacement method requires less effort than the volume-displacement method. The displacement volume of a soap bubble meter does not change with use; therefore, it requires only initial calibration upon receipt from the manufacturer. The soap-bubble meter can be used only within the volume range for which it was calibrated. A calibration procedure by the gravimetric method is presented here.

1. Secure a clean displacement tube to a ringstand, and attach a stopcock to the bottom (as shown in Figure 2.3).

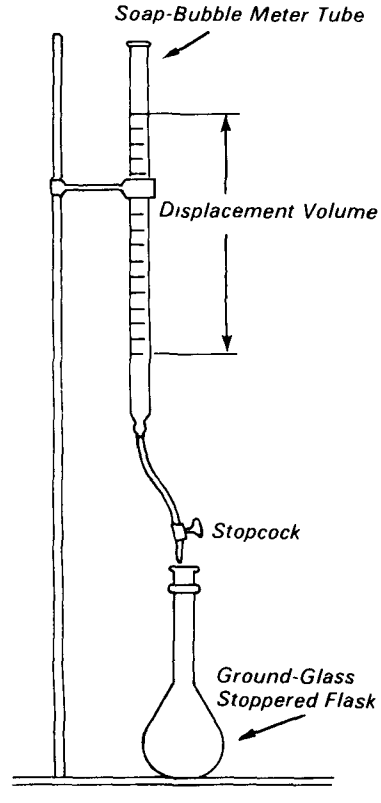


Figure 2.3 *Test apparatus for soap-bubble meter.*

2. Obtain an appropriately sized and stoppered groundglass volumetric flask that will contain the volume of the displacement tube of the soap-bubble meter.

3. Determine the weight of the flask and the stopper to the following specifications:

a. 10-ml flask - weigh to the nearest 0.001 g

b. 100-ml flask - weigh .... to the nearest 0.01 g

c. 1000-ml flask - weigh to the nearest 0.1 g

Record the weight on the calibration log, Figure 2.4; a blank form for the Handbook user is in Section 2.1.13.

4. Fill the displacement tube with distilled water, drain the system until all air bubbles are removed, and collect the water in a beaker and discard it.

5. Fill the displacement tube so that the bottom of the meniscus is at the top mark.

6. Determine the temperature of the water within the displacement tube, and record it in the log.

Table 2.1 *Saturation Vapor Pressure Over Water (°C, mm Hg)*

(Values for fractional degrees between 50 and 89 obtained by interpolation)

Temp °C	0.0	0.2	0.4	0.6	0.8
−15	1.436	1.414	1.390	1.368	1.345
−14	1.560	1.534	1.511	1.485	1.460
−13	1.691	1.665	1.637	1.611	1.585
−12	1.834	1.804	1.776	1.748	1.720
−11	1.987	1.955	1.924	1.893	1.863
−10	2.149	2.116	2.084	2.050	2.018
− 9	2.326	2.289	2.254	2.219	2.184
− 8	2.514	2.475	2.437	2.399	2.362
− 7	2.715	2.674	2.633	2.593	2.553
− 6	2.931	2.887	2.843	2.800	2.757
− 5	3.163	3.115	3.069	3.022	2.976
− 4	3.410	3.359	3.309	3.259	3.211
− 3	3.673	3.620	3.567	3.514	3.461
− 2	3.956	3.898	3.841	3.785	3.730
− 1	4.258	4.196	4.135	4 075	4.016
− 0	4.579	4.513	4.448	4.385	4.320
0	4.579	4.647	4.715	4.785	4.855
1	4.926	4.998	5.070	5.144	5.219
2	5.294	5.370	5.447	5.525	5.605
3	5.685	5.766	5.848	5.931	6.015
4	6.101	6.187	6.274	6.363	6.453
5	6.543	6.635	6.728	6.822	6.917
6	7.013	7.111	7.209	7.309	7.411
7	7.513	7.617	7.722	7.828	7.936
8	8.045	8.155	8.267	8.380	8.494
9	8.609	8.727	8.845	8.965	9.086
10	9.209	9.333	9.458	9.585	9.714
11	9.844	9.976	10.109	10.244	10.380
12	10.518	10.658	10.799	10.941	11.085
13	11.231	11.379	11.528	11.680	11.833
14	11.987	12.144	12.302	12.462	12.624
15	12.788	12.953	13.121	13.290	13.461
16	13.634	13.809	13.987	14.166	14.347
17	14.530	14.715	14.903	15.092	15.284
18	15.477	15.673	15.871	16.071	16.272
19	16.477	16.685	16.894	17.105	17.319
20	17.535	17.753	17.974	18.197	18.422
21	18.650	18.880	19.113	19.349	19.587
22	19.827	20.070	20.316	20.565	20.815
23	21.068	21.324	21.583	21.845	22.110
24	22.377	22.648	22.922	23.198	23.476
25	23.756	24.039	24.326	24.617	24.912
26	25.209	25.509	25.812	26.117	26.426
27	26.739	27.055	27.374	27.696	28.021
28	28.349	28.680	29.015	29.354	29 697
29	30.043	30.392	30.745	31.102	31.461
30	31.824	32.191	32.561	32.934	33.312
31	33.695	34.082	34.471	34.864	35.261
32	35.663	36.068	36.477	36.891	37.308
33	37.729	38.155	38.584	39.018	39.457
34	39.898	40.344	40.796	41.251	41.710
35	42.175	42.644	43.117	43.595	44.078
36	44.563	45.054	45.549	46.050	46.556
37	47.067	47.582	48.102	48.627	49.157
38	49.692	50.231	50.774	51.323	51.879

Temp °C	0.0	0.2	0.4	0.6	0.8
42	61.50	62.14	62.80	63.46	64.12
43	64.80	65.48	66.16	66.86	67 56
44	68.26	68.97	69.69	70.41	71.14
45	71.88	72 62	73.36	74.12	74.88
46	75.65	76.43	77.21	78.00	78.80
47	79.60	80.41	81.23	82.05	82.87
48	83.71	84.56	85.42	86.28	87.14
49	88.02	88.90	89.79	90.69	91.59
50	92.51	93.5	94.4	95 3	96.3
51	97.20	98.2	99.1	100.1	101.1
52	102.09	103.1	104.1	105.1	106.2
53	107 20	108.2	109.3	110.4	111.4
54	112.51	113.6	114.7	115.8	116.9
55	118.04	119 1	120.3	121.5	122.6
56	123.80	125.0	126.2	127.4	128.6
57	129.82	131.0	132.3	133.5	134.7
58	136.08	137.3	138.5	139.9	141.2
59	142.60	143.9	145.2	146.6	148.0
60	149.38	150.7	152.1	153.5	155.0
61	156.43	157.8	159.3	160.8	162.3
62	163.77	165.2	166.8	168.3	169.8
63	171.38	172.9	174.5	176.1	177.7
64	179.31	180.9	182.5	184.2	185.8
65	187.54	189.2	190.9	192.6	194.3
66	196.09	197.8	199.5	201.3	203.1
67	204.96	206.8	208.6	210.5	212.3
68	214.17	216.0	218.0	219.9	221.8
69	223.73	225.7	227.7	229.7	231.7
70	233.7	235.7	237.7	239.7	241.8
71	243.9	246.0	248.2	250.3	252.4
72	254.6	256.8	259.0	261 2	263.4
73	265.7	268.0	270.2	272.6	274.8
74	277.2	279.4	281.8	284.2	286.6
75	289.1	291.5	294.0	296.4	298.8
76	301.4	303.8	306.4	308.9	311.4
77	314.1	316.6	319.2	322.0	324.6
78	327.3	330.0	332.8	335.6	338.2
79	341.0	343.8	346.6	349.4	352.2
80	355.1	358.0	361.0	363.8	366.8
81	369.7	372.6	375.6	378.8	381.8
82	384.9	388.0	391.2	394.4	397.4
83	400.6	403.8	407.0	410.2	413.6
84	416.8	420.2	423.6	426.8	430.2
85	433.6	437.0	440.4	444.0	447.5
86	450.9	454.4	458.0	461.6	465.2
87	468.7	472.4	476.0	479.8	483.4
88	487.1	491.0	494.7	498.5	502.2
89	506.1	510.0	513.9	517.8	521.8
90	525.76	529.77	533.80	537.86	541.95
91	546.05	550.18	554.35	558.53	562.75
92	566.99	571.26	575.55	579.87	584.22
93	588.60	593.00	597.43	601.89	606.38
94	610.90	615.44	620.01	624.61	629.24
95	633.90	638.59	643.30	648.05	652.82
96	657.62	662.45	667.31	672.20	677.12
97	682.07	687.04	692.05	697.10	702.17
98	707.27	712.40	717.56	722.75	727.98

***Table 2.1** (continued) Saturation Vapor Pressure Over Water (°C, mm Hg)*
(Values for fractional degrees between 50 and 89 obtained by interpolation)

Temp °C	0.0	0.2	0.4	0.6	0.8	Temp °C	0.0	0.2	0.4	0.6	0.8
39	52.442	53.009	53.580	54.156	54.737	99	733.24	738.53	743.85	749.20	754.58
40	55.324	55.91	56.51	57.11	57.72	100	760.00	765.45	770.93	776.44	782.00
41	58.34	58.96	59.58	60.22	60.86	101	787.57	793.18	798.82	804.50	810.21

Meter serial number 45324 *Date* 2/29/79
Displacement volume[a] 100 ML *Calibrated by* J Doe

Test number	Water temperature, °C	Initial weight of flask (Wt_i), g	Final weight of water and flask (Wt_f), g	Displacement volume (V_d),[b] ml	Remarks
1	23	73.905	173.930	100.27	
2	23	73.905	173.935	100.27	
3	23	73.905	173.925	100.26	

[a]V = *displacement volume stated by manufacturer* = 100 *ml.*

[b]$V_d = \frac{Wt_f - Wt_i}{D_r} = \frac{173.93 - 73.905}{0.99756} = 100.27$; D_r = 0.99756 *g/ml (Table 2.2).*

$\overline{V_d} = \frac{V_{d1} \times V_{d2} \times V_{d3}}{3} = \frac{100.27 + 100.27 + 100.26}{3} = 100.267$

% error $= \frac{(V - \overline{V_d})\,100}{\overline{V_d}} = -0.266$, *not to exceed ±1%.*

***Figure 2.4** Soap-bubble meter calibration log.*

7. Drain the displacement volume into the weighed flask (Step 3), and immediately cap it with a ground-glass stopper.
8. Weigh the flask and its contents, and record the weight in the log.
9. Repeat Steps 3 through 8 twice.
10. Calculate the displacement volume (V_d), using Equation 2-4.

$$V_d = \frac{Wt_f - Wt_i}{D_r} \quad \text{Equation 2-4}$$

where
V_d = displacement volume, ml
Wt_f = final weight of water and flask, g
Wt_i = initial weight of flask, g
D_r = relative density of water at test temperature, g/ml.

The following example calculation is for a 100-ml displacement tube.
a. Water temperature = 23.0°C
b. Wt_i = 73.905 g
c. Wt_f = 173.930 g
d. D_r = 0.99756 (Table 2.2)

$$V_d = \frac{173.930 - 73.905}{0.99756} = 100.27 \text{ ml.}$$

11. Compute the average displacement volume ($\overline{V}_d$) from the three tests:

$$\overline{V}_d = \frac{V_{d1} + V_{d2} + V_{d3}}{3}$$

Equation 2-5

12. Compute the percent error as follows:

$$\% \text{ error} = \left(\frac{V - \overline{V}_d}{\overline{V}_d}\right) \times 100$$

Equation 2-6

where V is the displacement volume (ml) stated by the manufacturer. The example calculation of % error below assumes that V = 100 ml and V_d = 100.267:

$$\% \text{ error} = \left(\frac{100 - 100.267}{100.267}\right) \times 100 = -0.27\%.$$

The error should not exceed ±1 percent.

Use of the soap-bubble meter for the calibration of flow rate devices such as rotameters and mass-flow meters requires corrections for temperature, barometric pressure, and the vapor pressure of the soap bubble (which is considered to be the vapor pressure of water). Equation 2-3 is repeated here to assist the user with these corrections to the standard conditions of 760 mm (29.92 in.) Hg, 25°C (77°F), and 0% water vapor.

Flow rate at standard conditions

$$= \frac{\text{vol (ml)}}{\text{time (min)}} \times \frac{P - P_v}{760} \times \frac{298}{273 + T}$$

Equation 2-3 (repeated)

where

P = atmospheric pressure, mm Hg

P_v = vapor pressure of water (see Table 2.1), mm Hg

T = temperature of gas, °C

Example: Assume the temperature to be 20°C and the atmospheric pressure to be 710 mm Hg

Flow rate at standard conditions

$$= \frac{\text{vol (ml)}}{\text{time (min)}} \times \frac{710 - 17.54}{760} \times \frac{298}{273 + 20}$$

$$= \frac{\text{vol (ml)}}{\text{time (min)}} \times 0.927 = \text{ml/min.}$$

2.1.3 *Mass-Flow Meter Calibration Check* - Mass-flow meters operate on a thermal principle that depends on the mass flow of the gas and on its heat capacity to gauge the temperature within a heated conduit. Because these meters measure the true mass flow, they have the advantage of not requiring corrections for changes of temperature and pressure. Flow rate values are usually given in standard cubic centimeters of air per minute, which are measures of the volume occupied by a mass of air at standard temperature and pressure, as specified by the manufacturer

Mass-flow meters are not volume displacement devices; therefore, they require calibration at least quarterly against a displacement device such as a bubble meter or a wet-test meter, which serves as a secondary calibration standard. Before calibration of a mass flow meter against an already calibrated wet test meter, reference should be made to the manufacturer's instructions for the flow rate capacity. The following procedure should then be used.

1. Be sure that the mass flow meter is off. Use the adjustment screw below the meter face to set the pointer needle on zero.
2. Turn the meter on, and allow it to warm up for 1 h.
3. After the warmup period, adjust te electronic zero as follows:
   a. Plug the inlet and the outlet of the transducer.
   b. Use the adjust screw to set the electronic zero on the meter.
   c Unplug the ends of the transducer before connecting it to the test apparatus (as illustrated in Figure 2.5).
4. Turn the vacuum pump on, and use the needle valve to adjust the flow rate to approximately 75 percent of the full scale of the mass-flow meter.
5. Allow the system to equilibrate for approximately 10 revolutions of the wet-test meter.
6. Read the manometer on the wet-test meter in mm H_2O; convert to mm Hg (mm H_2O x 0.0738 = mm Hg); and record the Δp_m on the calibration log (Figure 2.6). Because the air passing through the calibration apparatus has been presaturated, no correction for water vapor is necessary
7. As the wet-test meter pointer passes zero, use a precision stopwatch to begin the timing. As the wet-test meter pointer passes the three-quarter revolution mark, take a reading and record the mass-flow meter reading in the log. As the wet-test meter pointer passes the starting point, stop the stopwatch and record the elapsed time (t).
8. Record the wet-test meter volume in the column headed by V_m, and record the wet-test meter fluid temperature (T_m) in K.
9. Calculate $P_m = P_b - \Delta P_m$ and use Equation 2-7 to calculate V_s by using the recorded value of P_m, T_m, and V_m; T_s = 298 K and P_s = 760 mm Hg. Record the V_s value.

$$V_s = \left(\frac{P_m T_s}{P_s T_m}\right) V_m \quad \text{Equation 2-7}$$

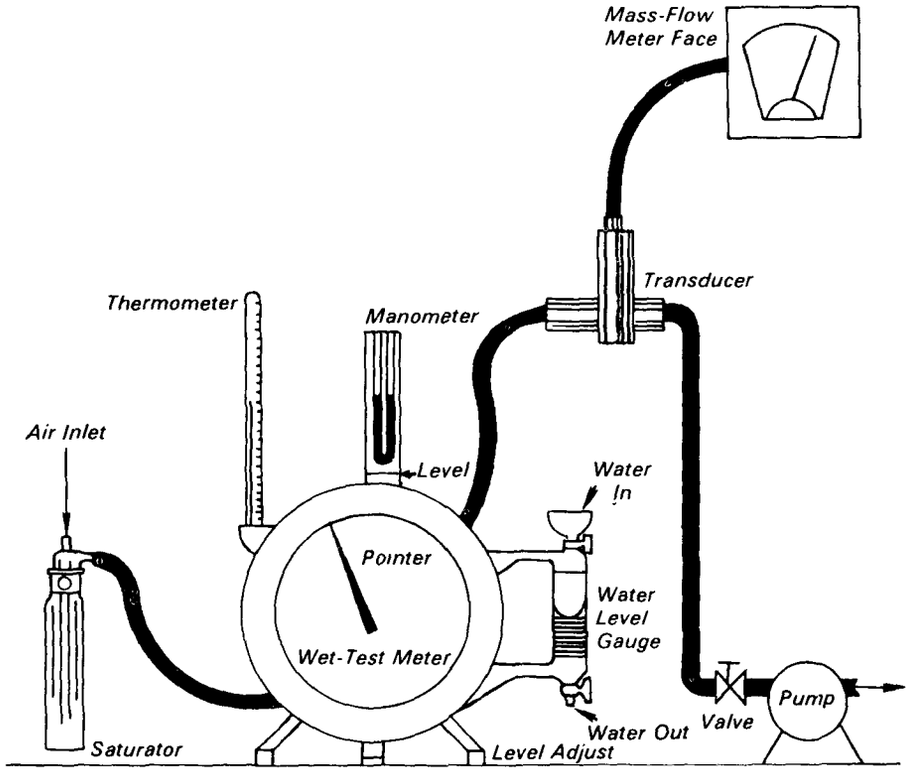


Figure 2.5 *Mass-flow meter calibration apparatus.*

Mass flow meter serial number 47897
Location LABORATORY
Barometric pressure (P_b) 750 mm Hg
Calibrated by JOE SMITH
mm Hg = 0.0738 x mm H_2O)

Calibrated With WET-TEST METER
Ambient room temperature 295 °K
Relative humidity 50%
Date 3-3-75

Test point	Wet-Test Meter Readings: Manometer reading (ΔP_m), mm Hg	$P_m = P_b - \Delta P_m$[a] mm Hg	Meter fluid temperature (T_m), K	Volume displaced (V_m), l	$V_s = \frac{P_m T_s V_m}{P_s T_m}$	Elapsed time (t), min	$Q_s = \frac{V_s}{t}$ l/min	Mass-flow meter scale
1	0.738	749.262	295	1.0	0.9959	2.0	0.498	0.5
2								
3								
4								
5								
6								
7								
8								
9								
10								

[a]If air is pushed through the calibration apparatus, Δp_m is to be added to P_b.

Figure 2.6 Mass-flow meter calibration log.

where
$P_m = P_b - \Delta P_m$ = measured barometric pressure corrected for internal meter pressure, mm Hg
P_s = pressure at standard conditions, 760 mm Hg
T_m = measured temperature of air, K
T_s = temperature at standard conditions, 25°C = 298 K and
V_m = measured volume from wet test meter.

10. Calculate the flow rate (Q_s) from V_s and t:

$$Q_s = \frac{V_s}{t} \quad \text{Equation 2-8}$$

where
Q_s = flow rate at standard conditions, liters/min
V_s = volume of gas at standard conditions, liters
t = time, min.

Record Q_s.

11 Plot Q_s versus the mass-flow meter readings on rectangular graph paper.

12. Repeat Steps 6 through 11 for five other flow rates within the range of the mass-flow meter.

13. Construct a best-fit curve for the points generated, and use this relationship for future work using the mass-flow meter.

2.1.4 *Calibration of Rotameter* - A commonly used method for measuring gas flow rates is the rotameter or variable-area flow meter. It is usually a round glass tube housing one or more floats that are free to move vertically up and down the tube axis On the sides are reference marks, which may be either linearly or exponentially inscribed on the tube As the gas flows up the tube, the float is displaced and continues to move upward until equilibrium is reached This occurs when the gravitational force of the float equals the buoyant force of the moving gas stream.

Float design will vary depending on the manufacturer and the flow rate desired. Most lower-range rotameters use spherical floats. Readings are conventionally taken at the widest point of the float.

Although the manufacturer generally provides reasonably accurate calibration curves, rotameters should be recalibrated at the conditions that will be used Rotameters separate from the train used as flow measuring devices must be calibrated against a previously calibrated wet-test meter, soap bubble meter, or mass-flow meter.

Rotameters can be calibrated by use of a bubble meter as a secondary standard as follows:

1 Assemble the equipment as shown in Figure 2.7. *Note* Rotameters calibrated in a vacuum situation should be used only in a similar (vacuum) situation.

2 Read and record room temperature and barometric pressure on the rotameter calibration data form (Figure 2 8 on following page).

3 Turn on vacuum pump

4 Adjust the needle valve until the rotameter float is about 20 percent of full scale

5 Touch the surface of the soap solution with the open end of the bubble meter so that a soap bubble will start to travel up the bubble meter tube. Repeat several times or until bubbles will travel the full length of the tube without breaking.

6 Touch the surface of the soap solution with the open end of the bubble meter so that a single bubble starts to travel up the bubble tube When the bubble passes the first line of graduated scale, start stopwatch Record time and volume displaced.

7. Repeat Step 6 two more times Record time and volume each time.

8. Calculate average time and volume displacement for three runs.

9. Correct average volume displacement to standard conditions of 760 mm Hg and 25°C by use of Equation 2-9,

$$V_s = V_m \left(\frac{P_b - P_v}{P_s}\right) \times \frac{T_s}{T_m} \quad \text{Equation 2-9}$$

where
V_m = measured volume from bubble meter, ml
P_b = barometric pressure, mm Hg
P_v = vapor pressure of water in soap bubble meter at the temperature employed, mm Hg (see Table 2.2)
P_s = pressure at standard conditions = 760 mm Hg
T_s = temperature at standard conditions, 298 K
T_m = temperature of soap bubble meter, K.

10. Divide the corrected volume displacement by the average time to determine the flow rate.

11. Repeat Steps 4 through 10 for each of five or more uniformly spaced points on the rotameter scale, going from low values to high values.

12. Plot the rotameter units versus the flow rate Q_s on linear graph paper, constructing a best fit smooth curve through the data points by use of a flexible rule A typical calibration relationship is presented in Figure 2.9. All data points should be within ±2 percent of the curve of best fit.

13 Should the rotameter be used in a field location where the barometric pressure and/or temperature is different than those conditions when the rotameter was calibrated, the following corrections must be applied to convert the flow rate to standard conditions. This correction factor is not advisable for conditions that differ greatly from those at which the rotameter was calibrated Greater accuracy can be obtained by developing calibration

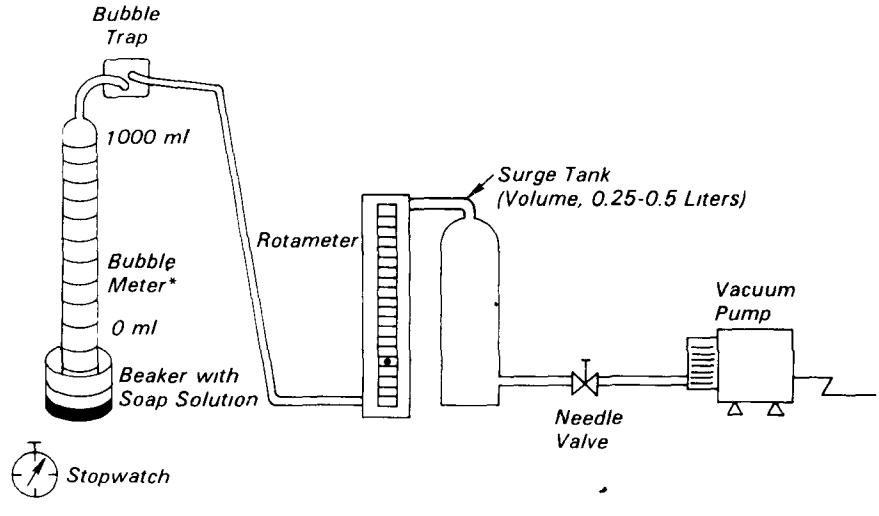


Figure 2.7 *Rotameter calibration apparatus.*

**Volume tubes available 10 ml to 1000 ml*

Rotameter serial number 7112-7278
Location Standards Lab, Notown, NC.
Barometric Pressure (P_b), mm Hg 750.4
Calibrated by TOM Brown

Calibrated with Bubble Meter
Room temperature 22 °C + 273 = 295 °K
Vapor pressure of H_2O (P_v), mm Hg 19.827
Date 6-7-78

Test point	Rotameter reading, units	Bubble displacement time, min	Average time (t), min	Volume displaced, ml	Volume at STP (V_s),[a] ml	$Q_s = \frac{V_s}{t}$ ml/min	Remarks
1	2.2	2.75	2.77	100	97.1	35.1	
2	2.2	2.77		100			
3	2.2	2.79		100			
4	4.8	1.14	1.14	100	97.1	85.2	
5	4.8	1.15		100			
6	4.8	1.13		100			
7	8.1	2.81	2.81	500	485.5	172.8	
8	8.1	2.80		500			
9	8.1	2.81		500			
10	10.9	1.93	1.94	500	485.5	250.3	
11	10.9	1.95		500			
12	10.9	1.94		500			
13	14.0	2.91	2.90	1000	971.0	334.8	
14	14.0	2.90		1000			
15	14.0	2.90		1000			

[a] $V_s = V_m \left(\frac{P_b - P_v}{P_s}\right) \times \frac{T_s}{T_m}$

Figure 2.8 Rotameter calibration data form.

Table 2.2 *Absolute Density of Water*
(Values numerically equal to absolute density of H_2O)

Temp, °C	Density, g/ml	Temp, °C	Density, g/ml
15	0.99913	25	0.99707
16	0.99887	26	0.99681
17	0.99880	27	0.99654
18	0.99862	28	0.99626
19	0.99843	29	0.99597
20	0.99823	30	0.99567
21	0.99802	31	0.99537
22	0.99780	32	0.99505
23	0.99756	33	0.99473
24	0.99732	34	0.99440

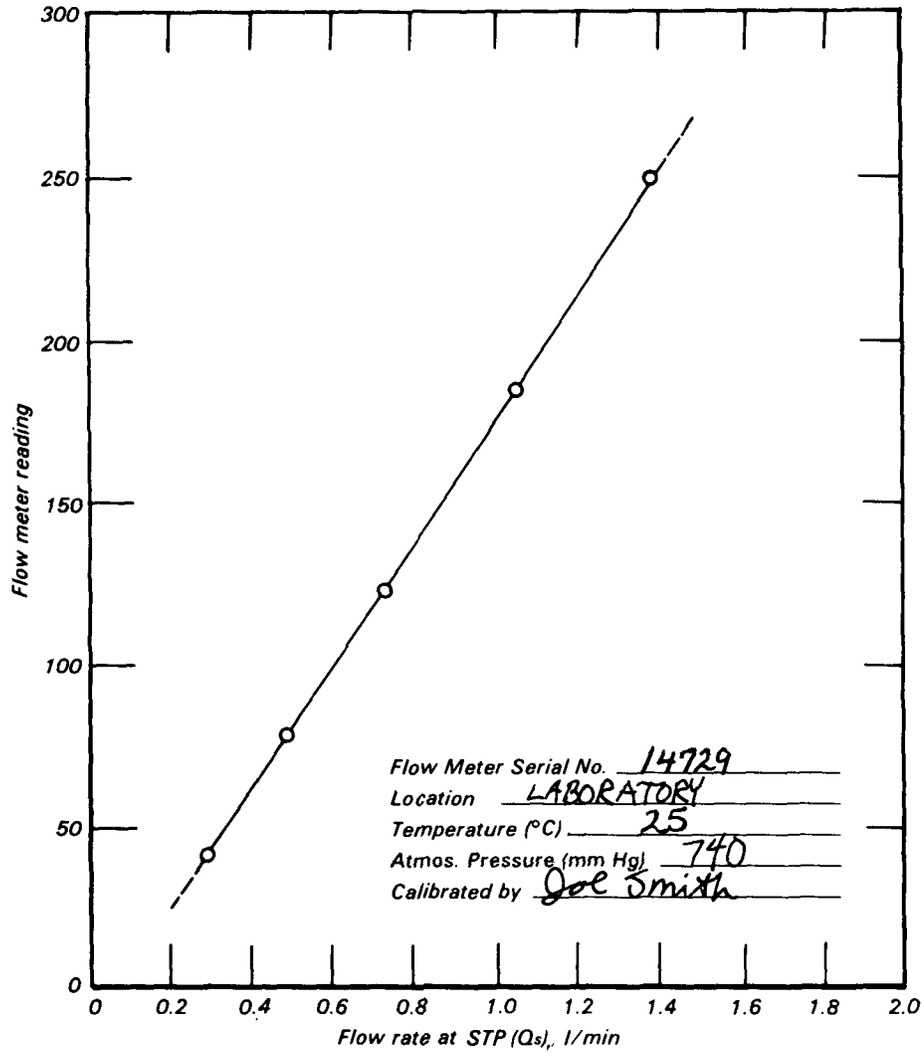


Figure 2.9 *Typical rotameter calibration curve.*

curves for expected conditions.

$$Q_s = Q_f \left(\frac{P_f}{760} \times \frac{298}{T_f} \right)^{1/2}$$

Equation 2-10

where

Q_s = flow rate corrected to standard conditions from field conditions, ml/min

Q_f = flow rate at field conditions from calibration curve, ml/min

P_f = barometric pressure at field conditions, mm Hg

T_f = temperature at field conditions, K.

2.2 Sampling Train Flow Control Devices

The rotameters and needle valves (short-term sampling only) or the critical orifices used as flow-control devices in the SO_2 sampling trains should be checked for the appropriate range of sampling rates, but they do not require strict calibration because their values cannot be used to determine the sample volume. The sample volume is determined from the sampling time and the sample flow rate measured before and after sampling by use of a flow measurement device connected to the inlet of the absorber.

Flow rate requirements for different sampling periods and typical hypodermic needle sizes that will give these flow rates are:

1. 30 minutes of sampling at 0.9 to 1.1 liters/min. Use a 1-inch 22-gauge hypodermic needle.
2. One hour of sampling at 450 to 550 cm^3/min. Use a 5/8-inch, 23-gauge, hypodermic needle.
3. 24-hours of sampling at 180 to 220 cm^3/min Use a 3/8-inch 27-gauge, hypodermic needle.

In the short-term sampling train only, a rotameter and needle valve covering the appropriate range may be used.

The flow control devices in the assembled sampling train should be checked to ensure that the appropriate range can be obtained before they are taken into the field. Any needle unable to give the accepted range should be discarded. The flow rates are checked by use of the procedures described for determining the flow rates before and after sampling in Section 2.1.4, Subsection 4 4.

Constant flow rates through hypodermic needles can be achieved only when critical flow conditions are met. These conditions exist when the absolute pressure downstream of the needle (P_d) is ≤ 0.45* of the absolute pressure upstream of the needle (P_u)—that is, when $P_d \leq 0.45\ P_u$. For the SO_2 sampling trains, the upstream pressure (P_u) is usually 25 mm (1.0 in.) Hg less than the barometric pressure, and the downstream pressure (P_d) is equal to the barometric pressure minus the pressure from the vacuum gauge (P_g).

Since the barometric pressure decreases with altitude, the critical flow conditions are satisfied at lower vacuum gauge readings at higher altitudes. Vacuum gauge readings for critical flows at several altitudes are shown in Table 2.3. A minimum safety

*Reference 8 of the Reference Method, Section 2 1 11, verifies the 0 45 for use with the hypodermic needle Reference 5 of Section 2.1.12 gives 0 53 as a purely theoretical value.

Table 2.3 Vacuum Gauge Readings to Achieve Critical Flow for Various Elections
(Assumed pressure drop across sampling train = 25 mm (1.0 in.) Hg)

Elevation above sea level		Standard barometric pressure		Gauge reading for critical flow	
m	ft	mm Hg	in. Hg	mm Hg	in. Hg
0	0	760	29.9	429	16.9
305	1000	732	28.8	414	16.3
610	2000	706	27.8	399	15.7
915	3000	680	26.8	385	15.2
1220	4000	656	25.8	372	14.6
1525	5000	632	24.9	359	14.1
1830	6000	609	24.0	346	13.6

factor of 20 percent of the gauge reading should be added to the table values to ensure critical flow during the total sampling period

Flow rates through hypodermic needles used as critical orifices are directly affected by upstream pressures, which are in turn affected by barometric pressures. Care must be exercised when needles are used at elevations that differ greatly from that at which they were checked.

2.3 Calibration of Analytical Balance

The balance calibration should be verifed when the balance is (1) first purchased, (2) any time it is moved or subjected to rough handling, and (3) during routine operations when a standard weight cannot be weighed within ±0.5 mg of its stated weight. If at any time, one or more of the standard weights cannot be measured within ±0.5 mg of its stated value, the manufacturer should be asked to recalibrate and adjust the balance. The results of all balance checks should be recorded in the log (Figure 2.10).

2.4 Calibration of Elapsed-Time Meter

The elapsed-time meter (synchronous motor, type 60 Hz) should be checked on site or in the laboratory every 6 mo against a timepiece of known accuracy. If the indicator shows any signs of being temperature-sensitive, it should be checked on site during each season of the year; a gain or loss of more than 2 min in a 24-h period warrants an adjustment or replacement of the indicator. Results of these checks should be recorded in the calibration log.

2.5 Calibration of On-Off Timer

The on-off timer should be calibrated and adjusted by using an already-calibrated elapsed-time meter as the reference. The calibration procedure should be performed quarterly, and the calibration data should be recorded in the timer log. (See Figure 2.11 for an example and Section 2.1 13 for a blank form.) An example calibration procedure is presented below.[4] Figure 2.12 is a wiring diagram for the calibration.

1. Plug a correctly wired timer into an electrical outlet.
2. Set the timer to the correct time.
3. Set the on and the off time trippers for the 24 h.
4. Plug the test light into one of the output plugs, and plug an elapsed-time meter into the other
5. Check the system by manually operating the switch on and off.
6. Allow the system to operate for the 24-h period, and determine the elapsed time from the elapsed-time meter. If the elapsed time is 24 h ±15 min, the timer is acceptable for field use; if not, adjust the tripper switches, and repeat the test.

Analytical Balance Quality Control Log

Date	Time	Class S Weights (g)			Technician
		0.5000	1 0000	2 0000	
7/29/74	11.07	0 5000	1 0002	2 0000	BSM
7/29/74	12·08	0.5002	1 0003	2 0001	DEK
7/29/74	2.40	0 5000	1 0000	1 9999	DEK
7/30/74	4:03	0.4996	0 9999	2 0002	JLK
7/31/74	9·57	0.4994	1 0000	2 0000	DEK
7/31/74	10 56	0 4995	0 9992	1 9993	DEK
7/31/74	11·57	0.4994	0 9994	1 9994	DEK
7/31/74	2 04	0.5001	1 0000	2.0002	DEK
7/31/74	3·05	0.5000	1.0000	2 0000	DEK
8/1/74	9:03	0.4998	0 9992	1 9992	DEK
8/1/74	10.05	0 4993	0 9992	1 9992	DEK
8/1/74	11:10	0.5000	1.0001	2 0001	DEK
8/1/74	12:12	0.4998	0 9997	1 9993	DEK
8/1/74	1 43	0.5000	1 0001	2 0002	DEK
8/1/74	2:42	0.5001	1 0001	2 0001	DEK
8/1/74	3 45	0 5001	1.0000	2 0001	DEK
8/2/74	8:54	0.5000	1 0001	2 0001	DEK
8/2/74	9·56	0 5000	1 0000	2.0001	DEK
8/2/74	10·59	0.5003	0 9999	1 9998	DEK
8/2/74	12·16	0.5001	1.0002	2 0002	DEK
8/2/74	1·55	0.4990	1 0002	2 0001	DEK
8/2/74	3·03	0 5000	0.9999	2 0001	DEK
8/2/74	4·00	0.5000	0 9998	1 9999	DEK
8/3/74	8·41	0 4999	0 9996	1 9998	DEK
8/3/74	11 15	0.5002	1.0002	2.0002	DEK
8/5/74	8.42	0.5001	1.0000	2 0000	DEK
8/5/74	9 45	0 5000	1 0000	2 0000	DEK
8/5/74	10 44	0.5000	1.0000	2.0000	DEK
8/5/74	11.46	0.5000	1.0001	2 0000	DEK
8/5/74	1:16	0 5001	1 0000	2.0000	DEK
8/5/74	2 21	0.5001	1.0000	2.0001	DEK
8/5/74	3·15	0.5000	1 0000	2 0001	DEK
8/6/74	9·37	0.4999	1.0000	2.0000	DEK
8/6/74	11 05	0.5000	0.9998	1.9994	DEK
8/6/74	12·10	0.4999	0 9998	1 9999	DEK
8/6/74	2 10	0.5000	0.9998	2 0000	DEK
8/6/74	3:09	0 5000	1 0000	2 0000	DEK
8/6/74	4·05	0.5000	1 0000	2 0000	DEK
8/7/74	8:50	0.5000	1 0002	2 0003	DEK
8/7/74	9:46	0.4996	0.9992	1 9990	DEK
8/7/74	1·10	0 5001	1 0000	2 0000	DEK
8/7/74	2:20	0.5001	1 0000	2.0000	DEK
8/7/74	3·25	0.5002	1.0001	2.0000	DEK
8/8/74	9:46	0.5000	1.0000	2 0000	DEK
9/24/74	3.50	0.5001	1 0001	2 0001	DEK
9/26/74	3:01	0.5001	1.0001	2 0001	DEK

Figure 2.10 *Example of an analytical balance performance record.*

Site location number	Timer number	Date		Elapsed-time indicator serial number	Test period	Elapsed-time indicator reading	Accuracy	Technician (signature)
		Start	Stop					
1141	4321	6/10/75	6/11/75	CW080G	24h	23h 53min	99.5	C. Jones

Figure 2.11. Example of a timer calibration log

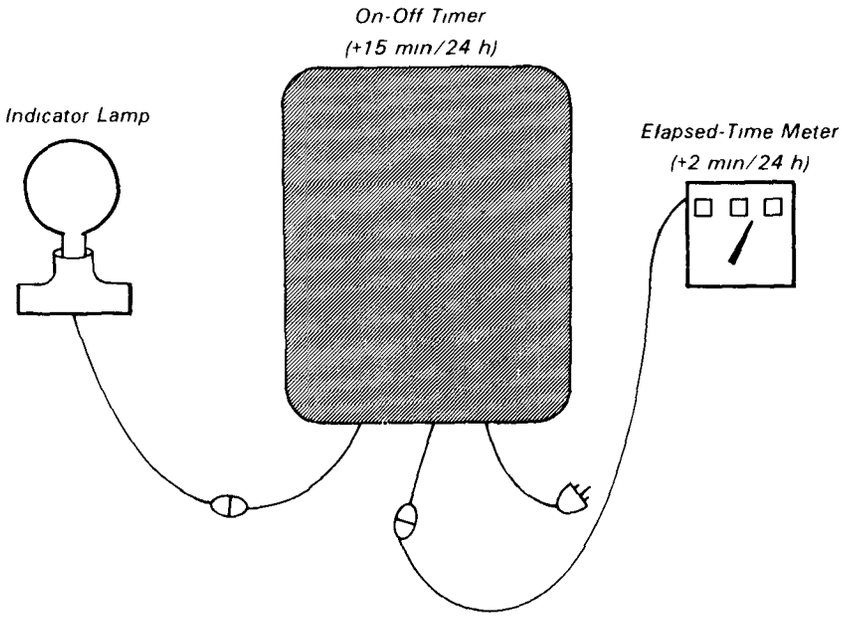


Figure 2.12 *Diagram of a timer calibration system.*

Table 2.4 *Activity Matrix for Calibration of Equipment*

Equipment	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Wet-test meter	% error ≤1% (Fig 2 2)	Check upon receipt and quarterly with liquid positive displacement (Subsec 2.1.1).	Adjust by manufacturer's instructions, or return to manufacturer.
Soap-bubble meter	% error ≤1% (Fig 2.4)	Calibrate upon receipt from manufacturer with gravimetric displacement (Subsec 2.1.2).	As above
Mass-flow meter	All data points within ±2% of best-fit curve	Calibrate quarterly with bubble or wet test meter (Subsec 2.1.3).	As above
Rotameter	As above	Calibrate quarterly with bubble meter (Subsec. 2.1.4).	As above
Flow control devices, rotameter and needle value or hypodermic needles	Appropriate range for sampling period: rotameter, 450 to 1100 cm^3/min; orifices, 900 to 1100 cm^2/min, 30-min sampling, 450 to 550 cm^3/min, 1- to 3-hour sampling, 180 to 220 cm^3/min, 24-hour sampling	Check flow rate initially and before and after each sampling period with calibrated flow measuring device.	Clean or replace rotameter; discard hypodermic needles.
Analytical balance	Standard weights ±0.5 mg of stated values	Verify calibration when first purchased, after moving or rough handling, and when a standard weight is not within ±0.5 mg of stated value.	Repeat check to verify malfunction; have manufacturer recalibrate and adjust as needed.
Elapsed-time meter	±2 min/24 h	Check every 6 mo with timepiece of known accuracy.	Adjust or replace.
On-off timer	±15 min/24 h	Use calibrated elapsed-time meter quarterly (Subsec 2.4).	Adjust the tripper switches; repeat test.

3.0 Preparation of Reagents

The quality control functions for preparation of reagents are summarized in Table 3.1 at the end of this section.

3.1 Distilled Water

The standard specification for reagent water is described in the ASTM designation D 1193-72; this document requires the Type-II grade of water, which is prepared by use of a still designed to produce a distillate having a conductivity of <1.0 micromho/ cm at 25°C (77°F) and a pH range of 6.6 to 7.2.

The following purity test should be performed after each lot of water reagent is prepared if the slope and intercept of the standard curve fail to meet the specified criteria (Section 2.1.5).

1. Add 0.20 ml of a potassium permanganate ($KMnO_4$) solution (0.316 g $KMnO_4$/liter) to a mixture of 500 ml of distilled water and 1 ml of sulfuric acid (H_2SO_4) in a stoppered bottle made of chemically resistant glass. If the $KMnO_4$ color (pink) does not disappear completely after standing for 1 h at room temperature, the water is suitable for use; if the color disappears, the water must be purified before using.
2. Water that fails the purity test can be purified as follows:
   a. Add 1 g each of $KMnO_4$ and barium hydroxide (BaOH) for each liter of distilled water.
   b. Redistill the water in an all-glass still.
   c. Perform the test for purity described above.
3. Repeat both the purification procedure and the test for purity until the slope and the intercept of the standard curve meet the specified limits.
4. Store the reagent water in an inert container with a vent guard. (A suitable guard is a drying tube filled with equal parts 8-20 mesh soda lime, oxalic acid, and 4-8 mesh calcium chloride separated from each other by a glass-wool plug.) Replace the vent guard drying materials every 30 days.

3.2 Absorbing Reagent

3.2.1 *Reagent Preparation* - The 0.04M potassium tetrachloromercurate (TCM) absorbing reagent should be prepared according to the following procedure.

1. Dissolve 10.86 g of mercuric chloride, 0.066 g EDTA (ethylenediaminetetraacetic acid disodium salt) and 6.0 g of potassium chloride in distilled water, and dilute to 1 liter. Usually it is necessary to prepare larger quantities of the absorbing reagent to meet the sampling requirements of the agency. *Warning:* The reagent is highly poisonous. Rubber gloves should be worn when preparing the absorbing reagent. If spilled on the skin, it must be flushed off with water immediately.
2. Label the reagent bottle, and include the date of preparation.

3.2.2 *Reagent pH Test* - For each lot of absorbing reagent prepared for sampling, the following pH test procedure should be conducted.

1. Standardize the pH meter with buffer solutions of pH 4.0 and pH 7.0.
2. Measure the pH of the absorbing reagent. The optimal pH is 4.0.
3. Discard the reagent if the pH is <3.0 or >5.0. Dispose of the absorbing solution according to one of the disposal techniques described in Section 2.1.5, Subsection 5.5.

3.2.3 *Reagent Storage* - The absorbing reagent should be stored in a toppered container, and the reagent should be discarded if it is >6 mo old (normally stable for 6 mo). It should be visually examined before each use and discarded if a precipitate is visible. The absorbing solution should be discarded in accordance with one of the disposal techniques described in Section 2.1.5, Subsection 5.5.

3.3 Sulfamic Acid (0.6%)

Sulfamic acid (0.6 g) should be dissolved in a 100-ml volumetric flask with water and diluted to the 100-ml mark. The solution should be kept in a glass- stoppered flask while not in use, and it should be prepared fresh daily.

3.4 Formaldehyde (0.2%)

Five milliliters (5 ml) of formaldehyde solution (36-38%) should be diluted to 1000 ml with distilled water. The 0.2% solution should be kept in a stopped container while not in use, and it should be prepared fresh daily.

3.5 Starch Indicator Solution

A starch solution for iodimetric determinations should be prepared by following these three steps:

1. Triturate 0.4 g of soluble starch and 0.002 g mercuric iodide (preservative) with a small amount of water to form a paste.
2. Add the paste slowly to 200 ml of boiling water, and continue the boiling until the solution is clear.
3. Allow to cool, and transfer to a glass-stoppered bottle.

Alternatively, a solution of stabilized starch for iodimetric determinations can be purchased commercially.

3.6 Stock Iodine Solution (0.1N)

The procedure for preparing the 0.1 N iodine solution is as follows.

1. Place 12.7 g of iodine in a 250-ml beaker.
2. Add 40 g of potassium iodide (KI) and 25 ml of water to the beaker.
3. Stir until dissolved.
4. Transfer the contents of the beaker to a 1000-ml flask, and dilute to the mark with distilled water. Keep the stock solution in a glass-stoppered dark bottle, and store in a cool place.

3.7 Working Iodine Solution (0.01N)

The approximately 0.01N iodine solution should be prepared by diluting 50 ml of the 0.1N stock solution to 500 ml with distilled water. The 0.01N working solution should be kept in a glass-stoppered dark bottle or dark flask, and it should be prepared fresh daily.

3.8 Hydrochloric Acid (1N)

The solution of 1N HCl should be prepared by slowly adding 86 ml of concentrated HCl (12N) to 500 ml of distilled water. After it has been allowed to cool, it should be diluted to 1000 ml with distilled water.

3.9 Stock Sodium Thiosulfate Solution (0.1N)

A 0.1N stock solution should be prepared by dissolving 25 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 100 ml of freshly boiled but cooled distilled water and by adding 0.1 g of sodium carbonate to the solution. The solution

should be allowed to stand 1 day before standardizing.

The procedure for standardizing against a potassium iodate (KIO_3) standard before each use is as follows:

1. Dry ACS reagent grade KIO_3 at 180°C (356°F) for 3 h in a drying oven.
2. Cool the dried KIO_3 in a desiccator.
3. Weigh and record the weight to the nearest 0.1 mg of the 1 5 g of the dried cooled KIO_3.
4. Add the weighed sample of KIO_3 to a 500-ml volumetric flask, and dilute to the 500-ml mark.
5. Pipette 50 ml of the KIO_3 solution into a 500-ml flask; add 2 g of KI and 10 ml of 1N hydrochloric acid (HCl).
6. Stopper the flask and wait 5 min before titrating to a pale yellow with the 0.1N stock thiosulfate solution.
7. Add 5 ml of a starch indicator solution, and continue the titration until the blue color disappears.
8. Calculate the normality (N_s) by using the following equation:

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

Equation 3-1

where

N_s = normality of stock thiosulfate solution
W = weight of KIO_3, g
M = volume of thiosulfate required, ml

$$2.80 = \frac{0.1\ (KIO_3 \text{ fraction used}) \times 10^3 \text{ (convert g to mg).}}{35.67 \text{ (equivalent weight of } KIO_3)}$$

Store the 0.1N sodium thiosulfate stock solution in a glass-stoppered flask.

3.10 Sodium Thiosulfate Titrant (0.01N)

The 0.1N stock thiosulfate solution (100 ml) should be accurately pipetted into a 1000-ml volumetric flask and diluted to the mark with freshly boiled but cooled distilled water. This 0.01N solution is not stable, and must be prepared fresh daily from the stock thiosulfate solution. It should be kept in a glass-stoppered flask or bottle when not in use. The normality of the sodium thiosulfate titrant (N_T) should be calculated as follows:

$$N_T = N_S \times 0.100$$

Equation 3-2

3.11 Standard Sulfite-TCM Solution

This solution is prepared by dissolving 0.30 g of sodium metabisulfite ($Na_2S_2O_5$) or 0.40 g of sodium sulfite (Na_2SO_3) in 500 ml of freshly boiled but cooled distilled water. (Because sulfite solution is unstable, water of the highest purity should be used to minimize the instability.) This solution contains the equivalent of 320 to 400 $\mu g\ SO_2$/ml; the actual concentration is determined by adding excess iodine and by back-titrating with the 0.01N standard sodium thiosulfate solution. The working sulfite-absorbing reagent solution (see Subsection 3.12) should be prepared while the iodine solution is being added to the flasks.

The procedure for standardizing the sulfite solution is as follows:

1. Label each of three 500-ml flasks with an A, and label three other flasks with a B.
2. Pipette 50 ml of the 0.01 working iodine solution into each of the six labelled 500-ml flasks.
3. To each A flask (blank), add 25 ml of distilled water; to each B flask (sample), pipette 25 ml of the standard sulfite solution.
4. Stopper the flasks, and allow the solutions to react for 5 min.
5. Use a 50-ml burette containing standardized 0.01N thiosulfate to titrate each flask to a pale yellow.
6. Add 5 ml of starch solution to each flask, and shake thoroughly; continue the titration until the blue color disappears.

Store the standardized sulfite-TCM solution in a glass-stoppered bottle or flask.

3.12 Working Sulfite-TCM Solution

A quantity of 5 ml of the standard solution (prepared above) should be pipetted into a 250-ml volumetric flask, and diluted to the mark with 0.04M absorbing reagent. The SO_2 concentration in the working solution should be calculated by using the data in Subsection 3.10, as follows:

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

Equation 3-3

where A and B are averages of the three replicate titrations, and

32,000 = milliequivalent weight of SO_2, μg
A = volume of thiosulfate needed for the blank, ml
B = volume of thiosulfate for the sample, ml
N_T = normality of thiosulfate titrant
0.02 = dilution factor
25 = vol. of standard sulfite solution, ml.

This solution is stable for 30 days at 5°C (41°F) if refrigerated. If not kept at 5°C, it should be prepared fresh daily.

3.13 Pararosaniline Stock Solution

Harleco Co. offers high purity pararosaniline (PRA) dye that can be used without purification for the preparation of the standard curve (described in Subsection 5.2) if the slope, the intercept, and wavelength of maximum absorbance are within specifications. If the specifications are not met, the dye must be purified.

3.13.1 *Dye Specifications* - Dye specifications are as follows:

1. The dye must have a maximum absorbance at a wavelength of 540 nm when assayed in a buffered solution of 0.1M sodium acetate-acetic acid.
2. The absorbance of the reagent blank, which is temperature-sensitive (0.015 absorbance unit/°C), must not exceed 0.170 at 22°C with a 1-cm optical path length when the blank is prepared according to the specified procedure.
3. The calibration curve (Subsection 5.2) must have a slope equal to 0.030 ±0.002 absorbance unit/$\mu g\ SO_2$ with a 1-cm optical path length when the dye is pure and the sulfite solution is properly standardized.

3.13.2 *Purification Procedure for PRA* - The following purification procedure is given in the event that the PRA does not meet the specifications.

1. Place 100 ml each of 1-butanol and 1N HCl in a 250-ml separatory funnel, shake, and allow to equilibrate. *Note:* Certain batches of 1-butanol contain oxidants that create an SO_2 demand. Check before using by placing 20 ml of 1-butanol and 5 ml of 20 percent KI in a 50-ml separatory funnel and shaking thoroughly. If a yellow color appears in the alcohol phase, either redistill the 1-butanol from the silver oxide and collect the middle fraction, or purchase a new supply of 1-butanol.
2. Weigh 100 mg of pararosaniline hydrochloride in a small beaker; add to it 50 ml of the equilibrated acid (drained from the bottom of the separatory funnel in Step 1); and then let the mixture of PRA and acid stand for several minutes.
3. Add to a 125-ml separatory funnel 50 ml of the equilibrated 1-butanol (drawn from the top of the separatory funnel in Step 1), transfer to the funnel the acid solution

containing the dye, and then extract. The violet impurity will transfer to the organic phase (top layer).

4. Transfer the lower aqueous phase from the separatory funnel into another separatory funnel, add 20 ml of 1-butanol, and extract again. Repeat the extraction procedure in Step 4 with three more 10-ml portions of 1-butanol This procedure usually removes most of the violet impurity that contributes to the blank, but the extracted phase (bottom) will still be red.

5. After the final extraction, filter the acid (bottom) phase through a cotton plug into a 50-ml volumetric flask, and dilute to the mark with 1N HCl. This PRA stock reagent will be yellowish red

3.13.3 *Assay of Pararosaniline Stock Solution* The following assay should be performed after each preparation or purchase of a new lot of PRA.

1. To prepare a buffer stock solution with a pH of 4.79, dissolve 13.61 g of sodium acetate trihydrate in distilled water in a 100-ml volumetric flask, add 5.70 ml of glacial acetic acid, and dilute to the mark with water.

2. Dilute 1 ml of the purified PRA stock solution (Subsection 3.13.2) to the mark in a 100-ml volumetric flask with distilled water.

3. Transfer a 5-ml aliquot to a 50-ml volumetric flask; add 5 ml of the acetate/acetic acid buffer solution (from Step 1); and dilute the mixture to the mark with distilled water. Let the mixture stand for 1 h.

4. Measure the absorbance at 540 nm with a spectrophotometer. Compute the percent purity of the PRA:

$$\% \text{ PRA} = \frac{AK}{W} \quad \text{Equation 3-4}$$

where

%PRA = PRA purity, %

A = measured absorbance of the final mixture, absorbance units.

K = conversion factor value (molar absorptivity), dependent on quality of spectrophotometer and associated equipment[5] (e.g., 1-cm cuvettes and a spectral band width half intensity of <11 nm, K = 21.3); *Note:* If these specifications are not met, the dye analysis will be incorrect;

W = weight of dye in 50 ml of PRA stock solution, g (e.g., if 100 mg is used to prepare 50 ml in the purification procedure, W = 0.100 g; and if 0.5 g is used to prepare 250 ml, W is still 0.100g; when obtained from commercial sources, use the stated concentration to compute W; for 0.20 percent concentration of 98 percent purity PRA, W = 0.098 g per 50 ml).

5. Record the results of the assay in a calibration log.

3.14 Pararosaniline Reagent

The procedure for preparing a pararosaniline reagent is as follows:

1. To a 250-ml volumetric flask, add 20 ml of PRA stock solution.

2. Add an additional 0.2 ml of stock solution for each percentage that the stock assayed below 100 percent.

3. Add 25 ml of 3M phosphoric acid. Dilute to the 250-ml mark with distilled water.

This reagent, stored in a glass-stoppered bottle, is stable for at least 9 mo.

Table 3.1 *Activity Matrix for Preparation of Reagents*

Reagent	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Distilled water	*$KMnO_4$ color (pink) persists after 1 h at room temperature*	*Test only if slope and intercept of standard curve fail to meet criteria (Sec. 2 1.5).*	*Purify the water.*
Water storage	*Inert container with vent guard*	*Visual check; cover and vent guard in place.*	*Replace vent guard every every 30 days.*
Absorbing reagent pH test	*$3.0 < pH < 5.0$; optimal pH of 4.0*	*Check new reagent before use with pH meter.*	*Discard; check chemicals; prepare new lot.*
Absorber reagent storage	*<6 mo after preparation; no precipitate*	*Visually check for preparation date and precipitate.*	*Discard.*
Sulfamic acid	*0.6%, keep in glass-stoppered flask*	*Gravimetric preparation; fresh daily*	*Prepare fresh reagent.*
Formaldehyde	*0.2%; keep in stoppered container*	*Volumetric preparation, fresh daily*	*As above*
Starch indicator solution	*2 g/liter; clear solution*	*Gravimetric preparation*	*As above*
Stock iodine solution	*0.1N; keep in glass stoppered dark bottle*	*As above*	*As above*
Working iodine solution	*0.01N; keep in glass-stoppered dark flask*	*Volumetric preparation; fresh daily*	*As above*
Hydrochloric acid	*1N keep in tightly sealed glass bottle*	*Volumetric preparation*	*As above*
Stock sodium thiosulfate	*0.1N; keep in glass-stoppered flask*	*Standardize before each use against KIO_3 standard*	*As above*
Sodium thiosulfate titrant	*0.01N, keep in glass-stoppered flask*	*Volumetric preparation; prepare daily*	*As above*
Standard sulfite-TCM solution	*320-400 μg SO_2/ml equivalent, store glass-stoppered flask*	*Standardize by titration.*	*As above*
Working sulfite-TCM solution	*Accurate preparation from standard stock solution*	*Volumetric preparation; prepare on day of use, or store <30 days @ 5°C (41°F).*	*As above*
Stock pararosaniline solution	*0.2% PRA; prepare according to Subsection 3.13.3*	*Assay at preparation; perform after each preparation, or purchase new lot of PRA.*	*As above*
PRA reagent	*Prepare according to Subsection 3.14*	*Discard after 9 months.*	*As above*

4.0 Sampling Procedure

The quality assurance activities for sampling are presented in Table 4 1 at the end of this section.

4.1 Selection of Sampling Train

A suitable sampling probe consists of a Teflon® or glass tubing and an inverted funnel of one of these materials. The funnel is oriented to preclude the sampling of precipitation and large particles. The residence time of the sample in the probe should be less than 20 seconds (see Section 7 of 40 CFR Part 58, Appendix E).

A midget impinger sampling train (Figure 4.1) is needed for short-term sampling (≤3 h). With this sampling train, the flow control is maintained either by a critical flow orifice or by a needle valve with a rotameter to indicate the flow rate. For short-term sampling (30 min or 1 h), a 30-ml all-glass midget impinger should be used, as specified in the Reference Method, Section 2.1.11 (Figure 4.2). The nozzle of the impinger should have an inside diameter of 1.0 mm (0.05 in.), and it should deliver 2.5 to 3.1 liters/min (0.09 to 0.11 ft^3/min) at 305 mm (12 in.) H_2O vacuum.

The sampling train commonly used for 24-h sampling (Figure 4.3) consists of polypropylene bubbler tubes and critical orifices for flow control. For 24-h sampling, the absorber selected should consist of:

1. A polypropylene container that is 164 mm (6.5 in.) in depth and 32 mm (1.26 in.) in diameter and has a permanent mark indicating 50 ml volume. (Available from Bel Art Products, Pequannock, New Jersey).
2. A two-port polypropylene tube closure (commercially available). Rubber stoppers are *not* acceptable.
3. A glass impinger tube that is 158 mm (6¼ in.) in length and 6 mm (0.24 in.) in diameter and has an outlet orifice diameter that fits a No. 79 jeweler drill. (No. 78 is too large.) The required orifice size is between 0.368 and 0.406 mm (0.014 and 0.016 in.).

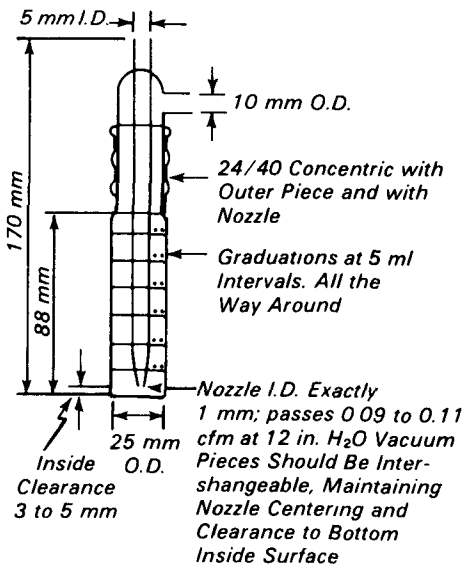


Figure 4.2 *Midget Impinger specifications.*

Clearance from the bottom of the absorber to the tip of the stem must be 6 ±2 mm.

4.2 Preparation of Sampling Train

4.2.1 *Cleaning the Absorber* - Before each use, the following procedure should be used for cleaning each absorber.

1. Wash in hot water.
2. Wash 1 h in an acid bath (1 part HNO_3, 2 parts HCl, 4 parts distilled H_2O).
3. Rinse with distilled water.
4. Air dry (drain).

4.2.2 *Dispensing the TCM* - The quantity of TCM absorbing reagent needed for the desired sampling period is transferred to the absorber as follows:

1. Transfer of 50 ml of TCM with an automatic reagent dispenser is acceptable for 24-h periods.
2. Transfer of 10 ml of TCM is required for 30-min and 1-h periods. *Warning:* TCM is highly poisonous. Wear rubber gloves when dispensing TCM. If spilled on the skin, flush with water immediately. Ship the TCM in test tubes with screw caps (Figure 4.4) that have Teflon or equivalent inner seals.

4.2.3 *Assembly of Absorber* - The absorber is assembled as follows:

1. After inspecting the impinger tip for damage during shipment and replacing if necessary, place the impinger stem in the outer sleeve of the all-glass unit for 30-min and 1-h sampling. Seal by placing a thin film of silicone stopcock grease around the ground-glass joint.
2. Assemble the absorber as shown in Figure 4.5 for 24-h sampling.

4.2.4 *Identifying the Sampling Apparatus* - A stick-on label should be used to mark the following information on each absorber.

1. Date of preparation
2. Sampling site number
3. Date to be used

Record the absorber and the orifice identifications in the laboratory log book.

4.2.5 *Packing for Shipment to the Field* - The absorber should be packed either in a wooden block container that has been predrilled for absorber

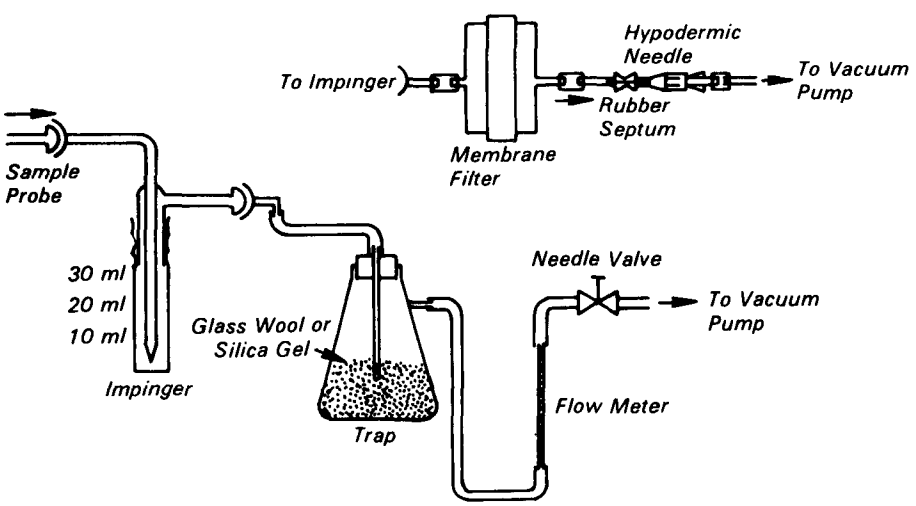
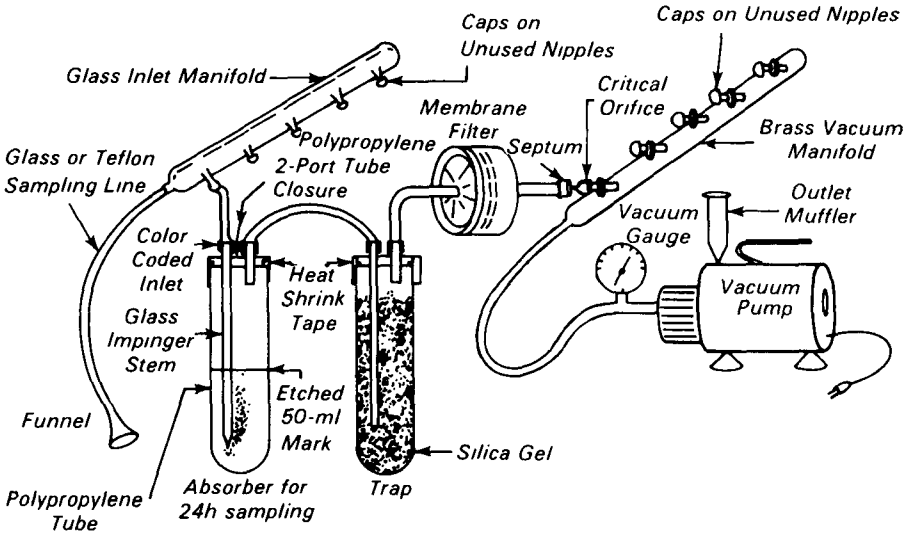


Figure 4.1 *Midget impinger sampling train.*



Note. A Midget Impinger is Used for 1-hour sampling.

Figure 4.3 *Twenty-four-hour sampling train.*

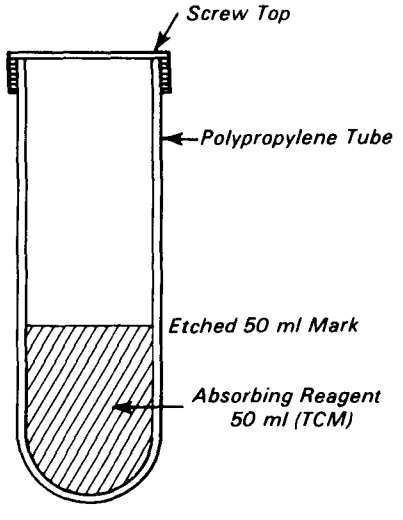


Figure 4.4 *Screw-top bubbler for shipment*

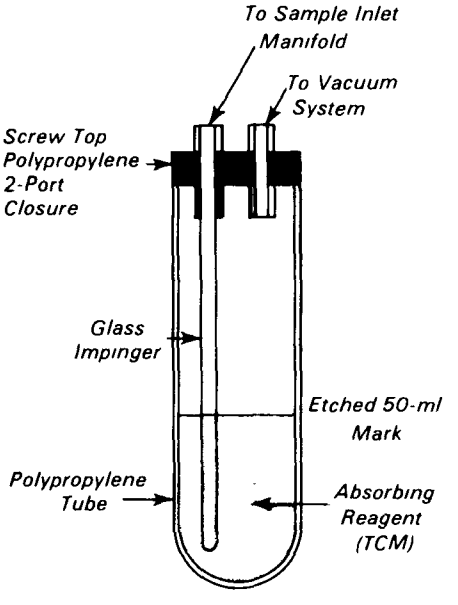


Figure 4.5 *Absorber for 24-hour sampling*

flasks according to the EPA-NASN design, or in a light-weight shipping container that has an "Etha foam" insert designed with appropriately sized holes to support the bubbler tubes. This insert can be used in a heavy-duty fiberboard container for shipment to the field, and it will reduce the shipping costs by a factor of approximately 5. *Caution:* Collected SO_2 samples must be shipped and stored at ≤5°C (≤41°F); therefore, the packing process described may be suitable for shipping absorber tubes to the field, but not for returning the collected SO_2 samples (unless ice packs are used).

4.2.6 *Connecting the 24-h Sampling System Components* - The sampler components shown in Figure 4.6 should be assembled as follows:

1. Attach the sample inlet line consisting of the Teflon® or glass tubing and the funnel, as shown.
2. Extend the funnel-and-sample inlet line out-of-doors through a window or other opening to avoid obstructions to air flow near the inlet. See Section 2.0.2 for siting guidelines.
3. Support and secure the tube and funnel in their positions so that they will not come loose during sampling. (The funnel should be hung down so that rain will not be drawn into the sampler.)
4. Use a temperature-controlled shelter. The temperature of the absorbing solution must be maintained at 15° ±10°C during sampling. As soon as possible following sampling and until analysis, the temperature of the collected sample must be maintained at 5° ±5°C. Where an extended period of time may elapse before the collected sample can be moved to the lower storage temperature, a collection temperature near the lower limit of the 15 ±10°C range should be used to minimize losses during this period. Thermoelectric coolers specifically designed for this temperature control are available commercially and normally operate in the range of 5° to 15°C. Small refrigerators can be modified to provide the required temperature control; however, inlet lines must be insulated from the lower temperatures to prevent condensation when sampling under humid conditions. A small heating pad may be necessary when sampling at low temperatures (<7°C) to prevent the absorbing solution from freezing. The thermostat in the shelter should be checked to ensure that it is operating properly. The absorbing solution must be shielded from light during and after sampling. Most commercially available sampler trains are enclosed in a light-proof box.
5. Use vacuum-type tubing to connect the metal vacuum manifold to the intake of the vacuum pump; place a pinch clamp on this section of tubing (as shown in Figure 4.6), but do not tighten it; and be sure all connections are airtight, but without constrictions in the tubing.
6. Electrically connect the vacuum pump to the timer switch (Figure 4.6); connect the timer to a 24-h 110-VAC outlet, and connect the sampler box to a 24-h outlet. A timer is recommended to initiate and stop sampling for the 24-hour period. The timer is not a required piece of equipment; however, without the timer a technician would be required to start and stop the sampling manually. An elapsed-time meter is

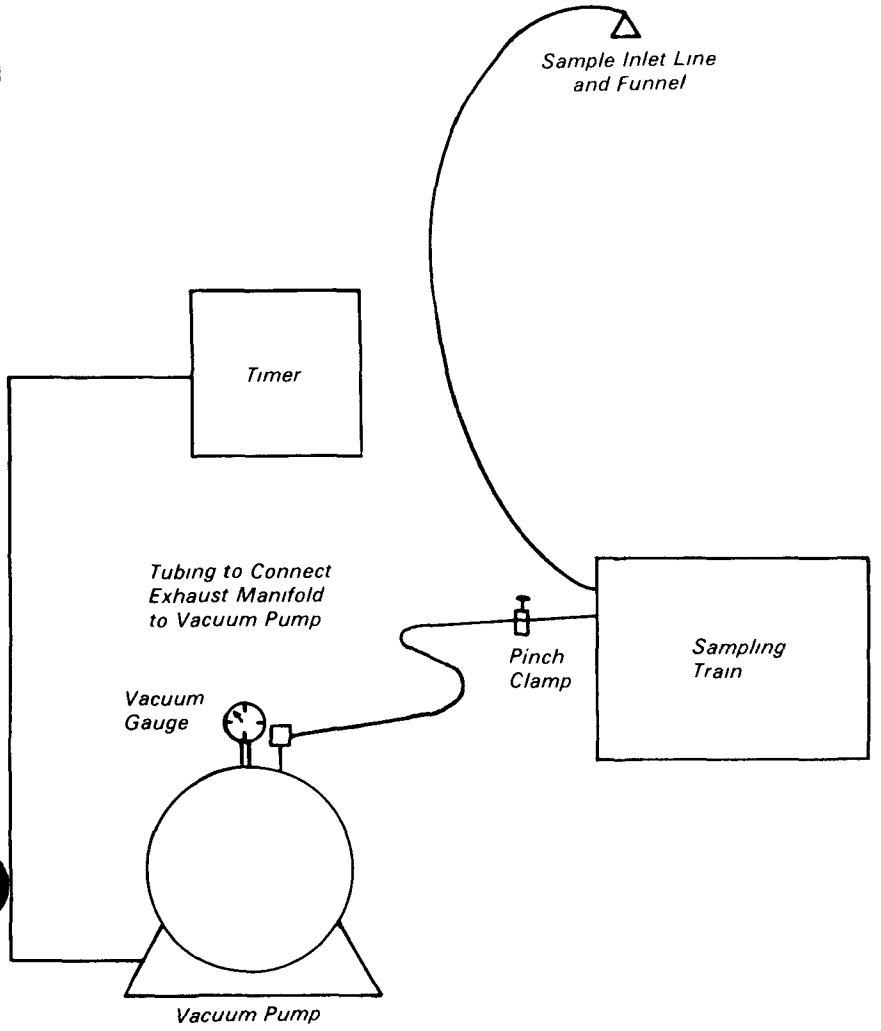


Figure 4.6 *Diagram of an SO_2 sampling apparatus.*

also recommended to determine the duration of the sampling period.

4.2.7 *Installing the Critical Orifice* - Tubing for the absorber and the sampling apparatus should be color-coded to facilitate proper positioning of absorbers and correct connections for tubes (Figure 4.7). Accordion-type tubing is used to connect the glass intake manifold to the impinger tube of the absorber; smooth tubing is used for all other connections. A step-by-step installation procedure for the 24-h bubbler is presented here.

1. Remove the used absorber from the sampling train by gently but firmly pulling the inlet and the outlet tubing from the absorber.
2. Exchange the reagent-filled absorber for the used absorber.
3. Transfer the caps from the reagent-filled absorber to the used absorber. *Note:* Always install the tube cap or the tubing on the impinger tube (color-coded side of absorber) first and remove it last; otherwise, some of the absorbing reagent/sample may be forced out of the impinger opening and lost.
4. Gently but firmly insert the accordion inlet tube from the glass manifold onto the color-coded tube (impinger tube) of the absorber lid, and be sure that the fit is airtight.
5. Gently but firmly insert the smooth tubing from the trap to the unpainted outlet tube of the absorber.
6. If the hypodermic needle is to be replaced, insert the new needle into the center of the rubber septum attached to the membrane filter unit (Figure 4.8). The needle must be put in straight. If the needle is accidently bent, it should be destroyed and discarded, and another needle should be used
7. Slide the base of the needle onto the metal vacuum manifold (Figure 4.9) Manipulate the needle and/or rotate the trap, if necessary, to obtain a tight connection
8. Leak-check the total system by activating the vacuum pump, capping off the plastic sample inlet nipple, and visually checking for bubbling Should a leak be detected, check all fittings for leaks. Heat-shrink material (as shown in Figure 4.3) can be used to retain the cap seals if there is any chance of the caps coming loose during sampling, shipment, or storage. (Also see Subsection 4.3.1.)
9. Shield the absorber from sunlight during and after sampling if the sampling train is not housed in a closed box. One means of accomplishing this is to wrap the absorber in aluminum foil.
10. Recheck the arrangement, alignment, and tightness of all connections, and verify the following points:

a. The accordion tubing from the glass manifold goes to the color-coded side of the absorber lid.
b. The needle is not bent or obstructed.
c. The needle fits the exhaust manifold tightly.
d. The inlet filter and tubing are connected tightly.
e. The vacuum pump connections are tight

4.3 Collection of the Sample

Operation of the sampling apparatus is started and stopped by the timer. Ranges of sample air flow rates to be used for different sampling periods are as follows

Sampling period, h	Flow rate, cm^3/min	Hypodermic needle size and gauge
1/2	900 to 1100	1 in., 22 gauge
1 to 3	450 to 550	5/8 in., 23 gauge
24	180 to 220	3/8 in., 27 gauge

Figure 4.7. Closeup view of absorber installation.

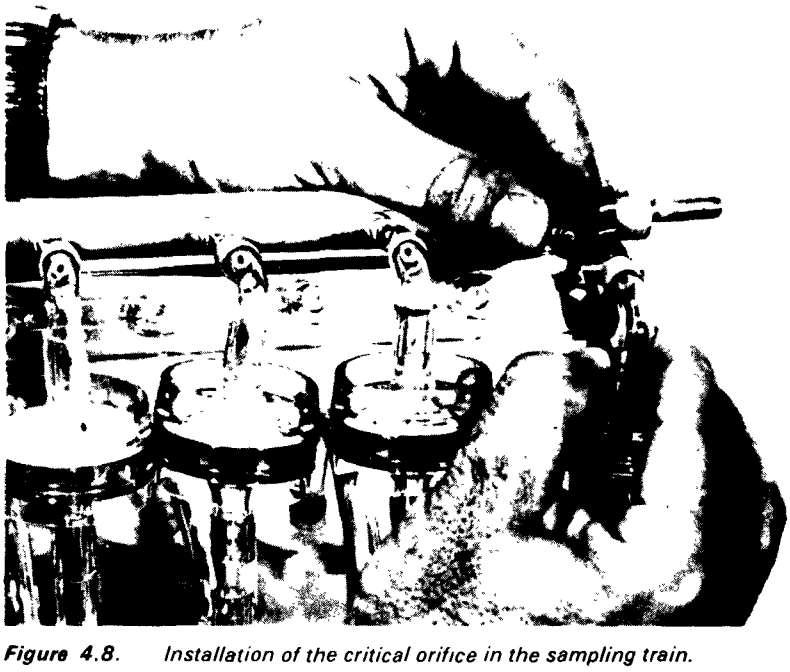


Figure 4.8. Installation of the critical orifice in the sampling train.

4.3.1 *Operational Check* - Procedural steps described in this subsection are performed by the operator prior to the actual collection of the sample. These operational checks can be performed any time before the sampling. Normally, they are performed immediately after the prior sample is removed.

1. If a rotameter equipped with a needle valve is used, adjust the system flow rate to the prescribed value on the sample record form (Figure 4.10). The manufacturer's calibration chart may be used to obtain this approximate setting. Proceed to step No. 7 below.

2. If a critical orifice is used, completely close the pinch clamp between the sampler and the vacuum pump or kink the tubing between the orifice and the vacuum pump.

3. Turn the vacuum pump on, and record the vacuum reading ("Start-Clamps," Figure 4.10).

4. If the vacuum gauge reading is below 530 mm (21 in.) Hg, make sure the pinch clamp (or kink) is closed and the tubing is securely connected to the pump inlet.

5. If the vacuum reading remains below the reference value (Step 4), repair or replace the pump.

6. Turn the vacuum pump off.

7. Open the pinch clamp (if necessary). Record the reading of the elapsed-time meter unless a bubble meter is used to measure the flow. If a bubble meter is to be used, record elapsed time after the initial flow measurement.

8. Leak-check and measure the initial flow rate at the inlet to the absorber by using one of the procedures in Subsection 4.4.

9. Turn on the vacuum pump and record the vacuum gauge reading on the sample record form in the space marked "Start-Open."

10. Gently lift the sampling train halfway out of the sampler box, and check to be sure the absorber is bubbling. If not, check for loose connections or a plugged line.

11. Turn the timer off, and set it for the sampling period.

12. Record the date and time on the sample record form.

4.3.2 *Postsampling Check* - Steps listed in this subsection are performed by the operator after the sample collection.

1. For apparatus with a rotameter:

a. Measure the final flow rate, using the same procedure as that used for the initial flow rate, and record on the sample record form.

b. Turn the timer switch off.

c. Record the elapsed-time meter reading.

2. For apparatus with a critical orifice:

a. Leak-check and measure the final flow rate, using the same procedure as that used for the initial flow rate, and record on sample record.

b. Record the vacuum gauge reading on the sample record form (in the space marked "End-Open") and record the elapsed-time meter reading.

Figure 4.9. Connecting the critical orifice to the exhaust manifold

c. Close the pinch clamp tightly.

d. Record the vacuum gauge reading on the sample record form in the space marked "End-Clamp."

e. Turn the time switch off

3 Check the condition of the membrane filter, and replace the filter if it is discolored or cracked The porosity of the filter should be 0 8 to 2 μm. It is used to protect the flow controller from particles during long-term sampling. This item is optional for short-term sampling Check the moisture trap and replace the silica gel if more than three-fourths of the indicator is pink Glass wool may be substituted for silica gel during the collection of short-term samples (1 hour or less), or for long-term (24-hour) samples if flow changes are not routinely encountered

4. If the ambient temperature is lower than the thermostat setting in the sampling box, check to be sure that the thermostat and the heater are functioning.

5. Record the average temperature of the absorbing solution for the sampling period For 30-min and 1-h samples, the temperature immediately before, after, or at any time during the sampling period is adequate. For 24-h samples, a recording thermometer is recommended for use within the sampling train shelter, record the mean of the readings from the recording thermometer kept in the sampling box. A minimum-maximum thermometer has also been used for this purpose, but it only provides an indication of the degree of temperature control within the sampling box; if the minimum-maximum thermometer readings are unavailable, record the normal thermostatic setting of the sampling box or the ambient temperature for the sampling period, whichever is greater. *Note*· Unfortunately, the SO_2-TCM complex is thermally unstable. The SO_2 concentration measured in an air sample depends greatly on the temperature of the TCM absorbing solution during sampling and after sample collection. That is, the SO_2 is lost from the collected samples at rates that are highly dependent on temperature and that are independent of concentration as long as EDTA is used as called for, as shown by the following[6]·

Temperature, °C	°F	Rate of SO_2 loss, %/day
20	68	0.9
30	86	5.0
40	104	25.0
50	122	73.6

The temperature of the absorbing solution during sampling must be maintained between 5° and 25°C. During storage and transport, the temperature must be maintained at 5° ±5°C

6 Record the barometric pressure for the sampling period (obtained with a calibrated instrument or from the local weather bureau)

7. Check the absorber for any reagent loss due to evaporation Mark the level of the solution with a piece of tape or a grease pencil. Record an estimate of the quantity of absorbing reagent on the sample record form or state under "Remarks" that there was no evaporation

4.3.3 *Sampling Time Period* - The sampling time period should be recorded on the sample record form. For 24-h samples, the sample must be voided if the sampling period is <23 h or >25 h. The actual sampling period must be known to within ±15 min (see Section 2.1 2)

4.3.4 *Sample Handling* - The procedure for sample handling is as follows:

1. First remove the accordion tubing (color-coded) from the absorber impinger tube.

2. For 24-h samples, estimate the volume of absorber reagent remaining in the absorber flask after sampling, mark the TCM level in the absorber with tape or some other easily removable indicator, and record the estimate on the sample record form. To assist in this estimation, mark the tubes at the 35- and 50-ml levels with a marking pen. If <35 ml of sampling reagent remains after sampling, void the sample, and indicate this on the form. If 50 ml of sampling reagent remains after sampling, state (under "Remarks" on the sample record form) that no evaporation occurred during the sampling.

3. If there is evidence of malfunction (e g , absorbing reagent forced out of absorber into the vacuum system), record this on the sample record form Normally, the sample is invalid under this circumstance

4. Place the tube caps first on the impinger tube (color coded) of the absorber and then on the suction tube Press caps firmly in place, and place the absorber in the shipping block. *Note:* For 30-min and 1-h samples collected in glass impingers, shake the absorber thoroughly, quantitatively transfer all of the exposed reagent to a test tube or small bottle with a Teflon-lined threaded cap, and place the sample in the shipping block

5 Record on the sample record form any pertinent observations relative to sources, weather

Gas Bubbler Data Record

Station Location
City & State SMELTER TOWN, UTAH
Site & Address 341 NORTH ST.
Project SMELTER *Site No* 12
Pollutant SO_2
Sampler ID No. 25 *Sample No.* 471
Type of Flow Measuring Device ROTAMETER
Identification Number of Device 23

	Open	Clamp
Vacuum Reading Start	24.0	24.8
Vacuum Reading End	24.0	24.8

	mo	day	yr	h	min
Start Sampling	6	5	81	24	0
Stop Sampling	6	6	81	23	57

Elapsed Time Start 0
Elapsed Time Stop 1437
Nominal Flow Rate 200 ml/min

Initial Flow 204 ml/min, 205, 206 *Final Flow* 203 ml/min, 204, 202 *% Difference* 1.0
Average 205 ml/min *Average* 203 ml/min
Average sample temperature 7.0 °C *Relative humidity* 55%
Ambient temperature: Start ___ °C, *Stop* ___ °C, *Average* 25 °C
Barometric pressure. Start ___ mm Hg, *Stop* ___ mm Hg, *Average* 749.0 mm Hg
REMARKS:

Meteorological conditions for use when anomaly occurs
WIND ___ *calm* ✓ *light* ___ *gusty*
VISIBILITY ✓ *clear* ___ *hazy*
SKY ✓ *clear* ___ *scattered* ___ *overcast*
HUMIDITY ___ *dry* ✓ *moderate* ___ *humid* ___ *rainy*
TEMP °F ___ *<20* ___ *20-40* ___ *41-60* ✓ *61-80* ___ *>80*

Sample collected within guidelines given below

J. M. Jones
Signature

Guidelines

Proper flow rate — *1/2-h samples - 900-1100 cm³/min*
1-h samples - 450-550 cm³/min
24-h samples - 180-220 cm³/min

24-h sampling — *23 h < sampling time < 25 h*
— *≥35 ml of absorbing reagent remain after sampling*
— *sampler timer accuracy ±15 min/24 h*

Figure 4.10. *Sample record form.*

conditions, etc., that might affect the SO_2 level.

6. Complete the sample record form in duplicate, return the original copy with the absorber in the shipping block, and file the duplicate in the site log book.

7. If samples must be stored before shipment for analysis, store them in a refrigerator or cooler at 5°C (41°F). A shipping container that can maintain a temperature of 5° ±5°C is used to transport the sample from the collection site to the analytical laboratory. Ice coolers or refrigerated shipping containers have been found to be satisfactory. The use of eutectic cold packs instead of ice will provide a better temperature control. Such equipment is commercially available from Cole-Parmer Company, 7425 North Oak Park Avenue, Chicago, Illinois 60648.

4.4 Determination of the Flow Rate of SO_2 Sampling Trains

The SO_2 sampling train that is used for short-term periods of 30 minutes and 1 hour normally has one of two flow control systems. One system has a needle valve and indicates the flow rate with a rotameter. The other uses various sizes of stainless steel hypodermic needles to control the flow. The 24-h sampling trains also use stainless steel hypodermic needles to control the flow. For short-term samples, the standard flow rate is determined at the sampling site at the initiation and completion of sample collection by use of a calibrated flow-measuring device connected to the inlet of the absorber. For 24-hour samples, the standard flow rate is determined at the time the absorber is placed in the sampling train and again when the absorber is

removed from the train for shipment to the analytical laboratory. A calibrated flow-measuring device connected to the inlet of the sampling train is used for this purpose. The flow rate determination must be made with all components of the sampling system in operation (e.g., the absorber temperature controller and any sample box heaters must be operating).

4.4.1 *Flow Rate Measurement* - Three step-by-step procedures for measuring the sampling flow rates are presented here. They involve the use of a mass-flow meter, a rotameter, or a soap-bubble meter. The reference method requires that the flow rate of each SO_2 sampling train be measured before and after each sampling period. The initial and final flow rates must agree within ±5 percent or the sample is voided. *Therefore, it is very important that the flow-measuring device selected have the appropriate range, accuracy, and readability to meet this specification.* The typical flow rates for 30-min, 1-hour, and 24-hour samples are 1000, 500, and 200 ml/min, respectively.

The range of a mass-flow meter used as a flow measuring device should be such that the measured flow is between 50 and 90 percent of full scale Regardless of the range, the mass-flow meter must have a readability and reproducibility of 1 percent of the measured flow to ensure that only samples from trains whose flow rate *did* change by more than 5 percent are invalidated. Mass-flow meters should be calibrated according to procedures given in Subsection 2.1.3.

Rotameters used as flow measuring devices should have a minimum scale of 6-in. (150 mm) with no less than 100 divisions The measured flow should be between 50 and 90 percent of full scale. If these conditions are met, only samples from the trains whose flow rate *did* change by more than 5 percent should be invalidated. Rotameters should be calibrated according to procedures presented in Subsection 2.1.4.

Bubble meters should be of a size that the volume is displaced in 10 to 30 seconds during the flow measurement. Bubble meters are calibrated according to procedures presented in Subsection 2 1.2

When flow measurements are made by inserting a mass-flow meter or rotameter between the probe and the absorber, the time required for the initial and final flow measurements should be included in the total sampling time.

Bubble meters are not as easily inserted between the probe and absorber inlet, and the solution in the bubble meter will absorb at least some of the SO_2. Therefore, the time required to do the initial and final flow measurements should *not* be included in the sampling time, and a charcoal scrubber should be inserted between the bubble meter and the absorber to ensure the removal of SO_2. Care must be exercised in the selection of the charcoal tube so that the pressure drop across the sampling system will not be increased enough to alter the sampling rate.

4.4.2 *With a Mass Flow Meter* - The following procedure should be used to measure the flow before and after sampling.

1. Assemble the equipment for sampling, as shown in Figure 4.11.
2. Be sure all connections are tight.
3. Be sure the absorber inlet line is connected to the mass-flow meter transducer outlet.
4. Zero the mass-flow meter.
5. Turn the vacuum pump on and adjust the needle valve to obtain approximately the desired flow (prior to sampling only). Record the vacuum reading on the sheet.
6. Check for bubbles in the sampling tube. Plug the inlet of the mass-flow meter, and check for zero flow on the rotameters. If a zero flow is not obtained, check for leaks. Unplug the inlet.
7. Read the flow rate on the mass-flow meter after the meter indicator has stabilized (about 30 s) and shut off the pump.
8. Turn the pump on, and repeat Step 7 two more times.
9. Average the three flow rates.

4.4.3 *With a Rotameter* - The following procedure should be used to measure the flow before and after sampling.

1. Assemble the equipment, as shown in Figure 4.12.
2. Place a new rubber septum on the tube (prior to sampling only).
3. Be sure all connections are tight.
4. Be sure the line from the surge tank outlet is connected to the inlet of the sampling tube absorber.
5. Turn the vacuum pump on, and check the vacuum by placing a finger over the end of the vacuum line. (The vacuum gauge should read at least 530 mm (21 in.) Hg at a barometric pressure of 760 mm (29.92 in.). Turn the vacuum pump off.
6. Insert a needle through the center of the septum, perpendicular to the plane of the septum face.
7. Turn the vacuum pump on. Slide the needle holder snugly into the recess at the base of the needle, and check for bubbles in the sampling tube. Plug the inlet to the rotameter and check to see that bubbling ceases in the absorber. If bubbling persists, check for leaks. Unplug the inlet.
8. Read the ball position on the rotameter; record the flow rate corrected to STP, 760 mm (29.92 in.) Hg and 25°C (77°F), from the rotameter calibration curve; and read the vacuum gauge to make sure the vacuum is sufficient during the flow measurement.
9. Repeat Step 8 two more times. Turn pump off and then back on after each run.
10. Record the ambient temperature and pressure or obtain the average for the sampling period from the local weather bureau.
11. Average the flow rates of the three runs.
12. If the rotameter is used in a field location where the barometric pressure and/or temperature is different from the conditions under which the rotameter was calibrated, apply the following corrections to convert the flow rate to standard conditions. This correction factor is not advisable for conditions that differ greatly from those at which the rotameter was calibrated. Greater accuracy can be obtained by developing calibration curves for expected conditions.

$$Q_s = Q_f \left(\frac{P_f}{760} \times \frac{298}{T_f} \right)^{1/2}$$

Equation 4-1

where

Q_s = flow rate corrected to standard conditions from field conditions, ml/min

Q_f = flow rate at field conditions from calibration curve, ml/min

P_f = barometric pressure at field conditions, mm Hg

T_f = temperature at field conditions, °K.

4.4.4 *With a Bubble Meter* - The following procedure should be used to measure the flow before and after the sampling.

1. Assemble the equipment for sampling, as shown in Figure 4.13.
2. Place a new rubber septum on the sampling tube only prior to sampling.
3. Be sure all connections are tight.

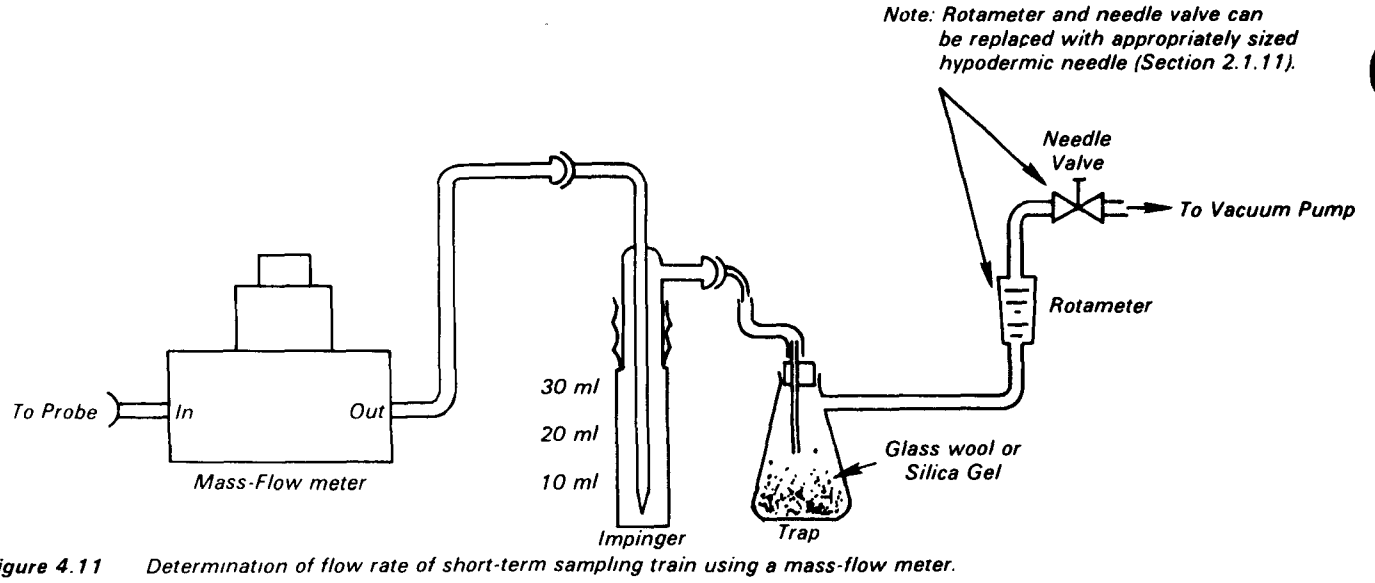
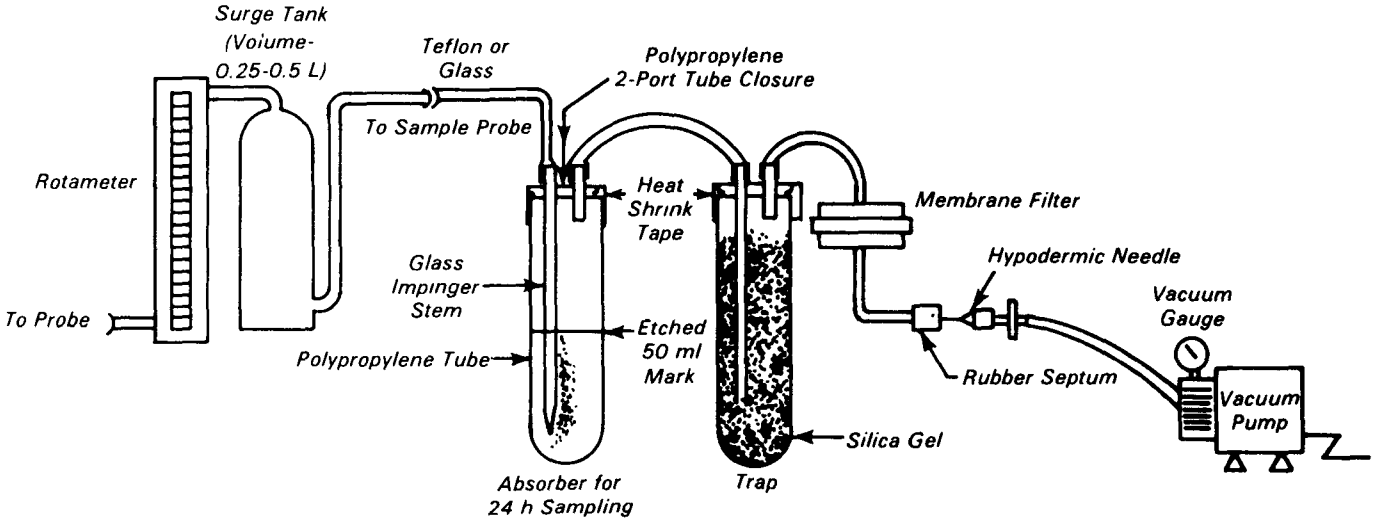


Figure 4.11 Determination of flow rate of short-term sampling train using a mass-flow meter.



Note A midget impinger is used for 1-hour sampling.

Figure 4.12 Determination of flow rate of long-term sampling train using a rotometer.

4. Be sure the charcoal tube is connected between the bubble meter and the inlet of the sampling tube impinger.

5. Turn the vacuum pump on and check the vacuum by placing a finger over the end of the vacuum line. (The vacuum gauge should read at least 530 mm (21 in.) Hg at a barometric pressure of 760 mm (29.92 in.) Hg. Turn the pump off.

6. Insert a needle through the center of the septum, perpendicular to the plane of the septum face.

7. Turn the vacuum pump on.

8. Slide the needle holder snugly into the recess at the base of the needle, and check for bubbles in the sampling tube. Plug the inlet to the bubble meter and check to see that bubbling ceases in the absorber. If bubbling persists, check for leaks. Unplug the inlet.

9. Touch the surface of the soap solution with the open end of the bubble meter so that a soap bubble will start to travel up the bubble meter tube. Repeat several times or until the bubble travels the full length of tube without breaking.

10. Touch the surface of the soap solution with the open end of bubble meter so that a single bubble starts to travel up the bubble tube. When the bubble passes the first line of the graduated scale, start the stopwatch and record the time and volume displaced. Read the vacuum gauge to make sure the vacuum is sufficient during flow measurement.

11. Repeat Step 10 two more times. Record the time and the volume each time.

12. Record the ambient temperature and pressure, or obtain the average for the sampling period from the local weather bureau.

13. Average the times and volume displacements for the three runs.

14. Divide the average volume displacement by the average time to determine the flow rate.

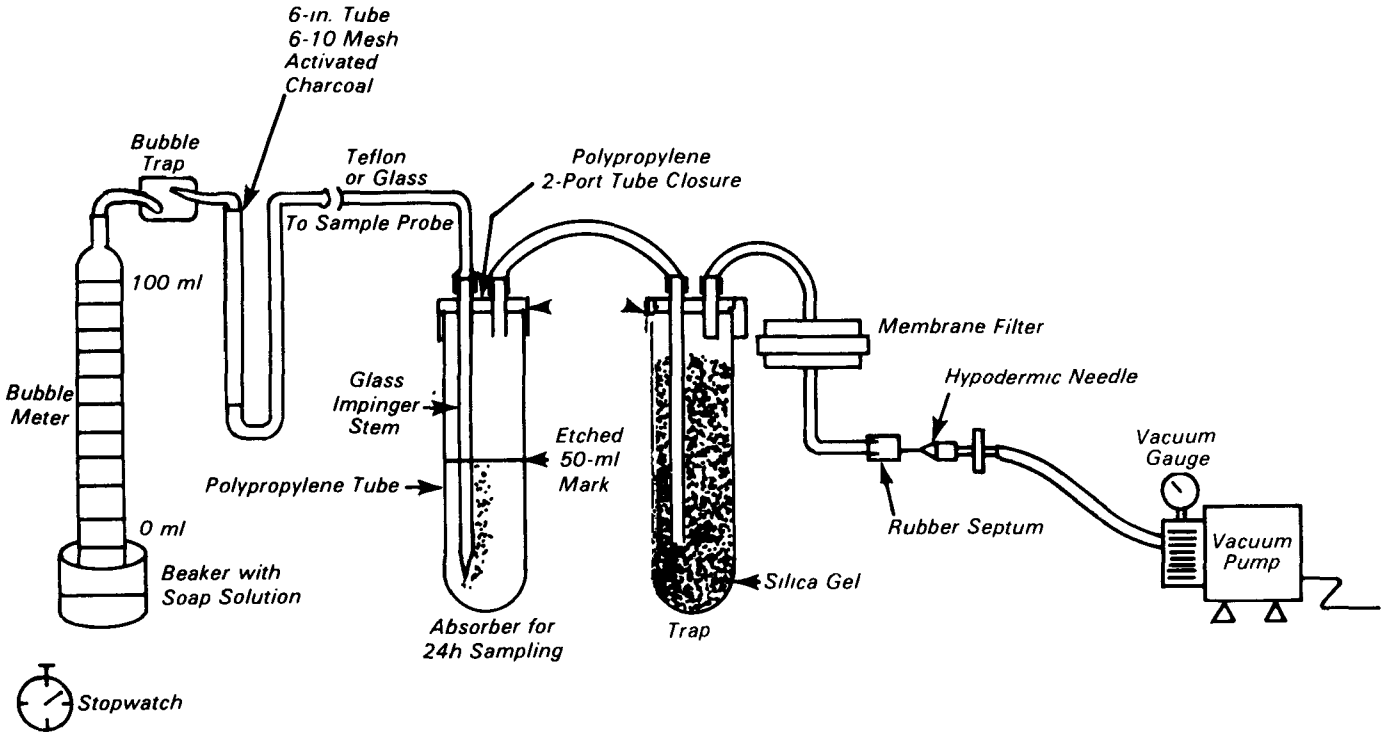


Figure 4.13 *Determination of flow rate of long-term sampling train using soap-bubble meter*

15. Correct the average flow rate to standard conditions of 760 mm (29.92 in.) Hg and 25°C (77°F), using Equation 4-2.

$$Q_{std} = Q_{act} \times \frac{P_b - (1-RH)P_{H2O}}{P_{std}} \times \frac{298.16}{(T_{meter} + 273.16)}$$

Equation 4-2

where

Q_{std} = flow rate at standard conditions, std liters/min (25°C and 760 mm Hg)

Q_{act} = flow rate at monitoring site conditions, liters/min

P_b = barometric pressure at monitoring site conditions, mm or in. Hg

RH = fractional relative humidity of the air being measured; determined with a sling psychrometer or similar device, or obtained from the local weather station.

P_{H2O} = vapor pressure of water at the temperature of the air in the flow or volume standard, in the same units as P_b (for wet volume standards only, i.e., bubble flowmeter of wet test meter, see Section 2.1.2; for dry standards, i.e., rotameter, P_{H2O} = 0)

P_{std} = standard barometric pressure, in the same units as P_b (760 mm Hg or 29.92 in. Hg)

T_{meter} = temperature of the air in the flow or volume standard, °C (e.g., bubble flowmeter)

If a barometer is not available, the following equation may be used to determine an average barometric pressure:

$$P_b = 760 - .076(H) \text{ mm Hg or } P_b = 29.92 - .0030(H) \text{ in. Hg}$$

Equation 4-3

where

H = sampling site elevation above sea level in meters.

4.5 Flow Rate Validation

4.5.1 *Initial Flow Rate* If the flow meter or the hypodermic needle in the sampling train has been calibrated, the initial flow rate (determined by one of the flow-measuring devices listed in Subsection 4.4) should be compared with the rate of the flow-controlling device to determine if the train is leak-free.

If the initial flow rate (Q_i) differs from the flow rate of the critical orifice or the flow rate indicated by the flowmeter in the sampling train (Q_c) by more than 5 percent (as determined by Equation 4-4), checks for leaks should be made and the Q_i should be determined.

$$\% \text{ Diff} = \frac{Q_i - Q_c}{Q_c} \times 100$$

Equation 4-4

4.5.2 *Final Flow Rate* The initial flow rate and the final flow rate must agree within ±5 percent for a valid sample to be collected. This check should be performed in the field when the final flow measurement is made so that any discrepancies can be determined at that time. Immediate onsite determination of the reasons for variable flow rates can prevent further data loss.

The sample should be invalidated if the difference between the initial (Q_i) and final (Q_f) flow rates is more than 5 percent as determined by Equation 4-5.

$$\% \text{ Diff} = \frac{Q_i - Q_f}{Q_f} \times 100$$

Equation 4-5

Table 4.1 *Activity Matrix for Sampling Procedure*

Activity	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Absorber selection	*1) Short-term, ≤3 h; 30-ml all-glass midget impinger* *2) 24-h sample; polypropylene tube and closure with glass impinger tube* *3) Orifice ID >#79 drill and <#78 drill*	*Visually check each sample.*	*Select proper absorber*
Cleaning absorber	*Clean absorber*	*Water and acid bath prior to each use*	*Clean it.*
Dispensing TCM	*1) Short-term period, 10 ml TCM* *2) 24-h period, 50 ml TCM*	*Visually check each sample.*	*Correct the discrepancy*
Assembly of absorber	*As diagrammed*	*Visually check.*	*Reassemble.*
Determination of flow rates before and after sampling	*Percent difference ≤5%*	*Calibrated flow measuring device (Sec. 2.1.2).*	*Void sample.*
Sample ID	*All required information*	*Visually check.*	*Complete the stick-on label/*
Packing for shipment	*Shipped in insulated cool-pack container*	*As above*	*Repack as appropriate.*
Sampler assembly, 24-h bubbler	*NASN specifications (Figs 4.6, 4.7, 4.8)*	*As above*	*Reassemble if necessary.*
Installation of absorber and critical orifice	*See Subsec. 4.2,6 and 4.2.7.*	*As above*	*Reassemble and/or select proper orifice.*
Collection of sample	*Air flow rate ±5% (Subsec. 4.3); absorbing solution at 15 ±10°C during sampling and prior to recovery*	*Initial and Final (Subsection 4.4). Check thermometer for each sample, Subsec. 4.3.2.*	*Void sample.* *Void sample.*
Storage of sample before analysis	*Store at 5° ±5°C*	*As above*	*Void sample.*

5.0 Analysis of Samples

The quality control functions for analysis of samples are summarized in Table 5 2 at the end of this section

5.1 *Verification of Field Record Form*

Procedures for verifying the field record are as follows:

1. Examine the sample record form, and invalidate the sample if vital information is missing and cannot be obtained from field personnel Remove the samples from the shipping container. If the shipping period exceeded 12 hours, verify that the sample temperature is below 10°C. If the temperature is above 10°C, invalidate the sample. Check to see that the initial and final flow rates meet the ±5 percent criterion (see Subsection 4.5.2). Invalidate the sample if the flow rates differ by more than 5 percent. If the flow rates differ by less than 5 percent, the average value will be used to determine the SO_2 concentration. Calculate the sample volume, using Equation 5-1

$$V_{std} = \left(\frac{Q_i + Q_f}{2}\right)t$$

Equation 5-1

where

V_{std} = sampling volume, std liters

Q_i = standard flow rate determined at the initiation of sampling, std liters/min

Q_f = standard flow rate determined at the completion of sampling, std liters/min

t = total sampling time, min.

2. Log the sample into the sample-receiving log book.

3. Verify the volume marked on the absorber and recorded on the sample record form against the sample volume received. If the volume received is more than 10 ml for long-term sampling (2 ml for short-term sampling) lower than the volume marked on the absorber, significant leakage has occurred. Void the sample. If valid samples have <50 ml of absorbing reagent, add distilled water to bring the volume to 50 ml and continue with the analysis. If samples have a volume of >50 ml, measure the volume with a graduated cylinder (Class A) and record the volume. Continue with the analysis. Valid short-term samples are ready for analysis. If samples are to be stored before analysis, place them in a refrigerator at 5°C

5.2 Colorimetric Analyses

The following step-by-step procedure should be used to obtain the calibration curve for the spectrophotometer and to show the relationship of the μg of SO_2 to the absorbance. Calibration Option 1 of the reference method is discussed. The procedure described is intended to be used with matched spectrophotometer cells. If an unmatched pair of cells is used, the correction listed in the reference method (Subsection 2.1.11) must be applied.

1 Prepare a dilute working sulfite-TCM solution by diluting 10 ml of the sulfite-TCM solution to 100 ml with TCM absorbing reagent.

2 Accurately pipette the indicated volumes (Table 5.1) of the sulfite-TCM solutions into six 25-ml volumetric flasks.

3. Add the indicated volumes of TCM absorbing reagent to bring the volume in each flask to 10 ml.

4. Add 1 ml of 0.6% sulfamic acid to each, and allow to stand 10 min.

5. Accurately pipet 2 ml of 0.2% formaldehyde to each.

6. Add 5 ml of PRA solution to each, and start the timer.

7. Add recently boiled and cooled distilled water to bring each flask to the 25-ml mark. Mix thoroughly.

8. Place all six flasks in a water bath for at least 30 min, but no longer than 60 min, at 20°±0.2°C (68°±0.4°F).

9. Allow at least 5 min for the spectrophotometer to warm up; adjust the zero control to bring the meter needle to infinity absorbance on the scale; standardize the light control by inserting a 1-cm cuvette filled with distilled water into the sample holder and adjusting the light control until the meter reads zero absorbance. *Note:* The wavelength scale should be checked with a standard wavelength filter traceable to the National Bureau of Standards initially and after each 160 hours of normal use or every 6 months, whichever occurs first. Use commerically available, optically matched 1-cm cuvettes.

10. Remove the six samples from the water bath, pour a portion of each (one at a time) into a cuvette, immediately read the absorbance at 548 nm, and record on the SO_2 Calibration Data Sheet (Figure 5.1). Compute the μg SO_2/flask, using the following equation:

$$\mu g\ SO_2 = V_{TCM/SO_2} \times C_{TCM/SO_2} \times D$$

Equation 5-2

where

V_{TCM/SO_2} = volume of sulfite-TCM solution used, ml

C_{TCM/SO_2} = concentration of sulfur dioxide in the working sulfite-TCM, μg SO_2/ml (from Equation 3-3)

D = dilution factor (D = 1 for the working sulfite-TCM solution; D = 0.1 for the diluted working sulfite-TCM solution).

11. Plot the absorbance (y-axis) and the μg of SO_2 (x-axis) contained in each 25-ml flask (Figure 5.2).

12. Use regression analysis to determine the slope, intercept, and correlation coefficient of the calibration curve. (Refer to Appendix J of Volume I of the Handbook[7] for discussion of linear regression analysis.) See Figure 5.3 for calculation of the linear regression parameters.

Table 5.1

Sulfite-TCM solution	*Volume of Sulfite-TCM solution, ml*	*Volume of TCM, ml*	*Approximate total[a] μg SO_2*
	0.0	*10.0*	*0.0*
Dilute working	*5.0*	*5.0*	*3.6*
Dilute working	*10.0*	*0.0*	*7.2*
Working	*2.0*	*8.0*	*14.4*
Working	*3.0*	*7.0*	*21.6*
Working	*4.0*	*6.0*	*28.8*

[a]*Based on working sulfite-TCM solution concentration of 7.20 μg SO_2/ml; the actual total μg SO_2 must be calculated by use of Equation 5-2 (shown in Step 10).*

SO_2 Calibration Data Sheet

Date 3-27-81 *Analyst* J. Smith

Instrument I D P.E. 180

Color Development Time 35 *min , Temperature* 20.1 °C

Wavelength 548 *nm µg SO_2/ml (Working sulfite-TCM solution)* 7.20 µg SO_2/ml.

$V_{TCM\ SO_2}$	D	µg SO_2	Absorbance
0	1	0.0	0.160
5	0 1	3.6	0.226
10	0.1	7.2	0.378
2	1	14.4	0.590
3	1	21.6	0.811
4	1	28.8	1.024

µg SO_2 = $V_{TCM\ SO_2}$ x $C_{TCM\ SO_2}$ x D

$V_{TCM\ SO}$ = volume of sulfite-TCM solution used, ml,

$C_{TCM\ SO_2}$ = concentration of SO_2 in the working sulfite-TCM solution, µg SO_2/ml; and

D = dilution factor

Regression analysis results.

	Measured	Criteria
Slope	0.03005	0 030±0.002 absorbance units/µg SO_2
Intercept	0.1595	<0 170 at 22°C (add 0.015 per °C above 22°C)
Correlation coefficient	0.99998	>0.998

Calibration factor B_s = $\frac{1}{slope}$ = 33.28 *µg SO_2/absorbance unit*

Figure 5.1 *SO_2 spectrophotometer calibration data.*

13. Check each new calibration curve for conformance with these criteria:

a. Slope is 0.03±0 002 absorbance units/µg SO_2. If not, repeat the calibration. If still outside the limits, restandardize the sulfite solution and check the dye.

b. The intercept is <0.17 absorbance units at 22°C (72°F) with a 1-cm optical path length, and the blank is ± 0 030 absorbance units of the regression intercept. If not, check the temperature of the water bath. If the new intercept still is outside the limits, check the chemicals from which the reagents were prepared and prepare new reagents

c. The correlation coefficient is greater than 0.998

14. File the calculations and the calibration curve in the calibration log book.

15 Determine the calibration factor, B_s (µg SO_2/absorbance units), which is the reciprocal of the slope.

5.3 Sample Analysis (24-h Sampling)

The following step-by-step procedure is to be used for analysis of field samples.

1. If no leakage occurred during sample shipment (as indicated by comparing the volume marked on the data form after sampling with the volume received), dilute the sample with distilled water to 50 ml If the volume is greater than 50 ml, measure the volume with a Class A graduated cylinder and record the volume.

2. If leakage occurred, invalidate the sample.

3. Pipette 10.0 ml of the sample into a 25-ml volumetric flask. *Note:* For shorter sampling periods (e g., 1 or 3 h), quantitatively transfer the entire 10 ml sample to increase the detection limit.

4 Delay the analysis for 20 min to allow any ozone to decompose.

5. Prepare a reagent blank by pipetting 10.0 ml of absorbing reagent into a 25-ml volumetric flask for use throughout the analytical procedure. Prepare two internal control standards containing approximately 5 and 15 µg of SO_2 and add absorbing reagent to bring the volume to 10 ml in 25-ml volumetric flasks.

6. Analyze the reagent blank and internal control standards before the first sample, after every subsequent 10th sample, and after the last sample. Each reagent blank absorbance should be within ±0.03 absorbance units of zero, and the measured value of each internal control standard must be within ± 1 µg of the true value

7 To each 25-ml flask add the following·

a. 1.0 ml of 0.6 percent sulfamic acid (allow to react for 10 min to destroy the nitrate from oxides of nitrogen).

SO_2 calibration curve
EPA pararosaniline reference method
Analyst J. Smith *Date* 3-27-81
Calibration Temperature 20.1°C
Calibration factor (B_S) 33.3
Slope^{-1} = $\frac{1}{0.30}$ = 33.3 μg SO_2/absorbance unit

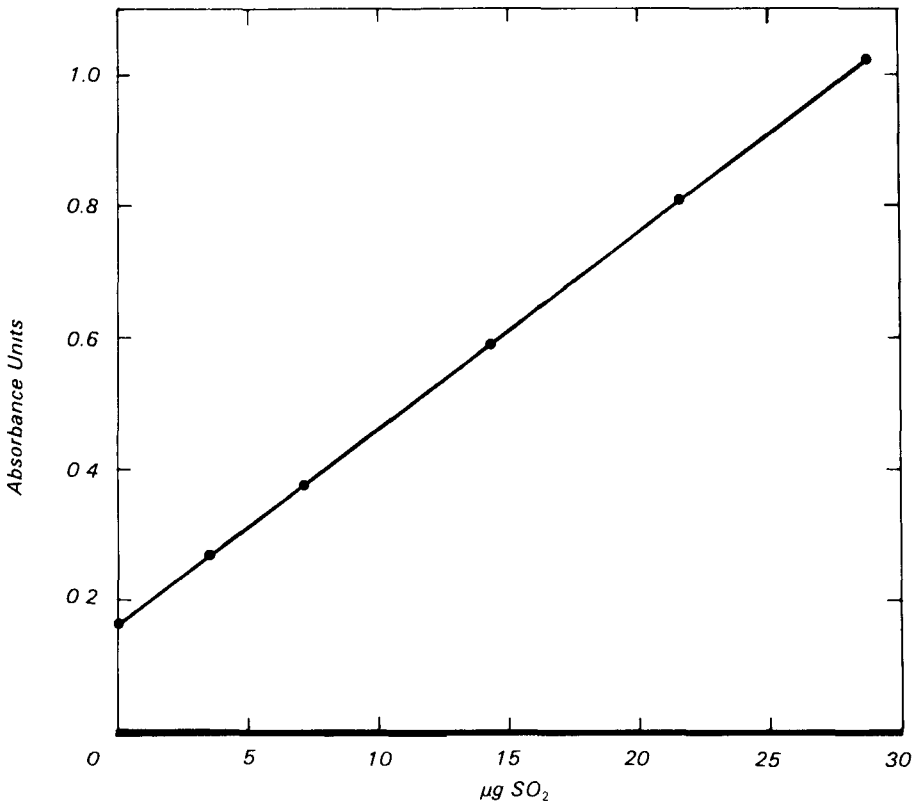


Figure 5.2 *Example of SO_2 calibration curve*

b. Pipette 2.0 ml of 0.2 percent formaldehyde solution.

c. Add 5.0 ml of PRA solution.

8. Start the laboratory timer previously set for 30 min.

9. Dilute all flasks to 25 ml with recently boiled and cooled distilled water, stopper them, and place them in a water bath at 20°±0.2°C (68±0.3°F).

10. Set the spectrophotometer wavelength to 548 nm, and allow at least 5 min for the spectrophotometer to warm up. If necessary, adjust the zero control to bring the meter needle to infinity on the absorbance scale. Standardize the light contol by inserting a cuvette filled with distilled water into the sample holder and by adjusting the light control until the meter reads zero absorbance.

11. Determine as quickly and accurately as possible, the absorbance of each sample of the internal control standard and of the reagent blank. Use distilled water, not the reagent blank, as the reference.

12. Record all absorbance units from the samples and the internal control standard on the laboratory data form. (Figures 5.4a and 5.4b.)

13. If the absorbance of the sample solution ranges between 1.0 and 2.0, the sample can be diluted 1:1 with a portion of the reagent blank and the absorbance redetermined within 5 minutes. Solutions with higher absorbances can be diluted up to sixfold with the reagent blank to obtain scale readings of less than 1.0 absorbance unit. It is recommended, however, that a smaller portion (<10 ml) of the original sample be reanalyzed (if possible) if the sample requires a dilution greater than 1:1.

14. Dispose of all reagents containing mercury by using one of the procedures described in Subsection 5.5. Until disposal, the discarded solutions can be stored in closed glass containers, and they should be left in a fume hood.

15. Immediately after their use, clean the cuvettes with isopropanol to avoid dye deposition on the cuvette walls.

16. Determine the pH of the samples in step 11. Maximum pH sensitivity is 1.6 ±0.1.[8]

17. Calculate the SO_2 concentration as follows.

$$\mu g\ SO_2/m^3 = \frac{10^3 (A - A_o) B_s}{V_R} \frac{V_b}{V_a} \times D \qquad \text{Equation 5-3}$$

10^3 = conversion of liters to m^3
A = sample absorbance
A_o = reagent blank absorbance
B_s = calibration factor, μg SO_2/absorbance unit
V_R = the sample air volume corrected to 25°C (77°F) and 760 mm Hg (29.92 in. Hg), liters,
V_a = volume of absorber solution analyzed, ml
V_b = total volume of solution in absorber, ml
D = dilution factor (if any) required to reduce sample absorbance below 1

And calculate the SO_2 concentration (ppm):

$$\text{ppm } SO_2 = \mu g\ SO_2/m^3 \times 3.82 \times 10^{-4}. \qquad \text{Equation 5-4}$$

18. If the absorbance of the blank is within ±0.03 absorbance units of the intercept and if the measured values of the internal control samples are within ±0.07 μg/ml SO_2 of the actual value, the analytical values determined for the field samples can be accepted as valid. If the reagent blank and/or the control sample falls outside the above limits, the reagent blank, the control sample, and the calibration curve should be checked by replication to verify that the above limits have been met before reanalyzing the field samples.

5.4 Quality Control Check of Analysis Procedure

It is recommended that each laboratory participate in the EPA national performance audit program as an independent quality control check on the analytical method. In this audit program, each participant receives five samples each 6 mo from the U.S. EPA Environmental Monitoring Systems Laboratory. If the results of these five analyses all fall within the acceptable range as published in the EPA survey report, the analysis procedure is considered to be in control. Otherwise, the laboratory should take corrective action and analyze a second set of samples to determine if the action taken has corrected the bias or imprecision of analytical results.

DATA FORM

For Hand Calculations

Calibration point number	*Micrograms SO_2 (x)*	*Absorbance units (y)*	x^2	xy	y^2
1	0.0	0.160	0	0	0.025600
2	3.6	0.266	12.96	0.9576	0.070756
3	7.2	0.378	51.84	2.7216	0.142884
4	14.4	0.590	207.36	8.4960	0.348100
5	21.6	0.811	466.56	17.5176	0.657721
6	28.8	1.024	829.44	29.4912	1.048576

$\Sigma x =$ 75.6 $\Sigma y =$ 3.229 Σx^2 1568.16 $\Sigma xy =$ 59.184 $\Sigma y^2 =$ 2.293637

$n =$ 6 *(number of calibration points)*

Calibration Slope, Intercept, and Correlation Coefficient. The method of least squares is used to calculate a calibration equation in the form of:

$$y = mx + b \qquad \textit{Equation 1}$$

where

y = corrected absorbance,
m = slope, absorbance units/μg SO_2,
x = micrograms of SO_2,
b = y intercept (absorbance units)

The slope (m), intercept (b), and correlation coefficient (r) are calculated as follows

$$m = \frac{n\Sigma xy - (\Sigma x)(\Sigma y)}{n\Sigma x^2 - (\Sigma x)^2} = \frac{(6)(59.184)-(75.6)(3.229)}{(6)(1568.16)-(75.6)^2} = 0.030050$$

$$b = \frac{\Sigma y - m\Sigma x}{n} = \frac{(3.229)-(0.030050)(75.6)}{(6)} = 0.1595$$

$$r = \sqrt{\frac{m(\Sigma xy - \Sigma x \Sigma y/n)}{\Sigma y^2 - (\Sigma y)^2/n}} = \sqrt{\frac{(0.030050)[(59.184)-(75.6)(3.229)/(6)]}{(2.29364)-(3.229)^2/(6)}}$$

$$= 0.99998$$

Figure 5.3. *Calculation of linear regression parameters*

The performance audit program is coordinated through the 10 EPA regional offices by the Quality Assurance Division of the Environmental Monitoring Systems Laboratory. To request further information about the program or to participate in the program, write to:

Ambient Air Audit Coordinator
Quality Assurance Division
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27709

A description of the audit material for SO_2 analysis is given in Section 2.0.10 of this Handbook.

5.5 Disposal of Mercury-Containing Solutions

The TCM absorbing solution and any reagents containing mercury compounds must be treated and disposed of by one of the two methods discussed below. Both methods remove greater than 99.99 percent of the mercury.

5.5.1 *Method for Forming an Amalgam* 1. Put the waste solution in an uncapped vessel and place it in a hood.

2. For each liter of waste solution, add approximately 10 g of sodium carbonate until neutralization has occurred (NaOH may have to be used).

3. Following neutralization, add 10 g of granular zinc or magnesium.

4. Stir the solution in a hood for 24 hours. Caution must be exercised, as hydrogen gas is evolved by this treatment process.

5. After the 24 hours of stirring, let the solution stand without further stirring to allow the mercury amalgam (solid black material) to settle to the bottom of the waste receptacle.

6. After the settling has occurred, decant and discard the supernatant liquid.

7. Quantitatively transfer the solid

Laboratory Data Log (Front)

SMELTER TOWN, UTAH
City Name 400 NORTH STREET
Site Address SO_2 NETWORK 24 HRS.
Project Time Interval

State Area Site: 46 09 000 01
Project Time Year: 02 7 76

Sampler Identification No. 016

Gas Bubbler - SO_2

Name Parameter Code: 4 2 4 0 1

Sampling Date Month	Sampling Date Day	St Hr	Conc µg/m³	Sample Number	Flow Rate cc/min Start	Flow Rate cc/min End	Flow Rate cc/min Average	Sampling Time	Air m³ Volume	Absorbance	B_s	Conc of Soln.
05	14	00	019	58	209	212	211	1440	303.8	.142	33.3	

If sulfite solutions used to prepare calibration curves, compute the SO_2 concentration in the sample

$$\mu g\ SO_2/m^3 = \frac{10^3 (A-A_o)\, B_s}{V_R} \frac{V_b}{V_a} \times D$$

A = sample absorbance
A_o = reagent blank absorbance
10^3 = conversion of l to cm³
V_R = sample volume corrected to 25°C and 760mm Hg, l
B_s = calibration factor, µg/absorbance unit
V_a = volume of absorber solution analyzed, ml
V_b = total volume of solution in absorber, ml
D = dilution factor (if any) required to reduce sample absorbance below 1

Handled in Accordance with Guidelines on Reverse Side of This Form

Joe Smith
Signature

Remarks:

Figure 5.4A Laboratory data log (front).

Preparation and Calibration	*Sample Analysis*	*Reagent Preparation*		
reagent water double-distilled and stored in a borosilicate glass vessel with vent guard	*Colorimetric analysis blank within ±0.03 absorbance calibration intercept, control sample absorbance within ±1 μg SO_2 of actual value*	*Reagent*	*Container*	*Frequency of Preparation*
		Sulfamic acid, 0.6%	*Glass stoppered*	*Before analysis*
		Formaldehyde, 0.2%	*Glass stoppered*	*Before analysis*
Absorbing reagent prepared every 6 mo, clear with 3 0 < pH < 5.0		*Working iodine, 0.1 N*	*Glass stoppered, dark*	*Before analysis*
		Stock iodine, 0.01N	*Glass stoppered, dark*	*Yearly*
24-h sampler with polypropylene tubes and closure with glass impinger, ½- and 1-h sample with with glass midget impinger	*Calibration curve for absorbance vs. μg SO_2/m^3 slope between 0 03 ±0.002 absorbance units/μg SO_2; intercept <0.17, all points within 0.04 μg SO_2/ml (1 μg SO_2) of best-fit curve*	*Sodium thiosulfate, 0.01N*	*Glass stoppered*	*Yearly*
		Stock sodium thiosulfate, 0 1N	*Glass stoppered*	*Yearly*
Check of flow-measuring device against specification.		*Working sulfite-TCM solution accurately prepared from standard solution prior to analysis, stable for 30 days at 5°C (41°F) if stored in dark glass-stoppered bottle*		
All data points within +2% of the best-fit calibration curve for flow-measuring rotameter		*Standard sulfite-ICM solution 320-400 μg SO_2/ml*		
Flow rate measured before and after each sampling period		*Pararosaniline (PRA) reagent 100% assay; stable if stored in dark glass-stoppered bottle*		
Rotameter cleaned and calibrated every 30 days of operation or every 6 mo		*Assayed PRA stock solution stored in dark glass-stoppered bottle; solution prepared if slope of calibration curve deviates from 0.03 ±0.002*		
Sample timer within ±15 min/24-h, checked every 6 mo		*Analytical balance performance within ±0.1 mg of manufacturer's specifications*		

Figure 5.4B *Laboratory data log (backside)*

material to a container and allow it to dry.

8. The solid material can be sent to a mercury reclaiming plant. It must not be discarded.

5.5.2 *Method Using Aluminum Foil Strips* 1. Put the waste solution in an uncapped vessel and place it in a hood.

2. For each liter of waste solution, add approximately 10 g of aluminum foil strips. If all the aluminum appears to be consumed and no gas is evolved, add an additional 10 g of foil. Repeat until the foil is no longer consumed and allow the gas to evolve for 24 hours.

3. Decant the supernatant liquid and discard.

4. Transfer to a storage container the elemental mercury that has settled to the bottom of the vessel.

5. The mercury can be sent to a mercury reclaiming plant. It must *not* be discarded.

Table 5.2 *Activity Matrix for Analysis of Samples*

Activity	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Verification of field record form	*All vital information obtained and verified*	*Visually inspect after each sampling period.*	*Obtain missing data or invalidate the sample.*
Flow rate check of system	*Difference in initial and final flow rates after sampling <5%*	*Repeat flow rate measurement after sampling.*	*Invalidate the sample.*
Calibration of spectrophotometer	*Each calibration curve: Slope 0.03 ±0.002 absorbance unit/μg SO_2; intercept <0.17 absorbance units; each correlation coefficient >0.998*	*Check the calibration curve after sampling*	*Repeat calibration and/or standardize the sulfite solution, and check dye; check water bath temp. and/or check chemicals used to prepare reagents; repeat reading for that point; average new and original values; replot*
Reagent blank and internal control standard	*Analysis in accordance with Subsec. 5.3; absorbance of blank within ±0.03 absorbance units of zero; measured value of each internal control standard within ±1 μg SO_2 actual value*	*Analyze a reagent blank and internal control standard before the first samples, after every subsequent 10th samples and after the last sample.*	*Take corrective action (recalibrate if necessary), and reanalyze the last 10 samples.*

6.0 Data Reduction, Validation, and Reporting

The quality control activities are summarized in Table 6.1 at the end of this section

6.1 Flow Rate Data Review

Samples should be invalidated if the difference between the initial and final flow rate is greater than 5 percent

6.2 SO_2 Data Review

The analytical data should be invalidated if any of the following conditions exist regarding SO_2 calibration.

1. Fresh reagents are not used.
2. The internal control samples were analyzed, and the results deviated by more than ± 1 μg SO_2 from the known value, but a new calibration curve was not constructed.
3. The slope of the final calibration curve was not within 0.03 ± 0.002 absorbance units/μg SO_2.
4. The intercept of the final calibration curve was not <0.17 at 22°C (72°F) with a 1-cm optical path length, and/or the blank was not within ± 0.03 of the regression intercept.
5. The correlation coefficient of the least square regression was <0.998.

6.3 Standardize Format Reporting

The standardized procedure for reporting is as follows:

1. Record the 24-h sample analytical results on the SAROAD daily data form (Figure 6.1).
2. Record the 30-min or the 1-h sample analytical results on the SAROAD hourly data form (Figure 6.2).
3. Refer to EPA-450/2-76-029, Dec. 1976, OAQPS Guidelines, AEROS Manual Series, Volume II: AEROS User's Manual, U.S. EPA Office of Air and Waste Management, Research Triangle Park, North Carolina.

24-Hour or Greater Sampling Interval

[2] Smelter Town Pollution Control
1 Agency

Smelter Town
City Name

400 North Street
Site Address

SO_2 Network — Project

24 hour — Time Interval

State		Area					Site	
4	6	0	9	0	0	0	0	1
2	3	4	5	6	7	8	9	10

Agency	Project		Time	Year		Month	
P	0	2	7	7	6	0	2
11	12	13	14	15	16	17	18

	Name PARAMETER Code	Name PARAMETER Code	Name PARAMETER Code	Name PARAMETER Code
	SO_2			
	4 2 4 0 1			
	23 24 25 26 27	37 38 39 40 41	51 52 53 54 55	65 66 67 68 69
	9 1 0 1 0			
	28 29 30 31 32	42 43 44 45 46	56 57 58 59 60	70 71 72 73 74

19	20	21	22	33	34	35	36	47	48	49	50	61	62	63	64	75	76	77	78
0	1	0	0	0	2	7	9												
0	2	0	0	0	2	2	8												
0	3																		
0	4																		
0	5																		
0	6																		
0	7																		
0	8																		
0	9																		
1	0																		
1	1																		
1	2																		
1	3																		
1	4																		
1	5																		
1	6																		
1	7																		
1	8																		
1	9																		
2	0																		
2	1																		
2	2																		
2	3																		
2	4																		
2	5																		
2	6																		
2	7																		
2	8																		
2	9																		
3	0																		
3	1																		
		DP→		4	3	2	1	4	3	2	1	4	3	2	1	4	3	2	1

Figure 6 1 SAROAD daily data form

Less Than 24-Hour Sampling Interval

1 Smelter Town
1 Agency

Smelter Town
City Name

400 North Street
Site Address

SO_2 Network
Project

ENVIRONMENTAL PROTECTION AGENCY
National Aerometric Data Bank
P.O. Box 12055
Research Triangle Park
North Carolina 27711

SO_2 — Parameter observed
Colorimetric — Method
hourly — Time interval of obs
PPM — Units of obs.

State	Area	Site
4	6	0 9 0 0 0 0 1
2	3	4 5 6 7 8 9 10

Agency	Project	Time	Year	Month
D	0 2	1	7 5	1 1
11	12 13	14	15 16	17 18

Parameter code	Method	Units	DP
4 2 4 0 1	1 4	0 7	2
23 24 25 26 27	28 29	30 31	32

Day	St	Hr	Rdg 1	Rdg 2	Rdg 3	Rdg 4	Rdg 5	Rdg 6	Rdg 7	Rdg 8	Rdg 9	Rdg 10	Rdg 11	Rdg 12
19 20	21	22	33 34 35 36	37 38 39 40	41 42 43 44	45 46 47 48	49 50 51 52	53 54 55 56	57 58 59 60	61 62 63 64	65 66 67 68	69 70 71 72	73 74 75 76	77 78 79 80
01	0	0	0000	0000	0005	0001	0001	0001	0015	0010	0005	0000	0000	0000
01	1	2	0000	0000	0000	0000	0040	0004	0003	0000	0000	0000	0000	0000

Figure 6.2 SAROAD hourly data form.

6.4 Filing the Calculations

1. Identify all of the sample calculations with the sample numbers and dates.
2. File the calculations in the laboratory data log book.

Table 6.1 *Activity Matrix for Data Reduction, Validation, and Reporting*

Activity	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Flow data	*Deviation in flow rates less than ±5%*	*Visually observe reported data*	*Void the sample*
SO_2 data	*Five conditions of Sub-sec 6.2 met*	*As above*	*As above*
Documentation and report of results	*All needed data available*	*As above*	*As above*

7.0 Maintenance

7.1 The 24-h Bubbler Train

Every 3 months or every 15 sampling periods, whichever occurs first, the following components should be replaced.

1. *Membrane filter* - Replace the membrane filter by removing the Tygon tubing from the inlet and outlet of the plastic filter holder (The filter and filter holder are disposable) Seal the new filter holder to prevent leakage by pulling the filter holder apart and coating the junction of the two halves with a thin layer of cyclohexanone and by rejoining the two halves and pressing them together until they are dry Connect the new filter in place

2 *Mist trap* - Change the trap by removing the Tygon tubing and replacing it with a clean dry trap Disassemble the trap that was removed, wash it, and allow it to dry before reassembling and using it again.

3. *Rubber septa* - Remove the old septa from the glass adapters, and replace them with new septa.

4. *Vacuum gauge* - Check the vacuum gauge against a calibrated vacuum guage or a mercury manometer. Replace the guage if it is defective. (not within ±25 mm (±1 in.) Hg).

5 *Vacuum tubing* - Replace the black vacuum tubing with a new section to minimize the possibility of leakage.

6 *Vacuum pump* - If the vacuum pump cannot provide >530 mm (>21 in) Hg vacuum at 760 mm (29.92 in.) atmospheric pressure, replace its carbon vanes or its diaphragm. At an atmospheric pressure of 760 mm, the 530 mm (21 in.) Hg vacuum provides a safety margin of 100 mm (3.9 in.) Hg vacuum

7.2 The Short-Term Sampling Train

Every 3 months or every 30 sampling periods, whichever occurs first, the following components should be serviced·

1 *Rotameters* - Disassemble and clean the rotameters with detergent, and rinse with distilled water and alcohol Recalibrate before use.

2 *Mist trap* - Clean the trap, and replace the glass wool

3 *Needle valve* - Inspect the valve for proper seating of the stem, check the valve-stem packing nut for proper tension, and clean the valve with detergent Rinse with distilled water and alcohol

4. *Vacuum pump* - Perform the same maintenance as that described in Subsection 7 1

5. *Vacuum tubing* - Perform the same maintenance as that described in Subsection 7 1

7.3 Calibration Equipment and Related Apparatus

Periodic maintenance requirements for equipment such as the mass -flow meters, soap-bubble meters, and spectrophotometers vary with the specific manufacturer. Thus, the manufacturer's recommendations should be followed as well as one's own experience.

Table 7.1 *Activity Matrix for Regular and Preventive Maintenance*

Equipment	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
24-h bubbler train	*Membrane filter, mist trap, rubber septa, and vacuum tubing replaced regularly.*	*Replace every 3 mo or after 15 sampling periods.*	*Implement maintenance actions.*
Vacuum gauge	*Readings correct within ± 25 4 mm (±1 in.) Hg*	*Check every 3 mo against calibrated vacuum gauge or Hg manometer.*	*Replace if defective.*
Vacuum pump	*Capability to provide at least 530 mm (21 in) Hg vacuum at STP.*	*Test the vacuum.*	*Replace carbon vanes or diaphragm; retest.*
Short-term sampling train	*Rotameter, mist trap needle valve, vacuum pump, and vacuum serviced regularly.*	*Clean every 3 mo or after 30 sampling periods.*	*Implement maintenance actions.*
Calibration equipment and related apparatus	*Maintained periodically according to manufacturer's recommendations.*	*Follow manufacturer's recommendations.*	*Implement maintenance actions.*

8.0 Auditing Procedure

An audit is an independent assessment of the accuracy of data. *Independence is achieved by having the audit made by an operator other than the one conducting the routine measurements and by using audit standards and equipment different from those routinely used in monitoring.*

The audit should be a true assessment of the measurement process under normal operations—that is, without any special preparation or adjustment of the system. Routine quality assurance checks conducted by the operator are necessary for obtaining and reporting good quality data, but they are not considered part of the auditing procedure.

Two types of audits are recommended herein—performance audits and system audits. Three performance audits and one system audit are detailed in Subsections 8.1 and 8.2 and summarized in Table 8.2 (at the end of this section). In addition to these audits, the precision of the entire measurement process is assessed by comparing the measurements made by collocated samplers, as described in Sections 2.0.9 and 2.1.9.

Proper implementation of an auditing program serves a twofold purpose: to ensure the integrity of the data and to assess the accuracy of the data. The technique for estimating the accuracy of the data is given in Section 2.0.8 of this volume.

8.1 Performance Audits

Performance audits conducted by another operator/analyst are quantitative evaluations of the quality of data produced by the total measurement system (sample collection, sample analysis, and data processing). The following three performance audits of individual variables are recommended:

1. Audit of flow rate for sample collection.
2. Audit of analysis process by use of reference samples (mandatory).
3. Audit of data processing. (Refer to Appendix A for auditing frequency.)

Auditing of 7 of 100 sampling periods for each site is suggested as a starting frequency for the first and third audits; frequency for the second audit is given in Subsection 8.1.2. Where one sample is collected every 6th day, one audit per month at each site is recommended; if the data are reported quarterly, this would mean auditing 3 of each 15 sampling periods. If the number of sampling periods is >15 but <50, four audits are recommended. These are the suggested starting frequencies; they should be altered if either experience or data quality indicate a need for change. For example, the frequency should be reduced if experience indicates that data are of good quality; the opposite would apply if the data were of poor quality

In a determination of the number of audits needed, it is more important to be sure that the audit sample is representative of the various conditions that may influence the data quality than to adhere to a fixed frequency. The supervisor will specify the frequencies according to mointoring requirements.

8.1.1 *Flow Rate Audit* - For 30-min, 1-h, and 24-h samples, a flow rate audit is recommended to assess the sampling collection phase of the measurement process. The audit should be performed as follows.

1. Have the regular operator prepare the sampler for sample collection as usual; this must include filling in the sample record form (Figure 4.10).
2. Have the operator compute the average sampled volume, $\overline{V}_m$, as measured by the regular flow measurement device and corrected to reference conditions (if necessary).
3. Insert the audit device in the sample inlet line and measure the flow in the usual manner at the beginning and at the end of the sampling period.
4. Calculate the average audited volume, $\overline{V}_a$, at reference conditions for the audit device ($\overline{V}_a = Q_a t$, where Q_a is the average audited flow rate in liters/minute and t is the sampling time in minutes).
5. Compute the percent difference, d (a measure of inaccuracy):

$$d = \left(\frac{\overline{V}_m - \overline{V}_a}{\overline{V}_a}\right) 100.$$

Equation 8-1

6. Record $\overline{V}_m$, $\overline{V}_a$, and d. It is recommended that the d's be plotted on the $\overline{X}$-and-R chart as illustrated in Figure 8.1. (Only the $\overline{X}$ chart is used for quality control of accuracy; the standard $\overline{X}$-and-R chart is used for convenience.) If d is greater than ±7% or if $\overline{V}_m/\overline{V}_a$ does not fall between 0.93 and 1.07, begin the troubleshooting and take corrective action before resuming the sampling. All flow rate data for the audit period is invalidated if an unexplained malfunction has occurred and resulted in errors in the flow rates.

8.1.2 *Audit of Analysis Process Using Reference Samples* - Reference (audit) samples should be included at ramdom at the recommended frequency among the samples awaiting analysis. If possible, they should not be recognizable to the analyst as reference samples. The audit procedure for the SO_2 method is as follows:

1. Prepare the audit solutions from a working sulfite-TCM solution, as described previously in Subsection 3.12 of Section 2.1.3. Prepare these audit samples independently from the standardized sulfite-TCM solution used in the routine analysis procedure. Prepare new sulfite-TCM audit samples every 30 days, and store them between 0° and 5°C.
2. Prepare the audit samples in each of the concentration ranges of 0.2 to 0.3, 0.5 to 0.6, and 0.8 to 0.9 μg SO_2/ml.* Analyze an audit sample in each of the three ranges at least once each day that samples are analyzed and at least twice per calendar quarter. The differences between the measured concentrations (μg SO_2/ml) and the audit concentrations are used to calculate the percent difference (a measure of inaccuracy) as described in Section 2.0.8. The calculation for percent difference for individual audit samples is also shown here at Item 3.
3. The agency/organization determines the percent difference (d) between the measured SO_2 concentration and the audit or known

*In the event that the absorption is plotted against the total SO_2 contained in 25 ml, the concentration ranges should be multiplied by 25. This same adjustment should be applied to all corresponding data in this section.

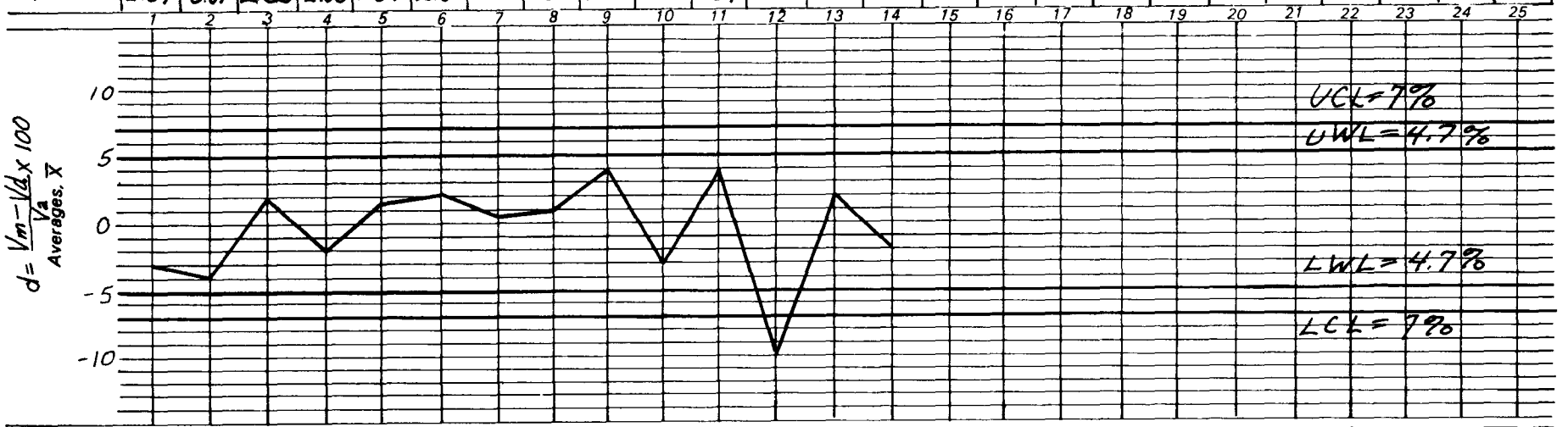
$\overline{X}$ and R Chart

Project Name: Flow Rate Audit

Measurement Performed: $d = 100(V_m - V_a)/V_a$, The Percent Difference in Measured & Audited Volumes

Measurement Units: V_m, V_a in l/min, d in %

			2-4	2-26	3-10	3-26	4-7	4-22	5-6	5-24	6-9	6-30	7-7	7-14	7-21	7-28
Measurement	Code	1	1st Quarter →						2nd Quarter →							
		2														
		3														
	Result	1	30.2	29.8	30.4	29	30.2	30	29.4	29.6	28.2	29.8	31.6	25.8	27.6	29.8
		2	31.1	31	29.7	29.6	29.8	29.3	29.2	29.3	27.1	30.6	30.2	28.8	27	30.5
		3														
Sum																
Average, $\overline{X}$																
diff, d			-2.89	-3.87	2.36	-2.03	1.34	2.39	0.68	1.02	4.06	-2.61	4.64	-10.4	2.2	-2.30



Ranges, R

Comments (Correct Action, etc.): Check Sampler Rotameter Calibration

Figure Example of an X-and-R chart audit flow rate using % D

values of concentration. The d is a measure of both the bias and the random error of the analytical phase of the SO_2 reference method. Calculate d by using Equation 8-2.

$$d = \frac{C_{SO_2}(M) - C_{SO_2}(A)}{C_{SO_2}(A)} \times 100$$

Equation 8-2

where

$C_{SO_2}(M)$ = concentration measured by the lab analyst $\mu g/ml$

$C_{SO_2}(A)$ = audit or known concentration of the audit sample, $\mu g/ml$.

The recommended control limits for the three audit sample ranges (0.2 to 0.3, 0.5 to 0.6, and 0.8 to 0.9 μg SO_2/ml) are the 90th percentile value for d based on the results of five audits (11/76, 4/77, 10/77, 4/78, and 10/78) performed by the Environmental Monitoring Systems Laboratory, USEPA, Research Triangle Park, North Carolina.[9, 10] By definition, 90 percent of the laboratory participants in the audit obtained values of d less than the values tabulated below. The control limits are expected to be exceeded by 10 percent of the laboratories to be audited, based on these five audits. The 90th percentile values and the known audit concentrations are given below for each audit concentration range.

Based on the results or these five audits, the recommended 90th percentile control limits for audit samples are ±33 percent for the 0.2 to 0.3 μg SO_2/ml concentration range and ±18 percent for both the 0.5 to 0.6 and the 0.8 to 0.9 μg SO_2/ml concentration ranges.

It is recommended that each laboratory participate in the EPA National Performance Audit program as described in Section 2.1.5, Subsection 5.4. This will serve as an independent audit of the analysis technique.

8.1.3 *Data Processing Audit* - The data processing audit is most conveniently performed soon after the original calculations have been completed, so that corrections can be made immediately and additional explanatory data can be retrieved from field personnel when necessary. The procedural steps are as follows.

1. The audit must be performed by an individual other than the one who originally reduced the data. The check should start with the raw data and continue through the recording of the concentration (μg SO_2/m^3) on the SAROAD form.
2. If the mass concentration of SO_2 computed by an audit does not agree with the original or indicated value within round-off error, the calculations for all samples collected since the previous audit should be checked and corrected. The audit value is always reported as the correct value, under the assumption that the audit should be checked if a discrepancy exists and corrected if necessary.
3. The audit and the original values and the percentage difference should be recorded in the laboratory log book and reported to the supervisor.

8.2 System Audit

A system audit is an onsite inspection and review of the quality assurance system used for the total measurement system (sample collection, sample analysis, data processing, etc.). A system audit is a qualitative appraisal of system quality.

A system audit should be conducted at the startup of a new monitoring system and thereafter as appropriate to ascertain significant changes in system operations. A checklist for use in a system audit is provided in Figure 8.2. These questions should be reviewed for their applicability to the particular local, State, or Federal agency being audited.

0.2 to 0.3 μg SO_2/ml

Audit date	*Known audit concentration μg SO_2/ml*		*90th percentile for d, %*
11/76	*0.259*		*33*
4/77	*0.289*		*32*
10/77	*0.338*		*35*

0.5 to 0.6 μg SO_2/ml

Audit date	*Known audit concentration μg SO_2/ml*		*90th percentile for d, %*
11/76	*0.617*		*24*
4/77	*0.688*		*17*
10/77	*0.562*		*18*
10/77	*0.562*	*duplicates*	*17*
10/78	*0.533*		*18*

0.8 to 0.9 μg SO_2/ml

Audit date	*Known audit concentration μg SO_2/ml*	*90th percentile for d, %*
11/76	*0.895*	*18*
4/77	*0.930*	*23*
10/77	*1.07*	*16*
4/78	*0.755*	*17*
10/78	*0.757*	*17*

1. What type of manual sampler is used for SO_2 collection?
   (a) RAC (b) 5-port (c) 2-port (d) other _____
2. Is a straight tube impinger used in the polypropylene sampling tube? yes
3. Is sample probe made of accepted material? Teflon® _____, Glass ✓
4. Is the probe (and manifold) located to prevent moisture condensation when sampling in humid conditions? yes
5. What method of analysis is used? Tolaval Rositer Is a copy available? yes (Method should be from 40 CFR 50, July 1, 1982, as amended 47 FR 54896, December 6, 1982 and 48 FR 17355, April 12, 1983
6. What quality of reagents is used to make up the chemicals for the SO_2 analysis? ACS reagent grade
   (They should be reagent grade or better
7. Is the sampling train routinely checked for leaks? yes
   How often? (a) Once a week (b) Once a month (c) Once a quarter (d) other each sampling period
8. What calibration check procedure is used for flow measuring device used in the field? Bubble meter see Sect. 2.1.2 Vol II
   Is a written copy available? yes
9. Are sampling flow rates determined before and after each sampling period? yes Is there an established procedure for discarding needles that are not within flow rate limits initially? yes If so, what are the limits? 180-220 ml/min (Any needle outside of 180 to 200 cm^3/min should be discarded for 24-h samples) Is the absorbing solution maintained at 15° ±10°C? yes Are samples voided? yes Do initial and final flow rates agree within ±5%? yes, voided (Void sample if they are not.)
10. Have calibration curves been made, and are they available? yes Is the calibration history of the analyses in a bound (or other type) of notebook, and is it readily available? yes
    (All laboratories must keep a bound notebook as a permanent record of the calibration history that indicates when the curves were made and what points were used to make them.)
11. Are collected samples shipped from the field to the laboratory in containers that prevent crushing, spilling, etc., and maintained at a temperature of 5°± 5°C? yes
12. How many days were there between sampling and analysis? 5 days (Commonly it is approximately 12 days, less than 12 is very good, but more than 12 may cause problems in analysis.)
13. Are samples stored in the dark until they are analyzed? yes At what temperature are the samples stored? 4 °C
14. What calculations were performed to obtain the final SO_2 concentration? see Section 2.1.5 Vol II
    (If possible, show the completed calculations.)
15. How were discrepancies in the data treated? _____
    _____ (There should be a format for taking care of data discrepancies.)
16. Are the data reported quarterly? yes If not, how often? _____

Figure 8.2 *Checklist for use by auditor for SO_2 method*

Table 8.1 *Activity Matrix for Auditing Procedure*

Audit	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Flow rate	$0.93 \leq \frac{V_m}{V_a} \leq 1.07$, where V_m = routinely measured sample volume, and V_a = audited volume	Once per 14 days of sampling or 1/mo, whichever is greater; calibrated flow measuring device.	Take corrective action before resuming sampling action noted on $\bar{X}$-and-R chart.
Audit of analysis process using audit samples	The value of d should be within ±33% for 0.2 to 0.3 μg SO_2/ml concentration range, and within ±18% for both the 0.5 to 0.6 and 0.8 to 0.9 μg SO_2/ml concentration ranges (Subsec. 8.1.2).	Analyze an audit sample in each of the three concentration ranges at least once each day and at least twice per calendar quarter that samples are analyzed (Subsec. 8.1.2).	Check calibration curve, if necessary; check a new reference sample, and if acceptable, resume analysis; calculate data accuracy per Sec. 2.0.8.
Data processing	The reported value should agree with the audited value within round-off error.	Once per 14 samples or 1/mo, whichever is greater; independent calcualtions from raw data to final recorded data.	Check and corret calculations for all samples collected since previous audit.
System audit	Method is described in this section of Handbook.	At the beginning of a new monitoring system, and periodically as appropriate; observation of procedures and use of a checklist.	Initiate improved methods and/or training programs.

9.0 Assessment of Monitoring Data for Precision and Accuracy

9.1 Precision

Collocated samplers should be used to assess the precision of the SO_2 Reference Method data. For each monitoring network, an additional sampler should be collocated from at least one site (two sites are required for SLAMS). A site with the highest expected geometric mean should be selected. The two samplers should be located at the same elevation and within 4 m of each other One of the two samplers should be identified as the one for normal routine monitoring, and the other as the duplicate sampler. The calibration, sampling, and analysis must be the same for both collocated samplers and for all other samplers in the network, and the collocated samplers must be operated when the routine samplers are operated.

The differences in concentrations ($\mu g/m^3$) recorded between the routine and the duplicate samplers are used to calculate precision (as described in Section 2.0.8 of this Handbook).

Based on a series of tests under well-controlled conditions in an EPA laboratory, the mean and standard deviations of SO_2 concentrations for several samples collected simultaneously by five sampling trains using a common manifold are given in the first two columns of Table 9 1 These results indicate that the standard deviation (s) is dependent on the average SO_2 concentrations ($\overline{X}$) for the five trains. In the third column of Table 9.1, the relative standard deviation (RSD, or the coefficient of variation) is computed and given as RSD = $100s/\overline{X}$. Columns 4 and 5 were obtained by multiplying the values in columns 2 and 3 by $3\sqrt{2}$. These values are the expected agreements between each two collocated samplers on the same manifold under well-controlled conditions, and they estimate the 3δ-control limits that correspond to values that should include about 99.7 percent of the differences between the two sample values under "ideal" laboratory conditions. The 3δ limits [expressed as percentages of the average concentration ($\overline{X}$) values in the last column of Table 9.1] are plotted in Figure 9.1. Values read from the smooth curve drawn through the data points with a minimum near 365 μg SO_2/m^3 would be the recommended 3σ limits under the *best* conditions of sampling and analysis.

Actual field data for collocated samplers show a trend similar to that in Figure 9.1; however, the 3σ limits are much larger. For concentrations >75 μg SO_2/m^3, the 3σ limits of agreement are about 45 percent of the average concentration; for low concentrations these limits often exceed 100 percent.

Based *on experimental data in Table 9.1 and on the actual field test data, poor agreement may be expected between collocated samplers when measured concentrations are <75 μg SO_2/m^3.*

9.2 Accuracy

The accuracy of the pararosaniline method for measurement of SO_2 is assessed as described in Section 2.1.8, Auditing Procedure. The accuracy of a single instrument is calculated as shown in Section 2.0.8 and 2.1.8 of this volume of the Handbook.

Table 9.1 *Experimental Data and Expected Agreement Between Two Collocated SO_2 Sampling Trains on a Common Manifold Under Well-Controlled Conditions*

Experimental data[a]			*Expected agreement between collocated (two) sampling trains*[b] *3σ-control limits*	
Average ($\overline{X}$), μg SO_2/m^3	*Standard deviation (s), μg SO_2/m^3*	*Relative standard deviation ($100s/\overline{X}$)*	*μg SO_2/m^3*	*Percentage of average concentration*
16.7	2.53	15.1	10.7	64
35.6	4.52	12.7	19.2	54
37.8	3.13	8 3	13.3	35
71 2	4.54	6 4	19.3	27
72.4	1.17	1 6	5.0	7
73.9	3.43	4.6	14.6	20
177	5.81	3.3	24.6	14
201	3.37	1.7	14.3	7
344	2 61	0.8	11.1	3
684	17.8	2 6	75.5	11
694	27 1	3.9	115	17
927	44.9	4.8	190	20

[a]*Based on 24-h samples obtained by one analyst using five trains on a common manifold. (Fuerst, R.G. Effect of Temperature on Stability of Sulfur Dioxide Samples. Unpublished research by the Environmental Monitoring and Support Laboratory, Research Triangle Park, N.C., March 1976).*

[b]*Results in columns 4 and 5 (calculated by multiplying the results in columns 2 and 3, respectively by $3\sqrt{2}$) were plotted as an eye-fitted smooth curve (Figure 9-1) to provide 3σ control limits which represent the best agreement that might be expected for collocated samplers using the SO_2 Reference Method.*

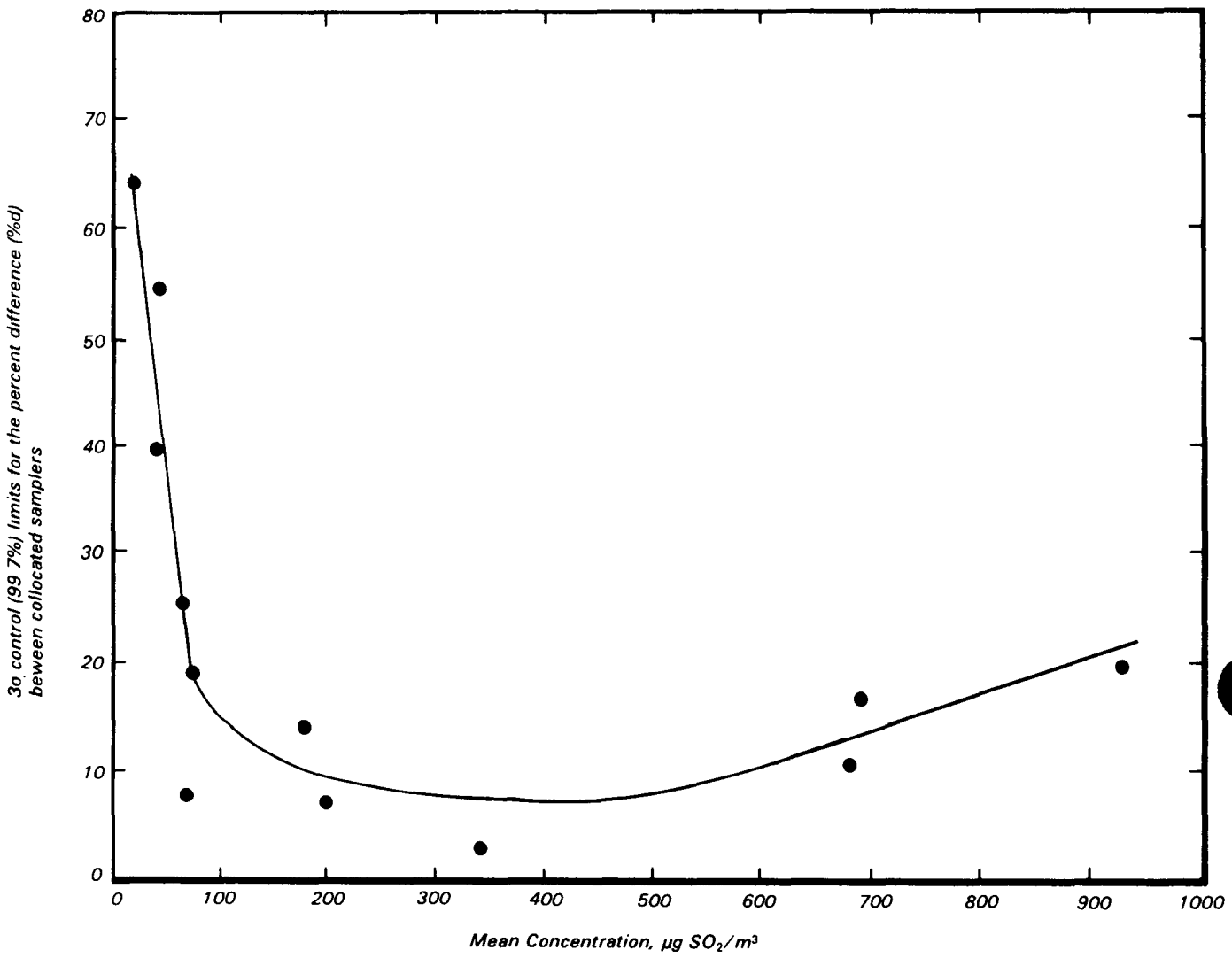


Figure 9.1 *Agreement between collocated (two) SO_2 sampling trains under well-controlled conditions (based on laboratory experimental data in Table 9.1).*

10.0 Recommended Standards for Establishing Traceability

Two considerations are essential to achieving data of the desired quality: (1) the measurement process must be in a state of statistical control at the time of the measurement, and (2) when the systematic errors are combined with the random variation (errors of measurement) the result must be a suitably small uncertainty. Evidence in support of good quality data is acquired by performing quality control checks and independent audits of the measurement process, documenting these data, and using materials, instruments, and measurement procedures that can be traced to an appropriate standard of reference

Data must be routinely obtained by repeat measurements of standard reference samples and primary, secondary, and/or working standards; and a condition of process control must be established. The working calibration standards should be traceable to standards of higher accuracy, such as those presented here.

1. Class-S weights (NBS specifications) are recommended for the analytical balance calibration. (See Section 2 1 2 for details on balance calibration checks)

2. Sulfur dioxide permeation tubes should be traceable to NBS Standard Reference Materials, Numbers 1625-1627 [11] (See Section 2 1 11, Subsection 10.3, for details on calibration using SO_2 permeation tubes.)

3. Reagents should be at least American Chemical Society (ACS) reagent-grade chemicals. Such reagents have been certified to contain impurities in concentrations below the specifications of the Committee of Analytical Reagents of the ACS. Each reagent bottle is identified by ACS with a batch number. Potassium iodate reagent must be of primary standard quality.

4 The complete absorbance scale should be checked with a calibrated set of NBS filters (SRM's 2101-2105[11]) periodically and anytime a control sample cannot be measured within the control limit assigned to it. (See Section 2.1.5 for details of spectrophotometer calibration)

5. The spectrophotometer should be checked for proper wavelength calibration throughout the range of the instrument. A Didymium Glass filter* may be used. This filter has five well-defined absorbance maxima between 400 and 900 mm. The known peak maximum at 585 mm should agree within ± 5 mm of the measured peak maximum or remedial action should be taken.

6. All calibrations of flow measurement devices are directly traceable to primary displacement methods.

*Available from Arthur H Thomas Company (Philadelphia, Pennsylvania)

11.0 Reference Method

Appendix A—Reference Method for the Determination of Sulfur Dioxide in the Atmosphere (Paraosaniline Method)

[Appendix A revised by 47 FR 54899, December 6, 1982]

1.0 Applicability

1.1 This method provides a measurement of the concentration of sulfur dioxide (SO_2) in ambient air for determining compliance with the primary and secondary national ambient air quality standards for sulfur oxides (sulfur dioxide) as specified in § 50.4 and § 50.5 of this chapter. The method is applicable to the measurement of ambient SO_2 concentrations using sampling periods ranging from 30 minutes to 24 hours. Additional quality assurance procedures and guidance are provided in Part 58, Appendixes A and B, of this chapter and in references 1 and 2.

2.0 Principle.

2.1 A measured volume of air is bubbled through a solution of 0.04 M potassium tetrachloromercurate (TCM). The SO_2 present in the air stream reacts with the TCM solution to form a stable monochlorosulfonatomercurate(3) complex. Once formed, this complex resists air oxidation (4, 5) and is stable in the presence of strong oxidants such as ozone and oxides of nitrogen. During subsequent analysis, the complex is reacted with acid-bleached pararosaniline dye and formaldehyde to form an intensely colored pararosaniline methyl sulfonic acid(6). The optical density of this species is determined spectrophotometrically at 548 nm and is directly related to the amount of SO_2 collected. The total volume of air sampled, corrected to EPA reference conditions (25°C, 760 mm Hg [101 kPa]), is determined from the measured flow rate and the sampling time. The concentration of SO_2 in the ambient air is computed and expressed in micrograms per standard cubic meter (ug/std m^3).

*40 CFR 50, July 1, 1982, as amended 47 FR 54896, December 6, 1982 and 48 FR 17355, April 22, 1983.

3.0 Range.

3.1 The lower limit of detection of SO_2 in 10 mL of TCM is 0.75 μg (based on collaborative test results) (7). This represents a concentration of 25 μg SO_2/m^3 (0.01 ppm) in an air sample of 30 standard liters (short-term sampling) and a concentration of 13 μg SO_2/m^3 (0.005 ppm) in an air sample of 288 standard liters (long-term sampling). Concentrations less than 25 μg SO_2/m^3 can be measured by sampling larger volumes of ambient air; however, the collection efficiency falls off rapidly at low concentrations (8.9). Beer's law is adhered to up to 34 μg of SO_2 in 25 mL of final solution. This upper limit of the analysis range represents a concentration of 1.130 μg SO_2/m^3 (0.43 ppm) in an air sample of 30 standard liters and a concentration of 590 μg SO_2/m^3 (0.23 ppm) in an air sample of 288 standard liters. Higher concentrations can be measured by collecting a smaller volume of air, by increasing the volume of absorbing solution, or by diluting a suitable portion of the collected sample with absorbing solution prior to analysis. [Corrected by 48 FR 17355, April 22, 1983]

4.0 Interferences.

4.1 The effects of the principal potential interferences have been minimized or eliminated in the following manner: Nitrogen oxides by the addition of sulfamic acid (10, 11) heavy metals by the addition of ethylenediamine tetracetic acid disodium salt (EDTA) and phosphoric acid. (10, 12) and ozone by time delay (10). Up to 60 μg Fe (III), 22 μg V (V), 10 μg Cu (II), 10 μg Mn (II), and 10μg Cr (III) in 10 mL absorbing reagent can be tolerated in the procedure (10). No significant interference has been encountered with 2.3 μg NH_3 (13).

5.0 Precision and Accuracy.

5.1 The precision of the analysis is 4.6 percent (at the 95 percent confidence level) based on the analysis of standard sulfite samples (10).

5.2 Collaborative test results (14) based on the analysis of synthetic test atmospheres (SO_2 in scrubbed air) using the 24-hour sampling procedure and the sulfite-TCM calibration procedure show that:

- The replication error varies linearly with concentration from ±2.5 $\mu g/m^3$ at concentrations of 100 $\mu g/m^3$ to ±7 $\mu g/m^3$ at concentrations of 400 $\mu g/m^3$.
- The day-to-day variability within an individual laboratory (repeatability) varies linearly with concentration from ±18.1 $\mu g/m^3$ at levels of 100 $\mu g/m^3$ to ±50.9 $\mu g/m^3$ at levels of 400 $\mu g/m^3$.
- The day-to-day variability between two or more laboratories (reproducibility) varies linearly with concentration from ±36.9 $\mu g/m^3$ at levels of 100 $\mu g/m^3$ to ±103.5 $\mu g/m^3$ at levels of 400 $\mu g/m^3$.
- The method has a concentration dependent bias which becomes significant at the 95 percent confidence level at the high concentration level. Observed values tend to be lower than the expected SO_2 concentration level.

6.0 Stability.

6.1 By sampling in a controlled temperature environment of 15° ±10°C, greater than 98.9 percent of the SO_2—TCM complex is retained at the completion of sampling (15). If kept at 5°C following the completion of sampling, the collected sample has been found to be stable for up to 30 days (10). The presence of EDTA enhances the stability of SO_2 in the TCM solution and the rate of decay is independent of the concentration of SO_2 (16).

7.0 Apparatus.

7.1 *Sampling.*

7.1.1 Sample probe: A sample probe meeting the requirements of Section 7 of 40 CFR Part 58, Appendix E (Teflon® or glass with residence time less than 20 sec.) is used to transport ambient air to the sampling train location. The end of the probe should be designed or oriented to preclude the sampling of precipitation, large particles, etc. A suitable probe can be constructed from Teflon® tubing connected to an inverted funnel.

7.1.2 Absorber—short-term sampling: An all glass midget impinger having a solution capacity of 30 mL and a stem clearance of 4±1 mm from the bottom of the vessel is used for sampling periods of 30 minutes and 1 hour (or any period considerably less than 24 hours). Such an impinger is shown in Figure 1. These impingers are commercially available from distributors such as Ace Glass, Incorporated.

7.1.3 Absorber—24-hour sampling: A polypropylene tube 32 mm in diameter and 164 mm long (available from Bel Art Products, Pequammock, NJ) is used as the absorber. The cap of the absorber must be a polypropylene cap with two ports (rubber stoppers are unacceptable because the absorbing reagent can react with the stopper to yield erroneously high SO_2 concentrations). A glass impinger stem, 6 mm in diameter and 158 mm long, is inserted into one port of the absorber cap. The tip of the stem is tapered to a small diameter orifice (0.4±0.1 mm) such that a No. 79 jeweler's drill bit will pass through the opening but a No. 78 drill bit will not. Clearance from the bottom of the absorber to the tip of the stem must be 6±2 mm. Glass stems can be fabricated by any reputable glass blower or can be obtained from a scientific supply firm. Upon receipt, the orifice test should be performed to verify the orifice size. The 50 mL volume level should be permanently marked on the absorber. The assembled absorber is shown in Figure 2.

7.1.4 Moisture trap: A moisture trap constructed of a glass trap as shown in Figure 1 or a polypropylene tube as shown in Figure 2 is placed between the absorber tube and flow control device to prevent entrained liquid from reaching the flow control device. The tube is packed with indicating silica gel as shown in Figure 2. Glass wool may be substituted for silica gel when collecting short-term samples (1 hour or less) as shown in Figure 1, or for long term (24 hour) samples if flow changes are not routinely encountered.

7.1.5 Cap seals: The absorber and moisture trap caps must seal securely to prevent leaks during use. Heat-shrink material as shown in Figure 2 can be used to retain the cap seals if there is any chance of the caps coming loose during sampling, shipment, or storage.

7.1.6 Flow control device: A calibrated rotameter and needle valve combination capable of maintaining and measuring air flow to within ±2 percent is suitable for short-term sampling but may not be used for long-term sampling. A critical orifice can be used for regulating flow rate for both long-term and short-term sampling. A 22-gauge hypodermic needle 25 mm long may be used as a critical orifice to yield a flow rate of approximately 1 L/min for a 30-minute sampling period. When sampling for 1 hour, a 23-gauge hypodermic needle 16 mm in length will provide a flow rate of approximately 0.5 L/min. Flow control for a 24-hour sample may be provide by a 27-gauge hypodermic needle critical orifice that is 9.5 mm in length. The flow rate should be in the range of 0.18 to 0.22 L/min.

7.1.7 Flow measurement device: Device calibrated as specified in 9.4.1 and used to measure sample flow rate at the monitoring site.

7.1.8 Membrane particle filter: A membrane filter of 0.8 to 2 μm porosity is used to protect the flow controller from particles during long-term sampling. This item is optional for short-term sampling.

7.1.9 Vacuum pump: A vacuum pump equipped with a vacuum gauge and capable of maintaining at least 70 kPa (0.7 atm) vacuum differential across the flow control device at the specified flow rate is required for sampling.

7.1.10 Temperature control device: The temperature of the absorbing solution during sampling must be maintained at 15° ± 10°C. As soon as possible following sampling and until analysis, the temperature of the collected sample must be maintained at 5° ± 5°C. Where an extended period of time may elapse before the collected sample can be moved to the lower storage temperature, a collection temperature near the lower limit of the 15 ± 10°C range should be used to minimize losses during this period. Thermoelectric coolers specifically designed for this temperature control are available commercially and normally operate in the range of 5° to 15°C. Small refrigerators can be modified to provide the required temperature control; however, inlet lines must be insulated from the lower temperatures to prevent condensation when sampling under humid conditions. A small heating pad may be necessary when sampling at low temperatures

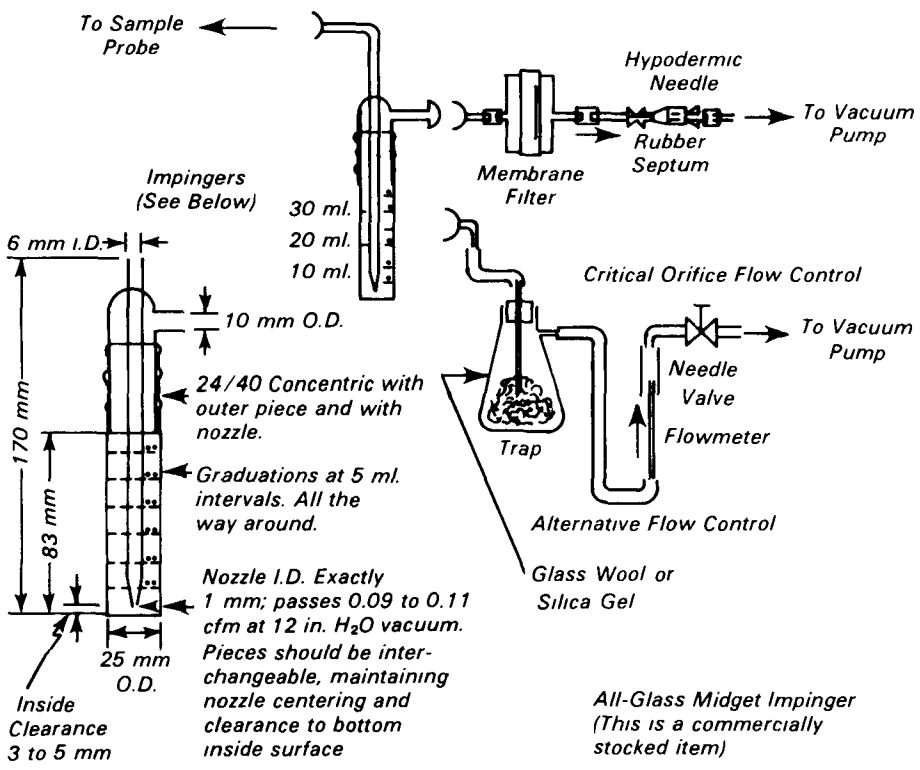


Figure 1. Short term sampling train.

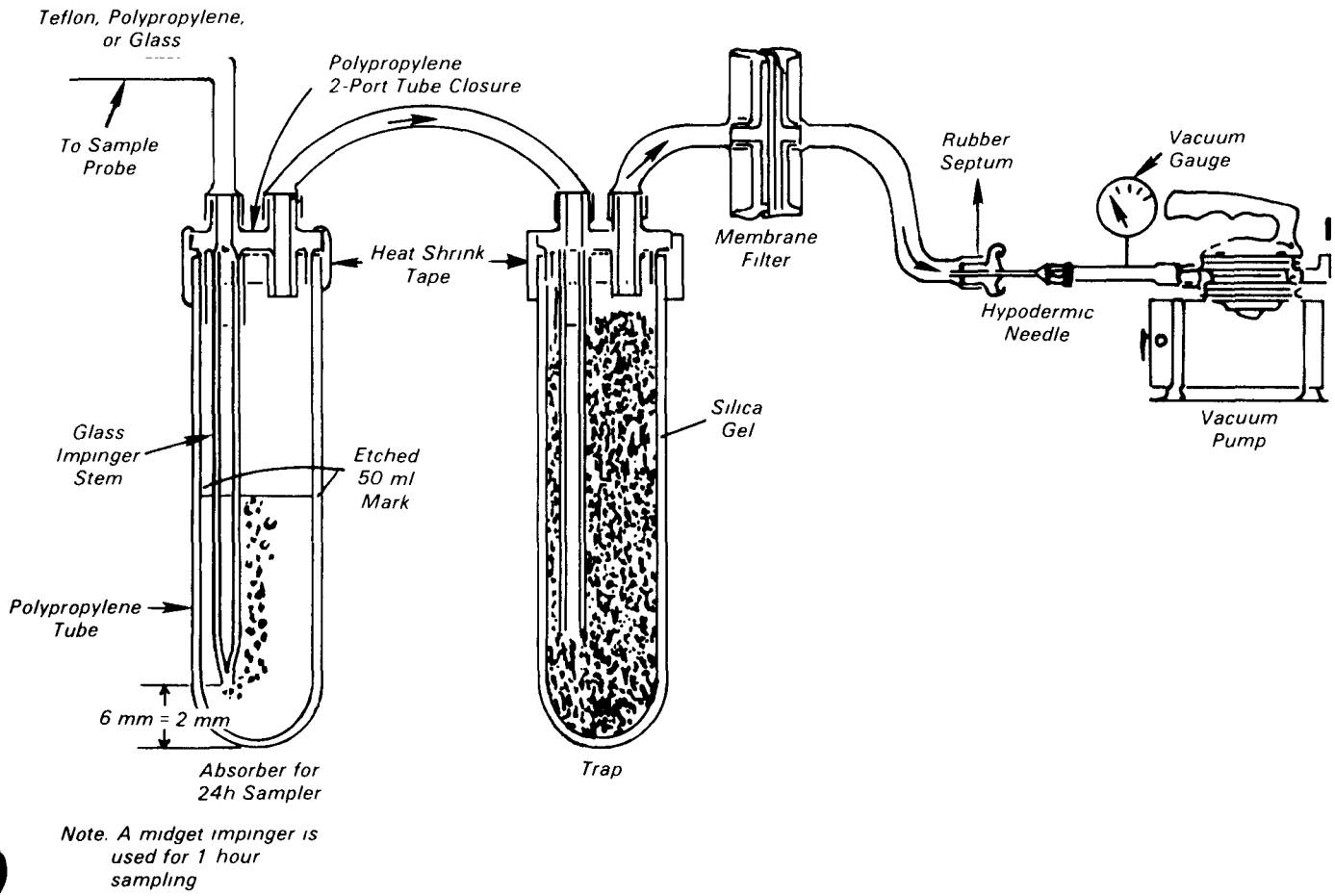


Figure 2. 24-Hour sampling system

(<7°C) to prevent the absorbing solution from freezing (17).

7.1.11 Sampling train container: The absorbing solution must be shielded from light during and after sampling. Most commercially available sampler trains are enclosed in a light-proof box.

7.1.12 Timer: A timer is recommended to initiate and to stop sampling for the 24-hour period. The timer is not a required piece of equipment; however, without the timer a technician would be required to start and stop the sampling manually. An elapsed time meter is also recommended to determine the duration of the sampling period.

7.2 *Shipping.*

7.2.1 Shipping container: A shipping container that can maintain a temperature of 5° ± 5°C is used for transporting the sample from the collection site to the analytical laboratory. Ice coolers or refrigerated shipping containers have been found to be satisfactory. The use of eutectic cold packs instead of ice will give a more stable temperature control. Such equipment is available from Cole-Parmer Company, 7425 North Oak Park Avenue, Chicago, IL 60648.

7.3 *Analysis.*

7.3.1 Spectrophotometer: A spectrophotometer suitable for measurement of absorbances at 548 nm with an effective spectral bandwidth of less than 15 nm is required for analysis If the spectrophotometer reads out in transmittance, convert to absorbance as follows.

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

where

A = Absorbance, and

T = transmittance ($0<T<1$).

A standard wavelength filter traceable to the National Bureau of Standards is used to verify the wavelength calibration according to the procedure enclosed with the filter. The wavelength calibration must be verified upon initial receipt of the instrument and after each 160 hours of normal use or every 6 months, whichever occurs first.

7.3.2 Spectrophotometer cells: A set of 1-cm path length cells suitable for use in the visible region is used during analysis. If the cells are unmatched, a matching correction factor must be determined according to Section 10.1.

7.3.3 Temperature control device: The color development step during analysis must be conducted in an environment that is in the range of 20° to 30°C and controlled to ±1°C. Both calibration and sample analysis must be performed under identical conditions (within 1°C). Adequate temperature control may be obtained by means of constant temperature baths, water baths with manual temperature control, or temperature controlled rooms.

7.3.4 Glassware: Class A volumetric glassware of various capacities is required for preparing and standardizing reagents and standards and for dispensing solutions during analysis. These included pipets, volumetric flasks, and burets.

7.3.5 TCM waste receptacle: A glass waste receptacle is required for the

storage of spent TCM solution. This vessel should be stoppered and stored in a hood at all times

8.0 Reagents.

8.1 *Sampling*

8.1.1 Distilled water: Purity of distilled water must be verified by the following procedure (18).

- Place 0.20 mL of potassium permanganate solution (0.316 g/L), 500 mL of distilled water, and 1mL of concentrated sulfuric acid in a chemically resistant glass bottle, stopper the bottle, and allow to stand.
- If the permanganate color (pink) does not disappear completely after a period of 1 hour at room temperature, the water is suitable for use.
- If the permanganate color does disappear, the water can be purified by redistilling with one crystal each of barium hydroxide and potassium permanganate in an all glass still.

8.1.2 Absorbing reagent (0.04 M potassium tetrachloromercurate [TCM]): Dissolve 10.86 g mercuric chloride, 0.066 g EDTA, and 6.0 g potassium chloride in distilled water and dilute to volume with distilled water in a 1,000-mL volumetric flask. (Caution: Mercuric chloride is highly poisonous. If spilled on skin, flush with water immediately.) The pH of this reagent should be between 3.0 and 5.0 (10). Check the pH of the absorbing solution by using pH indicating paper or a pH meter. If the pH of the solution is not between 3.0 and 5.0, dispose of the solution according to one of the disposal techniques described in Section 13.0. The absorbing reagent is normally stable for 6 months. If a precipitate forms, dispose of the reagent according to one of the procedures described in Section 13.0.

8.2 *Analysis.*

8.2.1 Sulfamic acid (0.6%): Dissolve 0.6 g sulfamic acid in 100 mL distilled water. Prepare fresh daily.

8.2.2 Formaldehyde (0.2%): Dilute 5 mL formaldehyde solution (36 to 38 percent) to 1,000 mL with distilled water. Prepare fresh daily.

8.2.3 Stock iodine solution (0.1N): Place 12.7 g resublimed iodine in a 250-mL beaker and add 40 g potassium iodide and 25 mL water. Stir until dissolved, transfer to a 1,000 mL volumetric flask and dilute to volume with distilled water.

8.2.4 Iodine solution (0.01N): Prepare approximately 0.01 N iodine solution by diluting 50 mL of stock iodine solution (Section 8.2.3) to 500 mL with distilled water.

8.2.5 Starch indicator solution Triturate 0.4 g soluble starch and 0.002 g mercuric iodide (preservative) with enough distilled water to form a paste. Add the paste slowly to 200 mL of boiling distilled water and continue boiling until clear. Cool and transfer the solution to a glass stoppered bottle.

8.2.6 1 N hydrochloric acid: Slowly and while stirring, add 86 mL of concentrated hydrochloric acid to 500 mL of distilled water.

Allow to cool and dilute to 1,000 ml with distilled water.

8.2.7 Potassium iodate solution: Accurately weigh to the nearest 0.1 mg, 1.5 g (record weight) of primary standard grade potassium iodate that has been previously dried at 180°C for at least 3 hours and cooled in a dessicator. Dissolve, then dilute to volume in a 500-mL volumetric flask with distilled water.

8.2.8 Stock sodium thiosulfate solution (0.1N): Prepare a stock solution by dissolving 25 g sodium thiosulfate ($Na_2S_2O_3 \cdot 5\ H_2O$) in 1,000 mL freshly boiled, cooled, distilled water and adding 0.1 g sodium carbonate to the solution. Allow the solution to stand at least 1 day before standardizing. To standardize, accurately pipet 50 mL of potassium iodate solution (Section 8.2.7) into a 500-mL iodine flask and add 2.0 g of potassium iodide and 10 mL of 1 N HCl. Stopper the flask and allow to stand for 5 minutes. Titrate the solution with stock sodium thiosulfate solution (Section 8.2.8) to a pale yellow color. Add 5 mL of starch solution (Section 8.2.5) and titrate until the blue color just disappears. Calculate the normality (N_s) of the stock sodium thiosulfate solution as follows:

$$N_s = \frac{W}{M} \times 2.80 \qquad (2)$$

where:

M = volume of thiosulfate required in mL, and

W = weight of potassium iodate in g (recorded weight in Section 8.2.7)s and

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

[Corrected by 48 FR 17355, April 22, 1983].

8.2.9 Working sodium thiosulfate titrant (0.01 N): Accurately pipet 100 mL of stock sodium thiosulfate solution (Section 8.2.8) into a 1,000-mL volumetric flask and dilute to volume with freshly boiled, cooled, distilled water. Calculate the normality of the working sodium thiosulfate titrant (N_T) as follows:

$$N_T = N_s \times 0.100 \qquad (3)$$

8.2.10 Standardized sulfite solution for the preparation of working sulfite-TCM solution: Dissolve 0.30 g sodium metabisulfite ($Na_2S_2O_5$) or 0.40 g sodium sulfite (Na_2SO_3) in 500 mL of recently boiled, cooled, distilled water. (Sulfite solution is unstable, it is therefore important to use water of the highest purity to minimize this instability.) This solution contains the equivalent of 320 to 400 $\mu g\ SO_2$/mL. The actual concentration of the solution is determined by adding excess iodine and back-titrating with standard sodium thiosulfate solution. To back-titrate, pipet 50 mL of the 0.01 N iodine solution (Section 8.2.4) into each of two 500-mL iodine flasks (A and B). To flask A (blank) add 25 mL distilled water, and to flask B (sample) pipet 25 mL sulfite solution. Stopper the flasks and allow to stand for 5 minutes. Prepare the working sulfite-TCM solution (Section 8 2.11) immediately prior to adding the iodine solution to the flasks. Using a buret containing standardized 0.01N thiosulfate titrant (Section 8.2.9), titrate the solution in each flask to a pale yellow color. Then add 5 mL starch solution (Section 8.2.5) and continue the titration until the blue color just disappears.

8.2.11 Working sulfite-TCM solution: Accurately pipet 5 mL of the standard sulfite solution (Section 8.2.10) into a 250-mL volumetric flask and dilute to volume with 0 04 M TCM. Calculate the concentration of sulfur dioxide in the working solution as follows:

$$C_{TCM/SO_2}\ (\mu g\ SO_2/mL) = \frac{(A - B)(N_T)(32{,}000)}{25} \times 0.02 \qquad (4)$$

where:

A = volume of thiosulfate titrant required for the blank, mL;

B = volume of thiosulfate titrant required for the sample, mL;
N_T = normality of the thiosulfate titrant, from equation (3),
32,000 = milliequivalent weight of SO_2, μg,
25 = volume of standard sulfite solution, mL; and
0.02 = dilution factor.

This solution is stable for 30 days if kept at 5°C (16). If not kept at 5°C, prepare fresh daily
[Corrected by 48 FR 17355, April 22, 1983]

8.2.12 Purified pararosaniline (PRA) stock solution (0.2% nominal):

8.2.12.1 Dye specifications—

- The dye must have a maximum absorbance at a wavelength of 540 nm when assayed in a buffered solution of 0.1 M sodium acetate-acetic acid;
- The absorbance of the reagent blank, which is temperature sensitive (0.015 absorbance unit/°C), must not exceed 0.170 at 22°C with a 1-cm optical path length when the blank is prepared according to the specified procedure;
- The calibration curve (Section 10.0) must have a slope equal to 0.030±0 002 absorbance unit/μg SO_2 with a 1-cm optical path length when the dye is pure and the sulfite solution is properly standardized

8.2.12.2 Preparation of stock PRA solution—A specially purified (99 to 100 percent pure) solution of pararosaniline, which meets the above specifications, is commercially available in the required 0.20 percent concentration (Harleco Co.). Alternatively, the dye may be purified, a stock solution prepared, and then assayed according to the procedure as described below (10).

8.2.12.3 Purification procedure for PRA—1. Place 100 mL each of 1-butanol and 1 N HCl in a large separatory funnel (250-mL) and allow to equilibrate. Note: Certain batches of 1-butanol contain oxidants that create an SO_2 demand. Before using, check by placing 20 mL of 1-butanol and 5 mL of 20 percent potassium iodide (KI) solution in a 50-mL separatory funnel and shake thoroughly. If a yellow color appears in the alcohol phase, redistill the 1-butanol from silver oxide and collect the middle fraction or purchase a new supply of 1-butanol.

2. Weigh 100 mg of pararosaniline hydrochloride dye (PRA) in a small beaker. Add 50 mL of the equilibrated acid (drain in acid from the bottom of the separatory funnel in 1.) to the beaker and let stand for several minutes. Discard the remaining acid phase in the separatory funnel.
3. To a 125-mL separatory funnel, add 50 mL of the equilibrated 1-butanol (draw the 1-butanol from the top of the separatory funnel in 1.). Transfer the acid solution (from 2.) containing the dye to the funnel and shake carefully to extract. The violet impurity will transfer to the organic phase.
4. Transfer the lower aqueous phase into another separatory funnel, add 20 mL of equilibrated 1-butanol, and extract again.
5. Repeat the extraction procedure with three more 10-mL portions of equilibrated 1-butanol.
6. After the final extraction, filter the acid phase through a cotton plug into a 50-mL volumetric flask and bring to volume with 1 N HCl. This stock reagent will be a yellowish red.
7. To check the purity of the PRA, perform the assay and adjustment of concentration (Section 8.2.12.4) and prepare a reagent blank (Section 11.2); the absorbance of this reagent blank at 540 nm should be less than 0.170 at 22°C. If the absorbance is greater than 0.170 under these conditions, further extractions should be performed.

8.2.12.4 PRA assay procedure— The concentration of pararosaniline hydrochloride (PRA) need be assayed only once after purification. It is also recommended that commercial solutions of pararosaniline be assayed when first purchased. The assay procedure is as follows (10).

1. Prepare 1 M acetate-acetic acid buffer stock solution with a pH of 4.79 by dissolving 13.61 g of sodium acetate trihydrate in distilled water in a 100-mL volumetric flask. Add 5.70 mL of glacial acetic acid and dilute to volume with distilled water.
2. Pipet 1 mL of the stock PRA solution obtained from the purification process or from a commercial source into a 100-mL volumetric flask and dilute to volume with distilled water.
3. Transfer a 5-mL aliquot of the diluted PRA solution from 2, into a 50-mL volumetric flask. Add 5 mL of 1 M acetate-acetic acid buffer solution from 1, and dilute the mixture to volume with distilled water. Let the mixture stand for 1 hour.
4. Measure the absorbance of the above solution at 540 nm with a spectrophotometer against a distilled water reference. Compute the percentage of nominal concentration of PRA by

$$\% \text{ PRA} = \frac{A \times K}{W} \qquad (5)$$

where:

A = measured absorbance of the final mixture (absorbance units);
W = weight in grams of the PRA dye used in the assay to prepare 50 mL of stock solution (for example, 0.100 g of dye was used to prepare 50 mL of solution in the purification procedure; when obtained from commercial sources, use the stated concentration to compute W: for 98% PRA, W = .098 g); and
K = 21.3 for spectrophotometers having a spectral bandwidth of less than 15 nm and a path length of 1 cm.

[Corrected by 48 FR 17355, April 22, 1983]

8.2.13 Pararosaniline reagent: To a 250-mL volumetric flask, add 20 mL of stock PRA solution. Add an additional 0.2 mL of stock solution for each percentage that the stock assays below 100 percent. Then add 25 mL of 3 M phosphoric acid and dilute to volume with distilled water. The reagent is stable for at least 9 months. Store away from heat and light.

9.0 Sampling Procedure.

9.1 *General Considerations.* Procedures are described for short-term sampling (30-minute and 1-hour) and for long-term sampling (24-hour). Different combinations of absorbing reagent volume, sampling rate, and sampling time can be selected to meet special needs. For combinations other than those specifically described, the conditions must be adjusted so that linearity is maintained between absorbance and concentration over the dynamic range. Absorbing reagent volumes less than 10 mL are not recommended. The collection efficiency is above 98 percent for the conditions described; however, the efficiency may be substantially lower when sampling concentrations below 25μg SO_2/m^3 (8,9).
[Corrected by 48 FR 17355, April 22, 1983]

9.2 *30-Minute and 1-Hour Sampling.*
Place 10 mL of TCM absorbing reagent in a midget impinger and seal the impinger with a thin film of silicon stopcock grease (around the ground glass joint). Insert the sealed impinger into the sampling train as shown in Figure 1, making sure that all connections between the various components are leak tight. Greaseless ball joint fittings, heat shrinkable Teflon® tubing, or Teflon® tube fittings may be used to attain leakfree conditions for portions of the sampling train that come into contact with air containing SO_2. Shield the absorbing reagent from direct sunlight by covering the impinger with aluminum foil or by enclosing the sampling train in a light-proof box. Determine the flow rate according to Section 9.4.2. Collect the sample at 1±0.10 L/min for 30-minute sampling or 0.500±0.05 L/min for 1-hour sampling. Record the exact sampling time in minutes, as the sample volume will later be determined using the sampling flow rate and the sampling time. Record the atmospheric pressure and temperature.

9.3 *24-Hour Sampling.*
Place 50 mL of TCM absorbing solution in a large absorber, close the cap, and, if needed, apply the heat shrink material as shown in Figure 3. Verify that the reagent level is at the 50 mL mark on the absorber. Insert the sealed absorber into the sampling train as shown in Figure 2. At this time verify that the absorber temperature is controlled to 15±10°C. During sampling, the absorber temperature must be controlled to prevent decomposition of the collected complex. From the onset of sampling until analysis, the absorbing solution must be protected from direct sunlight. Determine the flow rate according to Section 9.4.2. Collect the sample for 24 hours from midnight to midnight at a flow rate of 0.200±0.020 L/min. A start/stop timer is helpful for initiating and stopping sampling and an elapsed time meter will be useful for determining the sampling time.

9.4 *Flow Measurement.*

9.4.1 Calibration: Flow measuring devices used for the on-site flow measurements required in 9.4.2 must be calibrated against a reliable flow or volume standard such as an NBS traceable bubble flowmeter or calibrated wet test meter. Rotameters or critical orifices used in the sampling train may be calibrated, if desired, as a quality control check, but such calibration shall not replace the on-site flow measurements required by 9.4.2. In-line rotameters, if they are to be calibrated, should be calibrated *in situ,* with the appropriate volume of solution in the absorber.

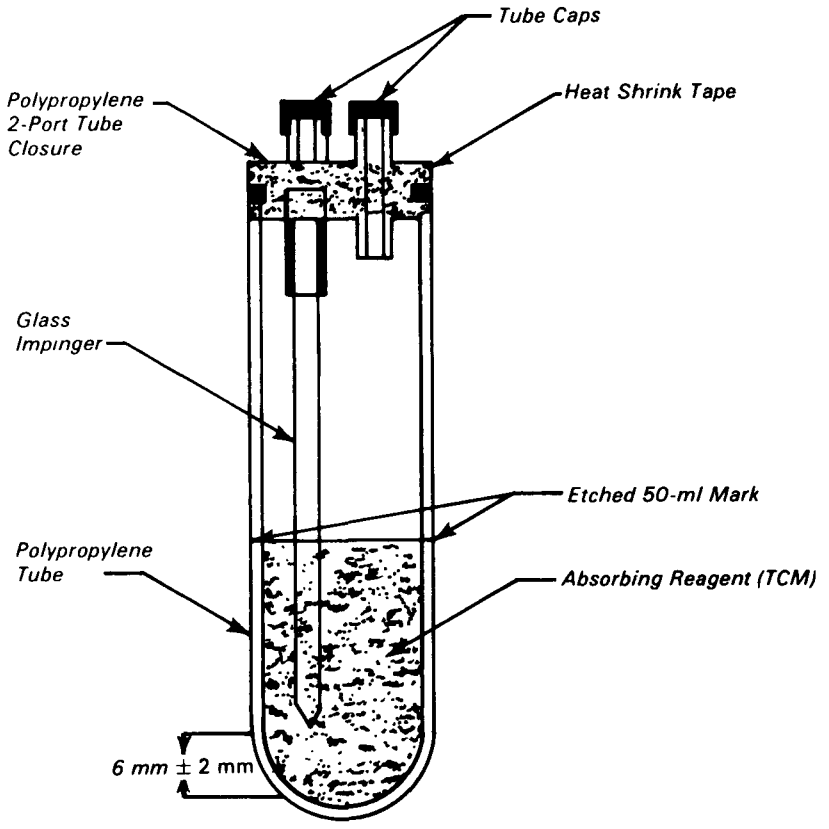


Figure 3. An absorber (24-hour sample) filled and assembled for shipment.

9.4.2 Determination of flow rate at sampling site: For short-term samples, the standard flow rate is determined at the sampling site at the initiation and completion of sample collection with a calibrated flow measuring device connected to the inlet of the absorber. For 24-hour samples, the standard flow rate is determined at the time the absorber is placed in the sampling train and again when the absorber is removed from the train for shipment to the analytical laboratory with a calibrated flow measuring device connected to the inlet of the sampling train. The flow rate determination must be made with all components of the sampling system in operation (e.g., the absorber temperature controller and any sample box heaters must also be operating). Equation 6 may be used to determine the standard flow rate when a calibrated positive displacement meter is used as the flow measuring device. Other types of calibrated flow measuring devices may also be used to determine the flow rate at the sampling site provided that the user applies any appropriate corrections to devices for which output is dependent on temperature or pressure.

$$Q_{std} = Q_{act} \times \frac{P_b - (1-RH)P_{H2O}}{P_{std}} \times \frac{298.16}{(T_{meter} + 273.16)} \qquad (6)$$

where
Q_{std} = flow rate at standard conditions, std L/min (25 C and 760 mm Hg);
Q_{act} = flow rate at monitoring site conditions, L/min;
P_b = barometric pressure at monitoring site conditions, mm Hg or kPa;
RH = fractional relative humidity of the air being measured;
P_{H2O} = barometric pressure of water at the temperature of the air in the flow or volume standard, in the same units as P_b (for wet volume standards only, i.e., bubble

flowmeter or wet test meter: for dry standards, i.e., dry test meter P_{H2O});

P_{std} = standard barometric pressure, in the same units as P_b (760 mm Hg or 101 kPa); and

T_{meter} = temperature of the air in the flow or volume standard, °C (e.g., bubble flowmeter).

[Corrected by 48 FR 17355, April 22, 1983]

If a barometer is not available, the following equation may be used to determine the barometric pressure:

P_b = 760 - .076 (H) mm Hg or

P_b = 101 - .01 (H)kPa (7)

where:

H = sampling site elevation above sea level in meters.

If the initial flow rate (Q_i) differs from the flow rate of the critical orifice or the flow rate indicated by the flowmeter in the sampling train (Q_c) by more than 5 percent as determined by equation (8), check for leaks and redetermine Q_i.

$$\% \text{ Diff} = \frac{Q_i - Q_c}{Q_i} \times 100 \quad (8)$$

Invalidate the sample if the difference between the initial (Q_i) and final (Q_f) flow rates is more than 5 percent as determined by equation (9):

$$\% \text{ Diff} = \frac{Q_i - Q_f}{Q_f} \times 100 \quad (9)$$

9.5 *Sample Storage and Shipment.* Remove the impinger or absorber from the sampling train and stopper immediately. Verify that the temperature of the absorber is not above 25°C. Mark the level of the solution with a temporary (e.g., grease pencil) mark. If the sample will not be analyzed within 12 hours of sampling, it must be stored at 5°±5°C until analysis. Analysis must occur within 30 days. If the sample is transported or shipped for a period exceeding 12 hours, it is recommended that thermal coolers using eutectic ice packs, refrigerated shipping containers, etc., be used for periods up to 48 hours (17) Measure the temperature of the absorber solution when the shipment is received. Invalidate the sample if the temperature is above 10°C. Store the sample at 5° ±5°C until it is analyzed.

10.0 Analytical Calibration.

10.1 *Spectrophotometer Cell Matching.* If unmatched spectrophotometer cells are used, an absorbance correction factor must be determined as follows

1. Fill all cells with distilled water and designate the one that has the lowest absorbance at 548 nm as the reference. (This reference cell should be marked as such and continually used for this purpose throughout all future analyses.)
2. Zero the spectrophotometer with the reference cell
3. Determine the absorbance of the remaining cells (A_c) in relation to the reference cell and record these values for future use. Mark all cells in a manner that adequately identifies the correction.

The corrected absorbance during future analyses using each cell is determined as follows:

$$A = A_{obs} - A_c \quad (10)$$

where:

A = corrected absorbance,

A_{obs} = uncorrected absorbance, and

A_c = cell correction.

[Corrected by 48 FR 17355, April 22, 1983]

10.2 *Static Calibration Procedure* [Option 1]. Prepare a dilute working sulfite-TCM solution by diluting 10 mL of the working sulfite-TCM solution (Section 8.2.11) to 100 mL with TCM absorbing reagent. Following the table below, accurately pipet the indicated volumes of the sulfite-TCM solutions into a series of 25-mL volumetric flasks. Add TCM absorbing reagent as indicated to bring the volume in each flask to 10 mL.

Sulfite-TCM Solution	*Volume of Sulfite-TCM Solution, mL*	*Volume of TCM, mL*	*Total µg SO_2 (approx.)**
working	*4.0*	*6.0*	*28.8*
working	*3.0*	*7.0*	*21.6*
working	*2.0*	*8.0*	*14.4*
dilute working	*10.0*	*0.0*	*7.2*
dilute working	*5.0*	*5.0*	*3.6*
-	*0.0*	*10.0*	*0.0*

**Based on working sulfite-TCM solution concentration of 7.2 µg SO_2/ml; the actual total µg SO_2 must be calculated using equation 11 below*

[10.2 table corrected by FR 17355, April 22, 1983]

To each volumetric flask, add 1 mL 0.6% sulfamic acid (Section 8.2.1), accurately pipet 2 mL 0.2% formaldehyde solution (Section 8.2.2), then add 5 mL pararosaniline solution (Section 8.2.13). Start a laboratory timer that has been set for 30 minutes. Bring all flasks to volume with recently boiled and cooled distilled water and mix thoroughly. The color must be developed (during the 30-minute period) in a temperature environment in the range of 20° to 30°C, which is controlled to ± 1°C. For increased precision, a constant temperature bath is recommended during the color development step. After 30 minutes, determine the corrected absorbance of each standard at 548 nm against a distilled water reference (Section 10.1). Denote this absorbance as (A). Distilled water is used in the reference cell rather than the reagant blank because of the temperature sensitivity of the reagent blank. Calculate the total micrograms SO_2 in each solution:

$$\mu g\ SO_2 = V_{TCM/SO2} \times C_{TCM/SO2} \times D \quad (11)$$

where:

$V_{TCM/SO2}$ = volume of sulfite-TCM solution used, mL;

$C_{TCM/SO2}$ = concentration of sulfur dioxide in the working sulfite-TCM, µg SO_2/mL (from equation 4); and

D = dilution factor (D = 1 for the working sulfite-TCM solution; D = 0.1 for the diluted working sulfite-TCM solution).

A calibration equation is determined using the method of linear least squares (Section 12.1). The total micrograms SO_2 contained in each solution is the x variable, and the corrected absorbance (eq. 10) associated with each solution is the y variable. For the calibration to be valid, the slope must be in the range of 0.030 ±0.002 absorbance unit/µg SO_2, the intercept as determined by the least squares method must be equal to or less than 0.170 absorbance unit when the color is developed at 22°C (add 0.015 to this 0.170 specificaion for each °C above 22°C) and the correlation coefficient must be greater than 0.998. If these criteria are not met, it may be the result of an impure dye and/or an improperly standardized sulfite-TCM solution. A calibration factor (B_s) is determined by calculating the reciprocal of the slope and is

subsequently used for calculating the sample concentration (Section 12.3) [Corrected by 48 FR 17355, April 22, 1983]

10.3 *Dynamic Calibration Procedures*
[Head corrected by 48 FR 17355, April 22, 1983]
(Option 2). Atmospheres containing accurately known concentrations of sulfur dioxide are prepared using permeation devices. In the systems for generating these atmospheres, the permeation device emits gaseous SO_2 at a known, low, constant rate, provided the temperature of the device is held constant (±0.1°C) and the device has been accurately calibrated at the temperature of use. The SO_2 permeating from the device is carried by a low flow of dry carrier gas to a mixing chamber where it is diluted with SO_2 free air to the desired concentration and supplied to a vented manifold. A typical system is shown schematically in Figure 4 and this system and other similar systems have been described in detail by O'Keeffe and Ortman (19), Scaringelli, Frey, and Saltzman (20), and Scaringelli, O'Keeffe, Rosenberg, and Bell (21). Permeation devices may be prepared or purchased and in both cases must be traceable either to a National Bureau of Standards (NBS) Standard Reference Material (SRM 1625, SRM 1626, SRM 1627) or to an NBS/EPA-approved commercially available Certified Reference Material (CRM) CRM's are described in Reference 22, and a list of CRM sources is available from the address shown for Reference 22. A recommended protocol for certifying a permeation device to an NBS SRM or CRM is given in Section 2.0.7 of Reference 2. Device permeation rates of 0 2 to 0.4 μg/min. inert gas flows of about 50 mL/min, and dilution air flow rates from 1.1 to 15 L/min conveniently yield standard atmospheres in the range of 25 to 600 μg SO_2/m^3 (0.010 to 0.230 ppm).

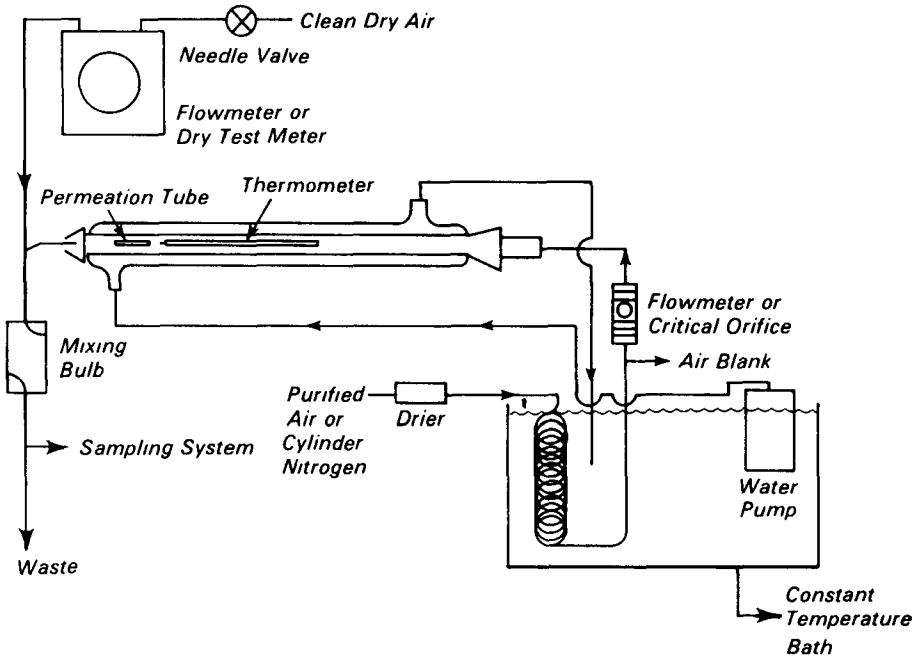


Figure 4. *Permeation tube schematic for laboratory use.*

10.3.1 Calibration Option 2A (30-minute and 1-hour samples): Generate a series of six standard atmospheres of SO_2 (e.g., 0, 50, 100, 200, 350, 500, 750 μg/m³) by adjusting the dilution flow rates appropriately. The concentration of SO_2 in each atmosphere is calculated as follows:

$$C_a = \frac{P_r \times 10^3}{(Q_d + Q_p)} \quad (12)$$

where:
C_a = concentration of SO_2 at standard conditions. μg/m³,
P_r = permeation rate, μg/min:
Q_d = flow rate of dilution air, std L/min, and
Q_p = flow rate of carrier gas across permeation device, std L/min.

[Corrected by 48 FR 17355, April 22, 1983]

Be sure that the total flow rate of the standard exceeds the flow demand of the sample train, with the excess flow vented at atmospheric pressure. Sample each atmosphere using similar apparatus as shown in Figure 1 and under the same conditions as field sampling (i.e., use same absorbing reagent volume and sample same volume of air at an equivalent flow rate). Due to the length of the sampling periods required, this method is not recommended for 24-hour sampling. At the completion of sampling, quantitatively transfer the contents of each impinger to one of a series of 25-mL volumetric flasks (if 10 mL of absorbing solution was used) using small amounts of distilled water for rinse (< 5mL). If >10 mL of absorbing solution was used, bring the absorber solution in each impinger to orginal volume with distilled H_2O and pipet 10-mL portions from each impinger into a series of 25-mL volumetric flasks. If the color development steps are not to be started within 12 hours of sampling, store the solutions at 5° ± 5°C. Calculate the total micrograms SO_2 in each solution as follows:

$$\mu g\ SO_2 = \frac{C_a \times Q_s \times t \times V_a \times 10^{-3}}{V_b} \quad (13)$$

where:
C_a = concentration of SO_2 in the standard atmosphere, μg/m³;
Q_s = sampling flow rate, std L/min;
t = sampling time, min;
V_a = volume of absorbing solution used for color development (10 mL); and
V_b = volume of absorbing solution used for sampling, mL.

Add the remaining reagents for color development in the same manner as in Section 10.2 for static solutions. Calculate a calibration equation and a calibration factor (B_g) according to Section 10.2, adhering to all the specified criteria.

10.3.2 Calibration option 2B (24-hour samples): Generate a standard atmosphere containing approximately 1,050 μg SO_2/m^3 and calculate the exact concentration according to equation 12. Set up a series of six absorbers according to Figure 2 and connect to a common manifold for sampling the standard atmosphere. Be

sure that the total flow rate of the standard exceeds the flow demand at the sample manifold, with the excess flow vented at atmospheric pressure. The absorbers are then allowed to sample the atmosphere for varying time periods to yield solutions containing 0, 0.2, 0.6, 1.0, 1.4, 1.8, and 2.2 $\mu g\ SO_2/mL$ solution. The sampling times required to attain these solution concentrations are calculated as follows:

$$t = \frac{V_b \times C_s}{C_a \times Q_s \times 10^{-3}} \quad (14)$$

where:

t = sampling time, min;
V_b = volume of absorbing solution used for sampling (50 mL);
C_s = desired concentration of SO_2 in the absorbing solution, $\mu g/mL$;
C_a = concentration of the standard atmosphere calculated according to equation 12, $\mu g/m^3$; and
Q_s = sampling flow rate, std L/min.

[Corrected by 48 FR 17335, April 22, 1983]

At the completion of sampling, bring the absorber solutions to original volume with distilled water. Pipet a 10-mL portion from each absorber into one of a series of 25-mL volumetric flasks. If the color development steps are not to be started within 12 hours of sampling, store the solutions at 5° ± 5°C. Add the remaining reagents for color development in the same manner as in Section 10.2 for static solutions. Calculate the total $\mu g\ SO_2$ in each standard as follows:

[Corrrected by 48 FR 17335, April 22, 1983]

$$\mu g\ SO_2 = \frac{C_a \times Q_s \times t \times V_a \times 10^{-3}}{V_b} \quad (15)$$

where:

V_a = volume of absorbing solution used for color development (10 mL).

All other parameters are defined in equation 14.

Calculate a calibration equation and a calibration factor (B_t) according to Section 10.2 adhering to all the specified criteria.

11.0 Sample Preparation and Analysis

11.1 *Sample Preparation.* Remove the samples from the shipping container. If the shipment period exceeded 12 hours from the completion of sampling, verify that the temperature is below 10°C. Also, compare the solution level to the temporary level mark on the absorber. If either the temperature is above 10°C or there was significant loss (more than 10 mL) of the sample during shipping, make an appropriate notation in the record and invalidate the sample. Prepare the samples for analysis as follows:

1. For 30-minute or 1-hour samples: Quantitatively transfer the entire 10 mL amount of absorbing solution to a 25-mL volumetric flask and rinse with a small amount (<5 mL) of distilled water.
2. For 24-hour samples: If the volume of the sample is less than the original 50-mL volume (permanent mark on the absorber), adjust the volume back to the original volume with distilled water to compensate for water lost to evaporation during sampling. If the final volume is greater than the original volume, the volume must be measured using a graduated cylinder. To analyze, pipet 10 mL of the solution into a 25-mL volumetric flask.

11.2 *Sample Analysis.* For each set of determinations, prepare a reagent blank by adding 10 mL TCM absorbing solution to a 25-mL volumetric flask, and two control standards containing approximately 5 and 15 $\mu g\ SO_2$, respectively. The control standards are prepared according to Section 10.2 or 10.3. The analysis is carried out as follows:

1. Allow the sample to stand 20 minutes after the completion of sampling to allow any ozone to decompose (if applicable).
2. To each 25-mL volumetric flask containing reagent blank, sample, or control standard, add 1 mL of 0.6% sulfamic acid (Section 8.2.1) and allow to react for 10 min.
3. Accurately pipet 2 mL of 0.2% formaldehyde solution (Section 8.2.2) and then 5 mL of pararosaniline solution (Section 8.2.13) into each flask. Start a laboratory timer set at 30 minutes.
4. Bring each flask to volume with recently boiled and cooled distilled water and mix thoroughly.
5. During the 30 minutes, the solutions must be in a temperature controlled environment in the range of 20° to 30°C maintained to ± 1°C. This temperature must also be within 1°C of that used during calibration.
6. After 30 minutes and before 60 minutes, determine the corrected absorbances (equation 10) of each solution at 548 nm using 1-cm optical path length cells against a distilled water reference (Section 10.1). *(Distilled water is used as a reference instead of the reagent blank because of the sensitivity of the reagent blank to temperature.)*
7. Do not allow the colored solution to stand in the cells because a film may be deposited. Clean the cells with isopropyl alcohol after use.
8. The reagent blank must be within 0.03 absorbance units of the intercept of the calibration equation determined in Section 10.

11.3 *Absorbance range.* If the absorbance of the sample solution ranges between 1.0 and 2.0, the sample can be diluted 1:1 with a portion of the reagent blank and the absorbance redetermined within 5 minutes. Solutions with higher absorbances can be diluted up to sixfold with the reagent blank in order to obtain scale readings of less than 1.0 absorbance unit. However, it is recommended that a smaller portion (<10 mL) of the original sample be reanalyzed (if possible) if the sample requires a dilution greater than 1:1.

11.4 *Reagent disposal.* All reagents containing mercury compounds must be stored and disposed of using one of the procedures contained in Section 13. Until disposal, the discarded solutions can be stored in closed glass containers and should be left in a fume hood.

12.0 Calculations

12.1 *Calibration Slope, Intercept, and Correlation Coefficient.* The method of least squares is used to calculate a calibration equation in the form of:

$$y = mx + b \quad (16)$$

where:

y = corrected absorbance,
m = slope, absorbance unit/$\mu g\ SO_2$
x = micrograms of SO_2
b = y intercept (absorbance units).

[Corrected by 48 FR 17355, April 22, 1983]

The slope (m), intercept (b), and correlation coefficient (r) are calculated as follows:

$$m = \frac{n\Sigma xy - (\Sigma x)(\Sigma y)}{n\Sigma x^2 - (\Sigma x)^2} \quad (17)$$

$$b = \frac{\Sigma y - m\Sigma x}{n} \quad (18)$$

$$r = \sqrt{\frac{m(\Sigma xy - \Sigma x\Sigma y/n)}{\Sigma y^2 - (\Sigma y)^2/n}} \quad (19)$$

where n is the number of calibration points.

A data form (Figure 5) is supplied for easily organizing calibration data when the slope, intercept, and correlation coefficient are calculated by hand.

12.2 *Total Sample Volume.* Determine the sampling volume at standard conditions as follows:

$$V_{std} = \frac{Q_i + Q_f}{2} \times t \quad (20)$$

where:

V_{std} = sampling volume in std L,
Q_i = standard flow rate determined at the initiation of sampling in std L/min,
Q_f = standard flow rate determined at the completion of sampling in std L/min, and
t = total sampling time, min.

[Corrected by 48 FR 17355, April 22, 1983]

12.3 *Sulfur Dioxide Concentration.* Calculate and report the concentration of each sample as follows:

$$\mu g\ SO_2/m^3 = \frac{(A - A_o)(B_x)(10^3)}{V_{std}} \times \frac{V_b}{V_a} \quad (21)$$

where:

A = corrected absorbance of the sample solution, from equation (10);
A_o = corrected absorbance of the reagent blank, using equation (10);
B_x = calibration factor equal to B_s B_g or B_t depending on the calibration procedure used, the reciprocal of the slope of the calibration equation;
V_a = volume of absorber solution analyzed, mL;
V_b = total volume of solution in absorber (see 11.1-2), mL; and
V_{std} = standard air volume sampled, std L (from Section 12.2).

DATA FORM

(For hand calculations)

Calibration point no.	Micrograms SO_2 (x)	Absorbance units (y)	x^2	xy	y^2
1					
2					
3					
4					
5					
6					

Σx = _____ Σy = _____ Σx^2 = _____
Σxy = _____ Σy^2 = _____
n = _____ *(number of pairs of coordinates)*

[Data Form corrected by 48 FR 17355, April 22, 1983]

Figure 5. *Data form for hand calculations.*

12.4 *Control Standards.* Calculate the analyzed micrograms of SO_2 in each control standard as follows:

$$C_a = (A - A_o) \times B_x \quad (22)$$

where:

C_a = analayzed μg SO_2 in each control standard,
A = corrected absorbance of the control standard, and
A_o = corrected absorbance of the reagent blank.

The difference between the true and analyzed values of the control standards must not be greater than 1 μg. If the difference is greater than 1 μg, the source of the discrepancy must be identified and corrected.

12.5 Conversion of $\mu g/m^3$ to ppm (v/v). If desired, the concentration of sulfur dioxide at reference conditions can be converted to ppm SO_2 (v/v) as follows:

$$ppm\ SO_2 = \frac{\mu g\ SO_2}{m^3} \times 3.82 \times 10^{-4} \quad (23)$$

[Corrected by 48 FR 17355, April 22, 1983]

13.0 Disposal of Mercury-Containing Solutions

13.1 The TCM absorbing solution and any reagents containing mercury compounds must be treated and disposed of by one of the methods discussed below. Both methods remove greater than 99.99 percent of the mercury.

13.2 Method for Forming an Amalgam.

1. Place the waste solution in an uncapped vessel in a hood.
2. For each liter of waste solution, add approximately 10 g of sodium carbonate until neutralization has occurred (NaOH may have to be used).
3. Following neutralization, add 10 g of granular zinc or magnesium.
4. Stir the solution in a hood for 24 hours. Caution must be exercised as hydrogen gas is evolved by this treatment process.
5. After 24 hours, allow the solution to stand without stirring to allow the mercury amalgam (solid black material) to settle to the bottom of the waste receptacle.

[Corrected by 48 FR 17355, April 22, 1983]

6. Upon settling, decant and discard the supernatant liquid.
7. Quantitatively transfer the solid material to a container and allow to dry.
8. The solid material can be sent to a mercury reclaiming plant. It must not be discarded.

13.3 *Method Using Aluminum Foil Strips.*

1. Place the waste solution in an uncapped vessel in a hood.
2. For each liter of waste solution, add approximately 10 g of aluminum foil strips. If all the aluminum is consumed and no gas is evolved, add an additional 10 g of foil. Repeat until the foil is no longer consumed and allow the gas to evolve for 24 hours.
3. Decant the supernatant liquid and discard.
4. Transfer the elemental mercury that has settled to the bottom of the vessel to a storage container.
5. The mercury can be sent to a mercury reclaiming plant. It must not be discarded.

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13.0 Data Forms

Blank data forms are provided on the following pages for the convenience of the Handbook user The customary descriptive title is centered at the top of the page; however, the usual section-page documentation in the top right-hand corner of each page has been replaced with a number in the lower right-hand corner that will enable the user to identify and refer to a similar filled-in form in a text section. For example, Form SO_2-1.1 indicates that the form is Figure 1.1 of the SO_2 method description. Any future revisions of these forms can be documented as 1.1A, 1 1B, etc. The following data forms are included:

Form	Title
1.1	Procurement Log
2.2	Wet Test Meter Calibration Log
2.4	Soap-Bubble Meter Calibration Log
2.6	Mass-Flow Meter Calibration Log
2.8	Rotameter Calibration Data Form
2.11	Timer Calibration Log
4.10	Gas Bubbler Data Record
5.1	SO_2 Calibration Data Sheet
5.3	Data Form for Hand Calculation
5.4A	Laboratory Data Log (Front)
5.4B	Laboratory Data Log (Back)
6.1	SAROAD Daily Data Form
6.2	SAROAD Hourly Data Form
8.1	$\bar{X}$-and-R Chart
8.2	Checklist for Use by Auditor for SO_2 Method

Procurement Log

Item description	*Quantity*	*Purchase order number*	*Vendor*	*Date*		*Cost*	*Disposition*	*Comments*
				Ordered	*Received*			

Wet Test Meter Calibration Log

Wet test meter: Manufacturer _____ *Calibrated by* _____

Model _____ *Date* _____

SN _____ *Test flask volume (V_t)* _____

Test Number	Barometric pressure (P_b), mm Hg	Water reservoir data: Temperature (T_r), °C	Water reservoir data: Temperature (T_r), K	Wet test meter data: Temperature (T_m), °C	Wet test meter data: Temperature (T_m), K	Wet test meter data: Manometer reading (ΔP_m), mm H_2O	Wet test meter data: Manometer reading (ΔP_m), mm Hg	Wet test meter data: Meter reading: Final (V_f), liters	Wet test meter data: Meter reading: initial (V_i), liters	Wet test meter data: Meter reading: V_m^{ind}, liters	V_m^{act} actual volume of meter, liters	Percent error, %

Calculations:

T_r = _____ °C + 273.2 = _____ K

T_m = _____ °C + 273.2 = _____ K

ΔP_m = _____ mm × H_2O x 0.0738 = _____ mm Hg

$V_m^{act} = \frac{T_m}{T_r} V_t$ = _____ *Note: If air is pushed through calibration system, ΔP_m is to be added to P_b.*

$$\text{Percent error} = \frac{V_m^{ind} - V_m^{act}}{V_m^{act}} \times 100 = 0.92$$

Average percent error not to exceed ±1%.

Soap Bubble Meter Calibration Log

Meter serial number _____ *Date* _____

Displacement volume[a] _____ *Calibrated by* _____

Test number	*Water temperature, °C*	*Initial weight of flask (Wt_i), g*	*Final weight of water and flask (Wt_f), g*	*Displacement volume (V_d),*[b] *ml*	*Remarks*

[a]*V = displacement volume stated by manufacturer = _____ ml*

[b]$V_d = \frac{Wt_f - Wt_i}{D_r}$ = _____ = _____; D_r = _____ *g/ml (Table 2 2).*

$\overline{V_d} = \frac{V_{d1} \times V_{d2} \times V_{d3}}{3}$ = _____ = _____

% error $= \frac{(V - \overline{V_d})\,100}{\overline{V_d}}$ = _____, *not to exceed ±1%*

Mass Flow Meter Calibration Log

Mass flow meter serial number _____ *Calibrated With* _____

Location _____ *Ambient room temperature* _____ °K

Barometric pressure (P_b) _____ *Relative humidity* _____

Calibrated by _____ *Date* _____

mm Hg = 0.0738 x mm H_2O)

Test point	Wet test meter readings				$V_s = \frac{P_m T_s V_m}{P_s T_m}$	Elapsed time (t), min	$Q_s = \frac{V_s}{t}$ l/min	Mass-flow meter scale
	Manometer reading (ΔP_m), mm Hg	$P_m = P_b - \Delta P_m^a$ mm Hg	Meter fluid temperature (T_m), K	Volume displaced (V_m), l				
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								

[a]*If air is pushed through the calibration apparatus, Δp_m is to be added to P_b.*

Rotameter Calibration Data From

Rotameter serial number _____ *Calibrated with* _____

Location _____ *Room temperature* _____ °C + 273 = _____ °K

Barometric Pressure (P_b), mm Hg _____ *Vapor pressure of H_2O (P_v), mm Hg* _____

Calibrated by _____ *Date* _____

Test point	Rotameter reading, units	Bubble displacement time, min	Average time (t), min	Volume displaced, ml	Volume at STP (V_s),[a] ml	$Q_s = \frac{V_s}{t}$ ml/min	Remarks
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							

[a] $V_s = V_m \left(\frac{P_b - P_v}{P_s}\right) \times \frac{T_s}{T_m}$

Timer Calibration Log

Site location number	Timer number	Date		Elapsed-time indicator serial number	Test period	Elapsed-time indicator reading	Accuracy	Technician (signature)
		Start	Stop					

Gas Bubbler Data Record

Station Location

City & State _____

Site & Address _____

Project _____ *Site No.* _____

Pollutant _____

Sampler ID No. _____ *Sample No.* _____

Vacuum Reading Start _____ *Open* _____ *Clamp*

Vacuum Reading End _____ _____

Start Sampling _____ _____ _____ _____ _____
mo day yr h min

Stop Sampling _____ _____ _____ _____ _____
mo day yr h min

Elapsed Time Start _____

Elapsed Time Stop _____

Nominal Flow Rate _____

Type of Flow Measuring Device _____

Identification Number of Device _____

Initial Flow _____ *Final Flow* _____ *% Difference* _____

_____ _____

_____ _____

Average _____ *Average* _____

Average sample temperature _____ °C *Relative humidity* _____

Ambient temperature: Start ____ °C, *Stop* ____ °C, *Average* ____ °C

Barometric pressure: Start ____ mm Hg, *Stop* ____ mm Hg, *Average* ____ mm Hg

REMARKS: _____

_____

Meteorological conditions for use when anomaly occurs.

WIND ____ *calm* ____ *light* ____ *gusty*

VISIBILITY ____ *clear* ____ *hazy*

SKY ____ *clear* ____ *scattered* ____ *overcast*

HUMIDITY ____ *dry* ____ *moderate* ____ *humid* ____ *rainy*

TEMP °F ____ *<20* ____ *20-40* ____ *41-60* ____ *61-80* ____ *>80*

Sample collected within guidelines given below.

Signature _____

Guidelines

Proper flow rate — 1/2-h samples - 900-1100 cm³/min
— 1-h samples - 450-550 cm³/min
— 24-h samples - 180-220 cm³/min

24-h sampling — 23 h < sampling time < 25 h
— ≥35 ml of absorbing reagent remain after sampling
— sampler timer accuracy ±15 min/24 h

SO_2 Calibration Data Sheet

Date _____ *Analyst* _____

Instrument I.D. _____

Color Development Time _____ *min, Temperature* _____ °C

Wavelength _____ *nm µg SO_2/ml (Working sulfite-TCM solution)* _____

$V_{TCM\ SO2}$	D	µg SO_2	Absorbance
0	1	0.0	
5	0 1		
10	0 1		
2	1		
3	1		
4	1		

$\mu g\ SO_2 = V_{TCM,SO2} \times C_{TCM\ SO2} \times D$

$V_{TCM\ SO}$ = volume of sulfite-TCM solution used, ml,

$C_{TCM\ SO2}$ = concentration of SO_2 in the working sulfite-TCM solution, µg SO_2/ml, and

D = dilution factor

Regression analysis results:

	Measured	Criteria
Slope	_____	0 030±0.002 absorbance units/µg SO_2
Intercept	_____	<0 170 at 22°C (add 0.015 per °C above 22°C)

Correlation coefficient _____ >0.998

Calibration factor $B_s = \frac{1}{slope}$ = _____ µg SO_2/absorbance unit

DATA FORM

For Hand Calculations

Calibration point number	Micrograms SO_2 (x)	Absorbance units (y)	x^2	xy	y^2
1					
2					
3					
4					
5					
6					

Σx = _____ Σy = _____ Σx^2 _____ Σxy = _____ Σy^2 = _____

n = _____ (number of calibration points)

Calibration Slope, Intercept, and Correlation Coefficient The method of least squares is used to calculate a calibration equation in the form of:

$$y = mx + b \qquad \textit{Equation 1}$$

where
- y = corrected absorbance,
- m = slope, absorbance units/μg SO_2
- x = micrograms of SO_2
- b = y intercept (absorbance units)

The slope (m), intercept (b), and correlation coefficient (r) are calculated as follows:

$$m = \frac{n\Sigma xy - (\Sigma x)(\Sigma y)}{n\Sigma x^2 - (\Sigma x)^2} = \frac{(\quad)(\quad) - (\quad)(\quad)}{(\quad)(\quad) - (\quad)^2} = _____$$

$$b = \frac{\Sigma y - m\Sigma x}{n} = \frac{(\quad) - (\quad)(\quad)}{(\quad)} = _____$$

$$r = \sqrt{\frac{m(\Sigma xy - \Sigma x\Sigma y/n)}{\Sigma y^2 - (\Sigma y)^2/n}} = \sqrt{\frac{(\quad)[(\quad)(\quad)(\quad)(\quad)]}{(\quad) - (\quad)^2 (\quad)}}$$

$$= _____$$

Laboratory Data Log (Front)

City Name

Site Address

State Area Site

Project Time Year

Sampler Identification No _____

Gas Bubbler - SO_2

Name Parameter Code: 4 2 4 0 1

Project	Sampling Date Month	Day	St Hr	Time Interval Conc µg/m³	Sample Number	Flow Rate cc/min Start	End	Average	Sampling Air m³ Time	Volume	Absorbance	B_s	Conc of Soln

If sulfite solutions used to prepare calibration curves, compute the SO_2 concentration in the sample:

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

A = sample absorbance
A_o = reagent blank absorbance.
10^3 = conversion of l to cm³.
V_R = sample volume corrected to 25°C and 760mm Hg, l.
B_s = calibration factor, µg/absorbance unit
V_a = volume of absorber solution analyzed, ml
V_b = total volume of solution in absorber, ml
D = dilution factor (if any) required to reduce sample absorbance below 1

Handled in Accordance with Guidelines on Reverse Side of This Form

_____
Signature

Remarks

Laboratory Data Log (Backside)

Preparation and Calibration	Sample Analysis	Reagent Preparation		
reagent water double-distilled and stored in a borosilicate glass vessel with vent guard	Colorimetric analysis blank within ±0.03 absorbance calibration intercept; control sample absorbance within ±1 μg SO_2 of actual value	Reagent	Container	Frequency of Preparation
		Sulfamic acid, 0 6%	Glass stoppered	Before analysis
		Formaldehyde, 0 2%	Glass stoppered	Before analysis
Absorbing reagent prepared every 6 mo, clear with 3.0 < pH < 5.0		Working iodine, 0 1N	Glass stoppered, dark	Before analysis
		Stock iodine, 0 01N	Glass stoppered, dark	Yearly
24-h sampler with polypropylene tubes and closure with glass impinger; ½- and 1-h sample with with glass midget impinger	Calibration curve for absorbance vs. μg SO_2/m^3 slope between 0.03 ±0.002 absorbance units/μg SO_2; intercept <0.17; all points within 0.04 μg SO_2/ml (1 μg SO_2) of best-fit curve	Sodium thiosulfate, 0.01N	Glass stoppered	Yearly
		Stock sodium thiosulfate, 0 1N	Glass stoppered	Yearly
Check of flow-measuring device against specification.		Working sulfite-TCM solution accurately prepared from standard solution prior to analysis; stable for 30 days at 5°C (41°F) if stored in dark glass-stoppered bottle		
All data points within +2% of the best-fit calibration curve for flow-measuring rotameter		Standard sulfite-ICM solution 320-400 μg SO_2/ml		
Flow rate measured before and after each sampling period		Pararosaniline (PRA) reagent 100% assay, stable if stored in dark glass-stoppered bottle		
Rotameter cleaned and calibrated every 30 days of operation or every 6 mo		Assayed PRA stock solution stored in dark glass-stoppered bottle, solution prepared if slope of calibration curve deviates from 0.03 ±0.002		
Sample timer within ±15 min/24-h; checked every 6 mo		Analytical balance performance within ±0 1 mg of manufacturer's specifications		

Saroad Daily Data Form

24-Hour or Greater Sampling Interval

2

1 Agency

City Name

Site Address

Project Time Interval

State Area Site

2 3 4 5 6 7 8 9 10

Agency Project Time Year Month

11 12 13 14 15 16 17 18

Name
PARAMETER
Code

23 24 25 26 27

28 29 30 31 32

Name
PARAMETER
Code

37 38 39 40 41

42 43 44 45 46

Name
PARAMETER
Code

51 52 53 54 55

56 57 58 59 60

Name
PARAMETER
Code

65 66 67 68 69

70 71 72 73 74

DP→ 4 3 2 1 0 4 3 2 1 0 4 3 2 1 0 4 3 2 1 0

Saroad Hourly Data Form

Less Than 24-Hour Sampling Interval

1 Agency

City Name

Site Address

Project

ENVIRONMENTAL PROTECTION AGENCY
National Aerometric Data Bank
P.O. Box 12055
Research Triangle Park
North Carolina 27711

Parameter observed

Method

Time interval of obs.

Units of obs.

State (2) Area (3 4 5) Site (6 7 8 9 10)

Agency (11) Project (12 13) Time (14) Year (15 16) Month (17 18)

Parameter code (23 24 25 26 27) Method (28 29) Units (30 31) DP (32)

Day (19 20)	St (21)	Hr (22)	Rdg 1 (33 34 35 36)	Rdg 2 (37 38 39 40)	Rdg 3 (41 42 43 44)	Rdg 4 (45 46 47 48)	Rdg 5 (49 50 51 52)	Rdg 6 (53 54 55 56)	Rdg 7 (57 58 59 60)	Rdg 8 (61 62 63 64)	Rdg 9 (65 66 67 68)	Rdg 10 (69 70 71 72)	Rdg 11 (73 74 75 76)	Rdg 12 (77 78 79 80)

$\overline{X}$ and R Chart

Project Name _____ Measurement Performed _____ Measurement Units _____

Measurement	Code	1																								
		2																								
		3																								
	Result	1																								
		2																								
		3																								
Sum																										
Average, $\overline{X}$																										
Range, R																										

Averages, $\overline{X}$																										

Ranges, R																										

Comments (Correct Action, etc.)																										

Checklist for Use by Auditor for SO_2 Method

1 *What type of manual sampler is used for SO_2 collection?*

(a) RAC (b) 5-port (c) 2-port (d) other _____

2 *Is a straight tube impinger used in the polypropylene sampling tube?* _____

3. *Is sample probe made of accepted material? Teflon®* _____ *, Glass* _____

4 *Is the probe (and manifold) located to prevent moisture condensation when sampling in humid conditions?* _____

5 *What method of analysis is used?* _____ *Is a copy available?* _____ *(Method should be from 40 CFR 50, July 1, 1982, as amended 47 FR 54896, December 6, 1982 and 48 FR 17355, April 22, 1983*

6 *What quality of reagents is used to make up the chemicals for the SO_2 analysis?* _____
(They should be reagent grade or better

7 *Is the sampling train routinely checked for leaks?* _____

How often? (a) Once a week (b) Once a month (c) Once a quarter (d) other _____

8. *What calibration check procedure is used for flow measuring device used in the field?* _____

Is a written copy available? _____

9 *Are sampling flow rates determined before and after each sampling period?* _____ *Is there an established procedure for discarding needles that are not within flow rate limits initially?* _____ *If so, what are the limits?* _____ *(Any needle outside of 180 to 200 cm^3/min should be discarded for 24-h samples). Is the absorbing solution maintained at 15° ±10°C?* _____ *Are samples voided?* _____ *Do initial and final flow rates agree within ±5%?* _____ *(Void sample if they are not)*

10. *Have calibration curves been made, and are they available?* _____ *Is the calibration history of the analyses in a bound (or other type) of notebook, and is it readily available?* _____
(All laboratories must keep a bound notebook as a permanent record of the calibration history that indicates when the curves were made and what points were used to make them)

11. *Are collected samples shipped from the field to the laboratory in containers that prevent crushing, spilling, etc., and maintained at a temperature of 5°± 5°C?* _____

12 *How many days were there between sampling and analysis?* _____ *days (Commonly it is approximately 12 days; less than 12 is very good, but more than 12 may cause problems in analysis)*

13. *Are samples stored in the dark until they are analyzed?* _____ *At what temperature are the samples stored?* _____ °C

14. *What calculations were performed to obtain the final SO_2 concentration?* _____
(If possible, show the completed calculations)

15. *How were discrepancies in the data treated?* _____

_____

_____ *(There should be a format for taking care of data discrepancies.)*

16. *Are the data reported quarterly?* _____ *If not, how often?* _____

United States
Environmental Protection
Agency

Environmental Monitoring Systems
Laboratory
Research Triangle Park NC 27711

Research and Development

EPA-600/4-77-027a

EPA

Test Method

Section 2.2
Reference Method for the Determination of Suspended Particulates in the Atmosphere (High-Volume Method)

Outline

Section	Documentation	Number of Pages
Summary	2.2	1
Method QA Highlights	2.2	1
Method Description		
1. Procurement of Equipment and Supplies	2.2.1	2
2. Calibration of Equipment	2.2.2	13
3. Filter Selection and Preparation	2.2.3	4
4. Sampling Procedure	2.2.4	8
5. Analysis of Samples	2.2.5	1
6. Calculations and Data Reporting	2.2.6	2
7. Maintenance	2.2.7	2
8. Auditing Procedure	2.2.8	4
9. Assessment of Monitoring Data for Precision and Accuracy	2.2.9	1
10. Recommended Standards for Establishing Traceability	2.2.10	1
11. Reference Method	2.2.11	10
12. References	2.2.12	1
13. Data Forms	2.2.13	10

Summary

Ambient air drawn into a covered housing and through a filter by a high-flow-rate blower at 1.1 to 1.7 m^3/min (39 to 60 ft^3/min) allows total suspended particulates (TSP) in sizes up to 25 to 50 μm (aerodynamic diameter) to collect on the filter surface. When operated within this range, the high-volume sampler is

capable of collecting TSP samples for 24-hour TSP concentrations ranging from 2 to 750 $\mu g/std\ m^3$ The mass concentration ($\mu g/m^3$)* in ambient air is computed by measuring both the mass of TSP collected and the (standard) volume of air sampled

This method provides a measurement of the mass concentration of total suspended particulate matter (TSP) in ambient air for determination of compliance with the primary and secondary National Ambient Air Quality Standards for Particulate Matter as specified in §50 6 and §50 7 of the Code of Federal Regulations, Title 40 The measurement process is nondestructive, and the size of the sample collected is usually adequate for subsequent chemical analysis Based on collaborative testing, the relative standard deviation (coefficient of variation) for single analyst precision (repeatability) of the method is 3 0 percent. The corresponding value for interlaboratory precision (reproducibility) is 3 7 percent

The absolute accuracy of the method is undefined because of the complex nature of atmospheric particulate matter and the difficulty in determining the "true" particulate matter concentration

This reference method appears in Title 40 of the Code of Federal Regulations, Part 50, Appendix B (as amended on December 6, 1982, (47 FR 54912) A complete copy of the Reference Method is reproduced in Section 2 2 11

Method QA Highlights

In this quality assurance document for the TSP Reference Method (high-volume sampler method), the procedures are designed to serve as guidelines for the development of agency quality assurance programs Because recordkeeping is a critical part of quality assurance activities, several data forms are included to aid in the documentation of necessary data The blank data forms (Section 2.2 13) may be used as they are, or they may serve as guidelines for preparing forms more appropriate to the individual agency, partially filled-in forms are interspersed throughout the text to illustrate their uses Activity matrices at the end of pertinent sections provide a review of the material covered in the text sections The material covered in this section for the TSP method is briefly summarized here.

1. *Procurement of Equipment* Section 2 2.1 describes the selection of equipment and the recommended procurement and calibration checks for the equipment. It also identifies the sections of this part of the Handbook that pertain to specific equipment and supplies. Figure 1.1 provides an example of a permanent procurement record.

2. *Calibration of Equipment* Section 2.2.2 provides detailed calibration procedures for the analytical balance, the relative humidity indicator, the elapsed-time meter, the flow-rate transfer standard, and the high-volume sampler. This section can be removed (along with the corresponding sections for the other methods of this volume of the Handbook) to serve as a calibration handbook. Table 2 2 at the end of the Section summarizes the acceptance limits for equipment calibration.

3. *Filter Selection and Preparation* Section 2.2.3 presents important considerations for the selection, identification, equilibration, weighing check, and handling of filters. The spectro-quality grade filter is recommended for use when additional chemical analyses are anticipated.

4. *Sampling Procedure* Section 2.2.4 details procedures for filter installation, performance of operational checks, sample handling, and data documentation. Several photographs are provided to clarify the installation procedure. Complete documentation of background information during the sampling is one of several quality assurance activities that are important to future data validation; particularly important are any unusual conditions existing during collection of the sample. Any such conditions should be noted.

5. *Analysis of Samples* Section 2.2.5 briefly describes verification of data from the field, sample inspection, filter equilibration, and the gravimetric analysis procedure. The analytical balance must be checked. The filter must be equilibrated in a controlled environment.

6. *Calculation and Data Reporting* Section 2.2 6 describes those activities pertaining to data calculations and reporting. The final data review, the data edit or validation, and the use of standardized reporting procedures are all important parts of a quality assurance program. Independent checks of the data and calculations are recommended to ensure that the reported data are both accurate and precise.

7. *Maintenance* Section 2.2.7 recommends periodic maintenance schedules to ensure that the equipment is capable of performing as specified.

8. *Assessment of Data for Accuracy and Precision* Sections 2.2.8 and 2.2.9 describe the assessment of the data for accuracy and precision, respectively. Independent audit activities provide accuracy checks of flow rate measurements, filter weighings, and data processing. The precision check is performed by using collocated samplers. The expected agreement between two collocated samplers is ±15%.

9. *Reference Information* Section 2.2.10 discusses the traceability of measurements to established standards of higher accuracy, a necessary prerequisite for obtaining accurate data.

Sections 2.2.11 and 2.2.12 contain the Reference Method and pertinent references.

Section 2.2.13 provides blank data forms for the convenience of the user.

*Although TSP is measured in micrograms per standard cubic meter, the "standard" is commonly omitted when reporting TSP measurements, by convention, $\mu g/m^3$ for TSP is understood to mean $\mu g/std\ m^3$

1.0 Procurement of Equipment and Supplies

Specifications for equipment and supplies for monitoring ambient air for total suspended particulates (TSP) are provided in the Reference Method, as reproduced in Section 2.2.11.

Upon receipt of the sampling equipment and supplies, appropriate procurement checks should be conducted to determine their acceptability, and their acceptability or rejection should be recorded in a procurement log. Figure 1.1 is an example of such a log, and Section 2.2.13 provides a blank copy for the Handbook user. This log will serve as a permanent record for future procurements and for any fiscal projections for future programs. It will also help to provide continuity of equipment and supplies Table 1-1 provides a matrix of the activities involved in the procurement of equipment and supplies.

The following list of equipment, apparatus, and supplies provides a reference to sections and subsections within this part of the Handbook to guide the user to specific checkout procedures. Here and throughout the balance of the text, "section" refers to the primary divisions of Section 2.2, "subsection" refers to the subdivisions within these sections

Item	Section	Subsection
Analytical balance	2.2.2	2.1
Relative humidity indicator	2.2.2	2.2
Elapsed-time meter	2.2.2	2.3
Timer	2.2.2	2.4
Flow rate transfer standard	2.2.2	2.5
Sampler	2.2.2	2.6
Filter	2.2.3	3.1, 3.3
Sampler motor	2.2.7	7.1
Faceplate gasket	2.2.7	7.2
Rotameter	2.2.7	7.3
Sampling head	2.2.7	7.4
Motor gasket	2.2.7	7.5
Flow transducer and recorder	2 2.7	7.6

Table 1.1 *Activity Matrix for Procurement of Equipment and Supplies*

Equipment	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Analytical balance	*Indicated weight = standard weight ±0.0005 g for three to five standard weights over sample filter weight range*	*On receipt, check against weights of known accuracy.*	*Request recalibration by manufacturer/supplier.*
Elapsed-time meter	*24 h ±2 min*	*On receipt, check against standard timepiece of known accuracy.*	*Adjust or reject.*
Timer	*24 h ±30 min*	*On receipt, check against elapsed-time meter.*	*Adjust or reject.*
Orifice calibration unit (flow transfer standard)	*Calibration flow rate = actual flow rate ±2%*	*On receipt, check against flow-rate primary standard.*	*Adopt new calibration curve if no evidence of damage; reject if damage is evident.*
Sampler	*Sampler complete; no evidence of damage; flow = 1.1 - 1.7 m^3/min*	*On receipt, observe visually and check operation of all components.*	*Reject or repair.*
Relative humidity indicator	*Indicator reading = psychrometer reading ±6%*	*On receipt, compare with* reading of a wet bulb/dry bulb psychrometer.	*Adjust or replace to attain* acceptance limits.

Item description	Quantity	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ordered	Received			
HI-VOL BRUSH SET	12	1782	GEN'L METAL	6-1-75	6-10-75	21	ACC.	
HI-VOL BRUSH SET	100	1782	GEN'L METAL	6-1-75	6-10-75	25	ACC.	

Figure 1.1. Example of a Procurement Log.

2.0 Calibration of Equipment

Before a TSP sampling program is undertaken, a wide variety of sampling and analysis equipment must be calibrated. The calibration activities are summarized in Table 2.2 at the end of this section. Many of these activities will also serve as initial acceptance checks. All data and calculations required for these activities should be recorded in a calibration log book in which a separate section is designated for each apparatus and sampler used in the program.

2.1 Analytical Balance

The calibration should be verified (1) when the analytical balance is first purchased, (2) any time it has been moved or subjected to rough handling, and (3) during routine operations when a standard weight cannot be weighed within ±0.5 mg of its stated weight. A set of three to five standard weights covering the range normally encountered in weighing filters should be weighed. If the weighed value of one or more of the standard weights does not agree within ±0.5 mg of the stated value, the balance should be recalibrated or adjusted by the manufacturer. The results of all balance checks should be recorded in a log book such as the one shown in Figure 2.1.

High-Volume Filter-Weighing Quality Control Log

		Glass-S weights, g			
Date	Time	0.5000	1.0000	2.0000	Technician
7/29/74	11:07	0.5000	1.0002	2.0000	BSM
7/29/74	12:08	0 5002	1.0003	2.0001	DEK
7/29/74	2·40	0 5000	1.0000	1 9999	DEK
7/30/74	4:03	0.4996	0 9999	2.0002	JLK
7/31/74	9.57	0 4997	1.0000	2.0000	DEK
7/31/74	10:56	0.4995	0.9996	1.9996	DEK
7/31/74	11.57	0.4996	0.9998	1.9998	DEK
7/31/74	2.04	0.5001	1.0000	2.0002	DEK
7/31/74	3:05	0.5000	1.0000	2.0000	DEK
8/1/74	9:03	0.4998	0 9997	1.9997	DEK
8/1/74	10·05	0 4999	0.9997	1.9997	DEK
8/1/74	11 10	0.5000	1.0001	2.0001	DEK
8/1/74	12 12	0.4998	0.9997	1.9998	DEK
8/1/74	1:43	0.5000	1.0001	2.0002	DEK
8/1/74	2 42	0 5001	1.0001	2.0001	DEK
8/1/74	3.45	0 5001	1.0000	2.0001	DEK
8/2/74	8:54	0.5000	1.0001	2.0001	DEK
8/2/74	9:56	0.5000	1.0000	2.0001	DEK
8/2/74	10·59	0 5003	0.9999	1.9998	DEK
8/2/74	12·16	0 5001	1.0002	2.0002	DEK
8/2/74	1:55	0 4999	1.0002	2.0001	DEK
8/2/74	3:03	0.5000	0.9999	2.0001	DEK
8/2/74	4:00	0.5000	0.9998	1.9999	DEK
8/3/74	8 41	0 4999	0.9996	1.9998	DEK
8/3/74	11 15	0.5002	1.0002	2.0002	DEK
8/5/74	8.42	0.5001	1.0000	2.0000	DEK
8/5/74	9.45	0 5000	1.0000	2.0000	DEK
8/5/74	10·44	0 5000	1.0000	2.0000	DEK
8/5/74	11·46	0 5000	1.0001	2.0000	DEK
8/5/74	1·16	0.5001	1.0000	2.0000	DEK
8/5/74	2 21	0 5001	1.0000	2.0001	DEK
8/5/74	3.15	0.5000	1.0000	2.0001	DEK
8/6/74	9.37	0.4999	1.0000	2.0000	DEK
8/6/74	11:05	0 5000	0.9998	1.9997	DEK
8/6/74	12.10	0 4999	0 9998	1.9999	DEK
8/6/74	2.10	0 5000	0.9998	2.0000	DEK
8/6/74	3·09	0 5000	1.0000	2.0000	DEK
8/6/74	4:05	0.5000	1.0000	2.0000	DEK
8/7/74	8·50	0.5000	1.0002	2.0003	DEK
8/7/74	9·46	0.4996	0.9998	1.9996	DEK
8/7/74	1·10	0 5001	1.0000	2.0000	DEK
8/7/74	2:20	0.5001	1.0000	2.0000	DEK
8/7/74	3 25	0.5002	1.0001	2.0000	DEK
8/8/74	9:46	0.5000	1.0000	2.0000	DEK
9/24/74	3:50	0 5001	1.0001	2.0001	DEK
9/26/74	3.01	0.5001	1.0001	2.0001	DEK

Figure 2.1. *Example of balance performance record*

2.2 Relative Humidity Indicator

The relative humidity indicator used for monitoring the filter conditioning environment should be checked against a wet bulb/dry psychrometer or the equivalent every 6 months. At least a two-point calibration should be made by comparing readings made in the conditioning environment against those made outdoors or perhaps just outside of the conditioning room. If the difference between the indicator and the corresponding psychrometer readings is within ±6%, it is all right to continue using the relative humidity indicator; if not, the indicator must be calibrated or a new one must be purchased Record the results of the relative humidity indicator checks in the calibration log book.

2.3 Elapsed-Time Meter

Every 6 months the elapsed-time meter should be checked against a timepiece of known accuracy, either on site or in the laboratory. If the indicator shows any signs of being temperature-sensitive, it should be checked on site during each season of the year. A gain or loss >2 min/24-h period warrants adjustment or replacement of the indicator The results of these checks should be recorded in the calibration log book.

2.4 On-Off Timer

The on-off timer should be calibrated and adjusted quarterly by using a calibrated elapsed-time meter as the reference. An example calibration procedure for one type is presented below Figure 2.2 depicts the connection diagram for calibration of a particular kind of timer The steps in the procedure are

1. Plug a correctly wired timer into an electrical outlet
2. Set the timer to the correct time
3. Set the on and off time-trippers for a 24-h test.
4. Plug the test light into one of the output plugs, and plug an elapsed-time meter into the other.
5. Check the system by manually turning the switch on and off.
6. Allow the system to operate for the 24-h test period, and determine the time elapsed on the elapsed-time meter. If the elapsed time is 24 h ±30 min, the timer is acceptable for field use; if not, adjust the tripper switches and repeat the test. Record the calibration data in a timer calibration log such as that shown in Figure 2.3 Section 2.2.13 provides a blank copy for the Handbook user.

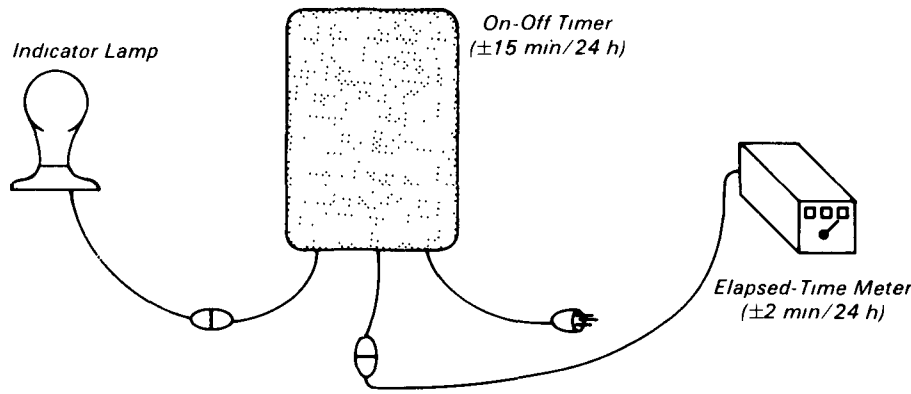


Figure 2.2. Diagram of a timer calibration system.

2.5 Flow Rate Transfer Standard

Calibration of the high-volume sampler's flow indicating or control device is necessary to establish traceability of the field measurement to a primary standard via a flow-rate transfer standard. The calibration procedure provided here applies to a conventional orifice-type flow transfer standard. Other types of transfer standards may be used if the manufacturer or user provides an appropriately modified calibration procedure that has been approved by EPA (see 40 CFR, Part 58, Appendix C, Section 2.8).

Upon receipt and at 1-year intervals, the calibration of the transfer standard orifices should be certified with a positive displacement standard volume meter (such as a Rootsmeter) traceable to the National Bureau of Standards (NBS). Orifice units should be visually inspected for signs of damage before each use, and they should be recalibrated if the inspection reveals any nicks or dents in the orifice.

The following equipment is required for certification of an orifice transfer standard.

1. Positive-displacement, standard volume meter (such as Rootsmeter) traceable to NBS.
2. High-volume air pump (high-volume sampler blower).
3. Resistance plates or variable voltage regulator.
4. Stopwatch
5. Thermometer
6. Barometer
7. Manometers [1 mercury (Hg), 1 water, or equivalent]

The following step-by-step procedure for certification of an orifice transfer standard is adapted from the Reference Method.[1] An orifice transfer standard certification worksheet (Figure 2.4) is provided for documentation of certification data.

1. Record on the certification worksheet the standard volume meter serial number; transfer standard type, model, and serial number; the person performing the certification, and the date

2. Observe the barometric pressure and record it as P_1 (item 8).

3. Read the ambient temperature in the vicinity of the standard volume meter and record it as T_1 (item 9) (K = °C + 273).

4. Connect the orifice transfer standard to the inlet of the standard volume meter. Connect the mercury manometer to measure the pressure at the inlet of the standard volume meter. Connect the orifice (water) manometer to the pressure tap on the orifice transfer standard Connect a high-volume air pump (such as a high-volume sampler blower) to the outlet side of the standard volume meter. (See Figure 2.5 for an example of the calibration setup.)

5. Check for leaks by temporarily clamping both manometer lines (to avoid fluid loss) and blocking the orifice with a large-diameter rubber stopper, wide cellophane tape, or other suitable means. Start the high-volume air pump and note any change in the standard volume meter reading. The reading should remain constant. If the reading changes, locate any leaks by listening for a whistling sound and/or retightening all connections, making sure that all gaskets are properly installed.

Site location number	Timer number	Date		Elapsed-time indicator serial number	Test period	Elapsed-time indicator reading	Accuracy	Technician (signature)
		Start	Stop					
1141	4321	6-10-75	6-11-75	CW 080G	24 hrs.	23 HRS, 53 MIN	99.5	C. Jones

Figure 2.3. *Example of a timer calibration log.*

Orifice Transfer Standard Certification Worksheet

	1	2	3	4	5	6	7	7a
Run No.	Meter reading start V_i (m^3)	Meter reading stop V_f (m^3)	Elapsed time t (min)	Volume measured V_m (m^3)	Differential pressure (at inlet to volume meter) ΔP (mm Hg or in)	(X) Flow rate Q_{std} (std m^3 min)	Pressure drop across orifice ΔH ☒ (in) or ☐ (cm) of water	$\sqrt{\Delta H \left(\frac{(Y)\ P_1}{P_{std}}\right) \frac{298}{T_1}}$
1	4958.00	4968.00	5.441	10.0	26.0	1 77	13.00	3.60
2	4970.00	4980.00	6.200	10.0	33.0	1.54	9.70	3.11
3	4982.00	4992.00	6 788	10.0	40.6	1.39	7 90	2.81
4	4993.00	5003.00	7.597	10.0	48 3	1.23	6.15	2 48
5	5004.00	5014.00	9.057	10 0	58.4	1.02	4.20	2.05
6								

Recorded Calibration Data

Standard volume meter No 462

Transfer standard type ☒ orifice ☐ other

Model No _____ Serial No 142

(8) P_1 750 mm Hg (or in) (10) P_{std} 760 mm Hg (or 29 92 in)

(9) T_1 295 K (11) T_{std} 298 K

By GREG MEINERS

Date: 3-28-83

Calculation Equations

(1) $V_m = V_f - V_i$

(2) $V_{std} = V_m \left(\frac{P_1 - \Delta P}{P_{std}}\right)\left(\frac{T_{std}}{T_1}\right)$

(3) $Q_{std} = \frac{V_{std}}{t}$

Least Squares Calculations

linear ($Y = mX + b$) regression equation of $Y = \sqrt{\Delta H\ (P_1/P_{std})\ (298/T_1)}$ on $X = Q_{std}$ for Orifice Calibration Unit (i e , $\sqrt{\Delta H (P_1/P_{std})\ (298/T_1)} = mQ_{std} + b$)

Slope (m) = 2.062 Intercept (b) = −0.056 Correlation coefficient (r) = 0.99995

To use for subsequent calibration: $X = \frac{1}{m}(Y-b)$,

$$Q_{std} = \frac{1}{m}\left[\sqrt{\Delta H \left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)} - b\right]$$

Figure 2.4. Example of orifice transfer standard certification worksheet.

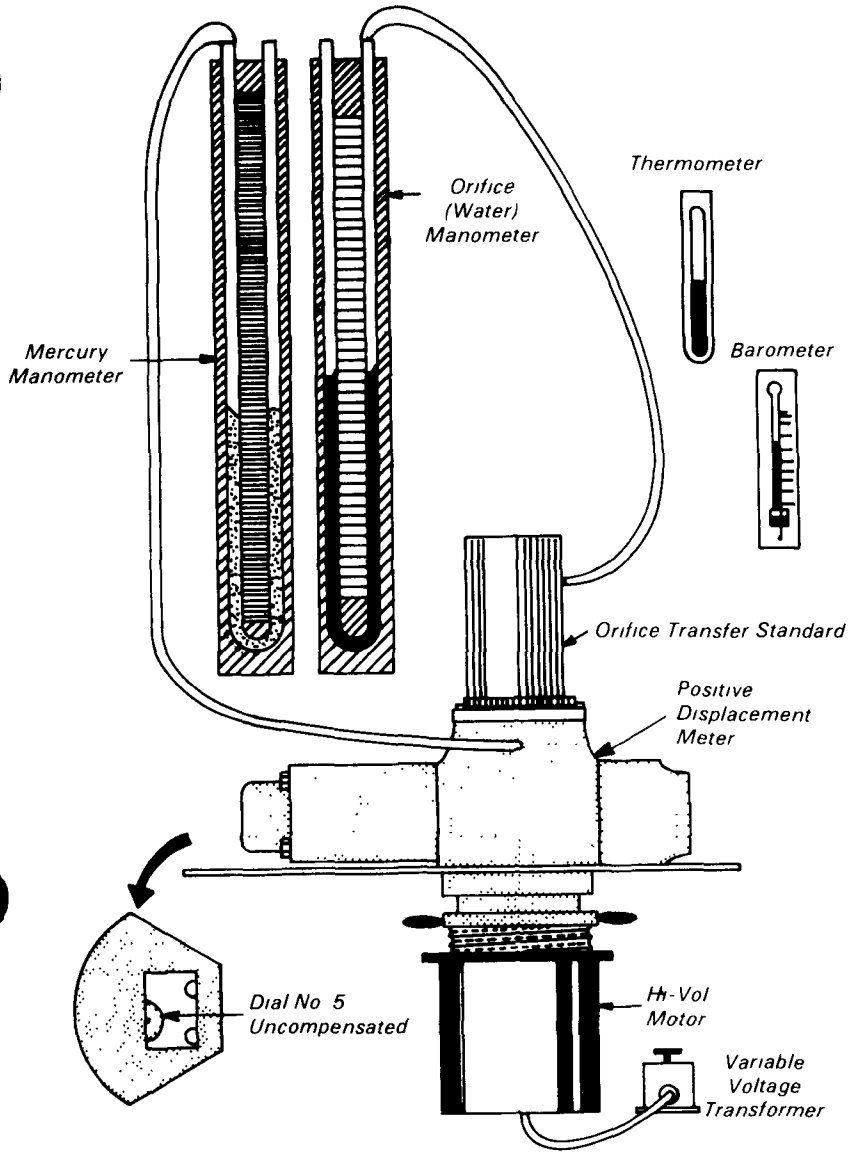


Figure 2.5. Example of orifice transfer standard calibration setup

6. Check the level of the positive displacement meter table, and adjust the legs if necessary.

7. After satisfactorily completing the leak check, shut off motor, unclamp both manometer lines, and zero the water and mercury manometers by sliding their scales until the zero is even with the meniscus, as illustrated in Figure 2 6

8. Achieve the appropriate flow rate through the system, either by means of the variable flow resistance in the transfer standard or by varying the voltage to the air pump. (Use of resistance plates is discouraged because the leak check must be repeated each time a new resistance plate is installed) At least five evenly distributed different but constant flow rates are required, at least three of which must be in the specified flow rate interval (1.1 to 1.7 m^3/min [39-60 ft^3/min]).

9 Start the blower motor, adjust the flow, and allow the system to run for at least 1 min to attain a constant motor speed Observe the standard volume meter dial reading and simultaneously start the stopwatch Error in reading the meter dial can be minimized by starting and stopping the stopwatch on whole numbers (e.g , 0046.00)

10 Record the initial meter reading (V_i) in Column 1 Maintain this constant flow rate until at least 3 m^3 of air have passed through the standard volume meter Record the standard volume meter inlet pressure manometer reading as ΔP (Column 5), and the orifice manometer reading as ΔH (Column 7). Be sure to indicate the correct units of measurement.

11 After at least 3 m^3 of air have passed through the system, note the standard volume meter reading and simultaneously stop the stopwatch Record the final meter reading (V_f) in Column 2 and the elapsed time (t) in Column 3

12 Calculate the volume measured by the primary standard volume meter (Vm) at meter conditions of temperature and pressure (using Equation 1 of the work sheet) and record in Column 4

$$V_m = V_f - V_i \qquad \text{Equation 2-1}$$

13 Correct this volume to standard volume (std m^3) by using Equation 2 of the work sheet.

$$V_{std} = V_m \left(\frac{P_1 - \Delta P}{P_{std}}\right)\left(\frac{T_{std}}{T_1}\right) \qquad \text{Equation 2-2}$$

where:

V_{std} = standard volume, std m^3,

V_m = actual volume measured by the primary standard volume meter, m^3 (Column 4 of work sheet)

P_1 = barometric pressure during calibration, mm (in.) Hg (Item 8 of work sheet)

ΔP = differential pressure at inlet to primary standard volume meter, mm (in) Hg (Column 5 of work sheet)

P_{std} = 760 mm Hg (29 92 in Hg)

T_{std} = 298 K

T_1 = ambient temperature during calibration, K (Item 9 of work sheet).

14. Calculate the standard volumetric flow rate (std m^3/min) by using Equation 3 of the work sheet·

$$Q_{std} = \frac{V_{std}}{t} \qquad \text{Equation 2-3}$$

where:

Q_{std} = standard volumetric flow rate, std m^3/min at 760 mm Hg and 298 K

t = elapsed time, minutes

15 Record Q_{std} to the nearest 0.01 std m^3/min in column 6 of the work sheet. Repeat steps 9 through 15 for at least four additional constant flow rates evenly spaced over the approximate range of 1.0 to 1.8 std m^3/min (35-64 ft^3/min).

16. For each flow, compute $\sqrt{\Delta H\,(P_1/P_{std})\,(298/T_1)}$ (Column 7a), and plot these values against Q_{std} as shown in Figure 2.7. Be sure to use consistent units (mm or in. Hg) for barometric pressure. Draw the orifice transfer standard certification curve or calculate the linear least squares slope (m) and intercept (b) of the certification curve:

$$\sqrt{\Delta H\,(P_1/P_{std})\,(298/T_1)} = m\,Q_{std} + b.$$

A certification graph should be readable to 0.02 std m^3/min.

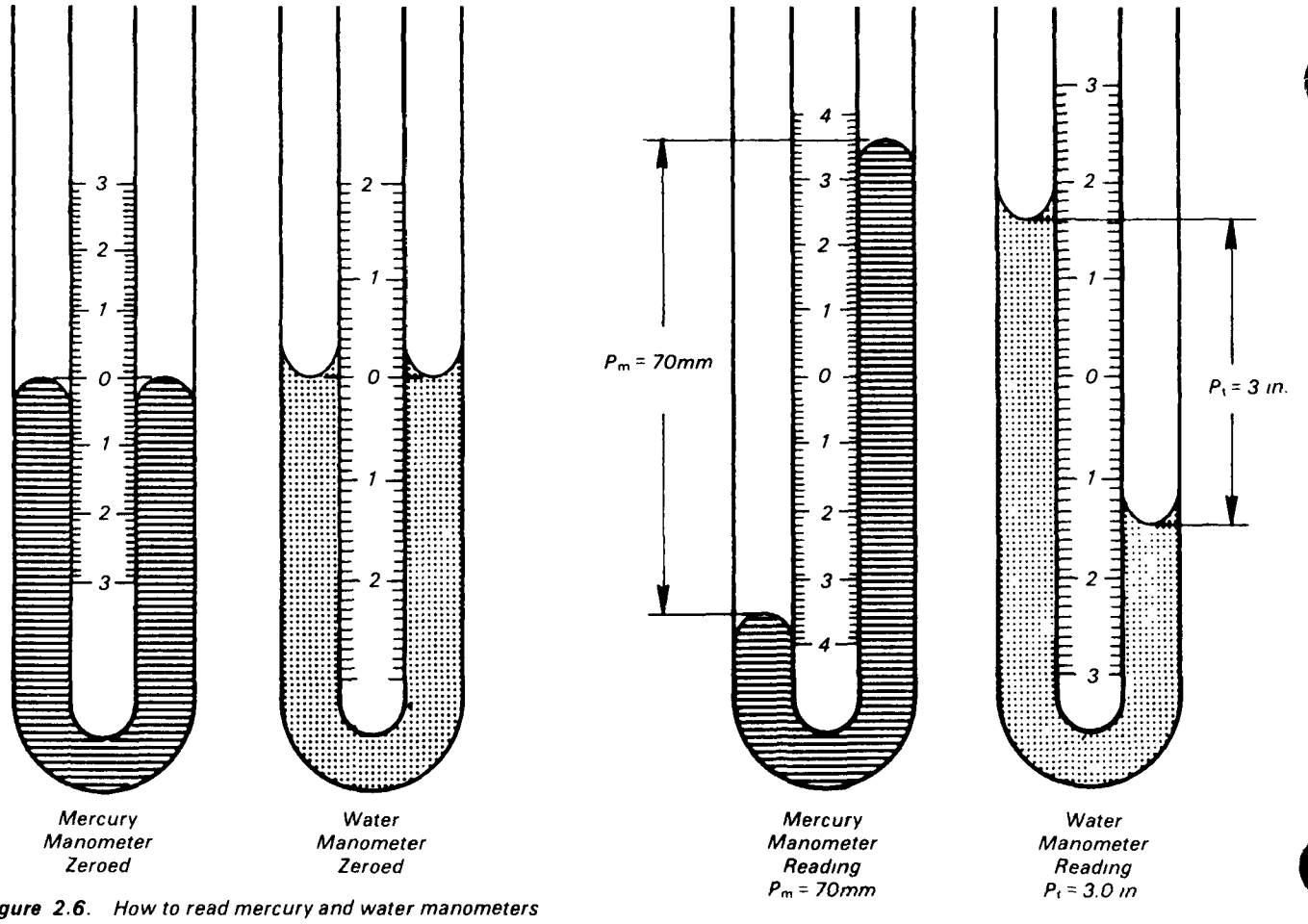


Figure 2.6. How to read mercury and water manometers

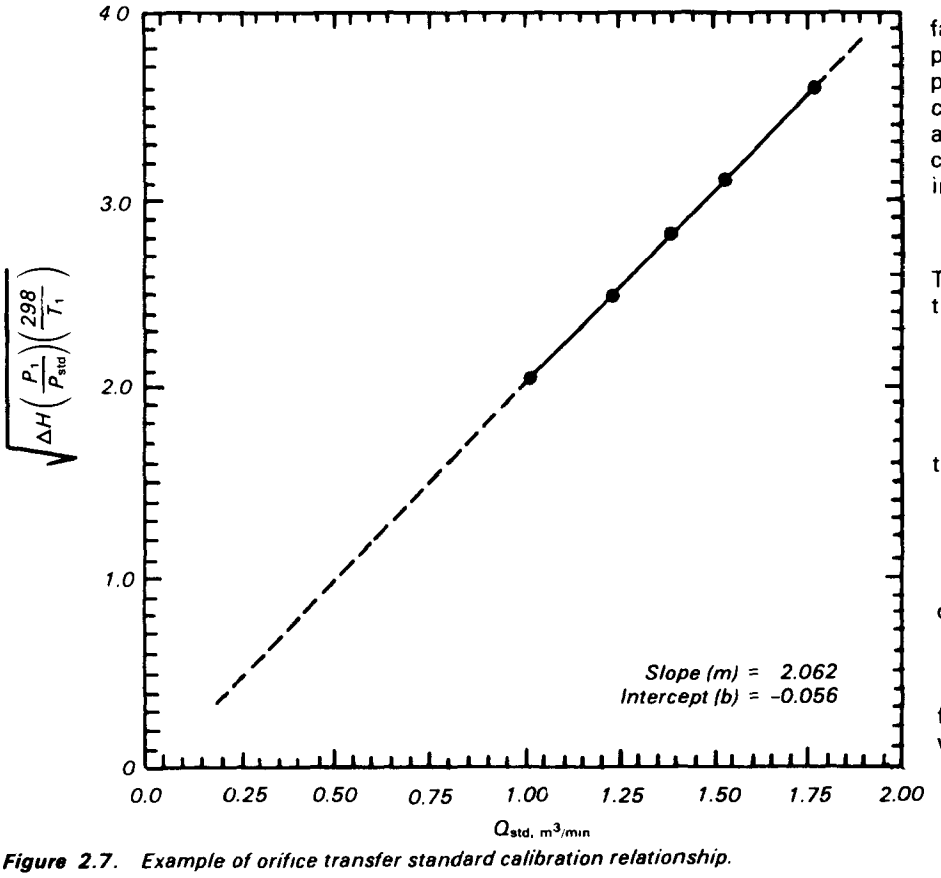


Figure 2.7. Example of orifice transfer standard calibration relationship.

17. If any calibration point does not fall within ±2% of the line, rerun that point, recalculate, and replot. The percent deviation can be calculated by comparing each Y from Column 7a against the corresponding Y_{cal} calculated from the slope and intercept using Equation 2-4:

$$Y_{cal} = m\ Q_{std} + b$$

Equation 2-4

The percent deviation for each point is then calculated using Equation 2-5.

$$\%\ \text{deviation} = \frac{Y - Y_{cal}}{Y_{cal}} \times 100$$

Equation 2-5

18. For subsequent use of the transfer standard, calculate Q_{std} as

$$Q_{std} = \frac{1}{m}\left[\sqrt{\Delta H\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)} - b\right]$$

Equation 2-6

or determine Q_{std} for each value of:

$$\sqrt{\Delta H\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$$

from the certification graph.

where:

P_2 = barometric pressure at time of Hi-Vol calibration

T_2 = temperature at time of Hi-Vol calibration

2.6 Calibration of High-Volume Sampler

Each high-volume sampler must incorporate a flow rate measurement device capable of indicating the total sampler flow rate This device may be an electronic mass flowmeter, an orifice or orifices located in the sample air stream together with a suitable pressure indicator (such as a manometer or an aneroid pressure gauge), or any other type of flow indicator (including a rotameter) having comparable precision and accuracy It must be possible to calibrate the flow rate measurement device to a flow rate that is readable (in corresponding units) to the nearest 0 02 std m^3/min A pressure recorder with an orifice device that provides a continuous record of the flow may be used.

The concentration of TSP in the ambient air is computed as the mass of collected particles, divided by the volume of air sampled, corrected to standard conditions of 760 mm Hg and 298 K, and then expressed in micrograms per standard cubic meter (μg/std m^3). When samples are collected at temperatures and pressures significantly different from standard conditions, the corrected concentrations may differ substantially from actual concentrations (micrograms per actual cubic meter), particularly at high elevations.

Calibration of a high-volume sampler refers to calibration of the sampler's flow rate indicator so that it provides accurate measurements of the sample flow rate from which the volume of the sampled air can be calculated. Details of the calibration procedure vary somewhat depending on (1) the type of flow indicator used, (2) whether the sampler is equipped with an automatic flow controller, and (3) whether the calibration is to incorporate the geographical average barometric pressure and seasonal average temperature at the sampling site. The basic procedure for nonflow-controlled samplers is given in Subsection 2.6 2, whereas the variations in the procedure necessary for flow-controlled samplers are presented in Subsection 2 6.3.

Orifice-type flow indicators are sensitive to changes in both temperature and barometric pressure. Because ambient temperature and barometric pressure vary from day to day, the calibration procedure contains a formula to correct for this variability. Errors resulting from normal daily fluctuation are relatively small, however, compared with barometric differences due to elevation and seasonal temperature changes. Thus, if the modest errors due to daily changes are acceptable, the average barometric pressure for a given elevation and the seasonal average temperature for that location can be incorporated directly into the sampler calibration with little error being introduced in the calculated flow rate.

When this is done, the sampler is calibrated for the average temperature and pressure conditions at the site, and no further temperature or pressure corrections are needed for the flow indicator reading to be used to determine the sampler flow rate. The relationship between the flow indicator reading and the standard volume flow rate then becomes a very simple one. This relationship also can be easily reduced to a simple three-column table (indicator reading, winter flow rate, and summer flow rate) suitable for use even by nontechnically oriented operators

The average barometric pressure for a site can be estimated from the altitude of the site, either by using an altitude-pressure table or by reducing the sea level pressure of 760 mm Hg by 26 mm Hg for each 305 m (1000 ft) of altitude. The average pressure could also be determined by averaging onsite barometer readings or nearby weather station or airport measurements (station pressure, uncorrected) over several months. The seasonal average temperature for a site can be estimated from onsite temperature readings or nearby weather station records over the season. Ideally, the average temperature should reflect the temperature at the time of day at which the flow indicator would normally be read; however, an average determined from 24-hour mean temperature records would be acceptable For most sites, two seasonal average temperatures (summer and winter) are sufficient; for sites where climatic changes are severe, however, four seasonal average temperatures may be needed to accommodate the changes. Where computers are used to process TSP data, monthly average temperatures could be used. Ideally, the seasonal average temperature should generally be within ±15°C of the local ambient temperature at the time the flow indicator is read. If daily temperature changes at the site are too drastic to be represented by a seasonal average (±15°C) actual temperature corrections should be used each time a flow reading is obtained.

Once a decision has been made on whether to incorporate an average barometric pressure and a seasonal average temperature into the calibration, the appropriate expression for plotting or calculating the sampler calibration can be selected from Table 2.1. The use of this expression is explained in Subsection 2.6.2.

2.6.1 *Calibration Schedule* - High-volume-sampler flow-rate devices should be calibrated with a certified flow-rate transfer standard such as an orifice calibration unit (1) upon receipt, (2) after motor maintenance, (3) any time the flow rate device is repaired or replaced, and (4) any time the difference between the sample flow rate and a one-point audit deviates more than ±7 percent.

2.6.2 *Sampler Calibration Procedure* - The procedures for multipoint calibration of a high-volume sampler are specified in 40 CFR 50, Appendix B (reproduced in Section 2.2.11). To facilitate these procedures, calculation data forms have been developed to aid in making the calibrations. These forms also may be used for the calibration of other types of high-volume flow measuring devices,

Table 2.1. *Expressions for Plotting Sampler Calibration Curves*

Type of sampler flow rate measuring device	*For actual pressure and temperature corrections*	*For incorporation of geographic average pressure and seasonal average temperature*
Mass flowmeter	1	1
Orifice and pressure indicator	$\sqrt{1\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$\sqrt{1\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$
Rotameter, or orifice and pressure recorder having square root scale[a]	$\sqrt{1\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$\sqrt{1\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$

[a]*This scale is recognizable by its nonuniform divisions; it is the most commonly available for high-volume samplers.*

provided the appropriate equations and procedures are followed

Documentation of all data on the flow-rate transfer standard for the high-volume site sampler, and the calibration procedures are of primary importance The validity of the data collected by the instrument is dependent on the quality of the calibration; thus the calibration must be performed with a transfer standard that meets all conditions specified in Subsection 2 5

The following procedure, which involves the use of the forms shown in Figures 2 8 and 2.9, is given to aid in the collection and documentation of calibration data This procedure applies primarily to a conventional orifice-type flow transfer standard and an orifice-type flow indicator with a flow recorder in the sampler (the most common type), as shown in Figure 2 10

1 Record the official name and address of the station on the form; where appropriate, the name and address should be the same as that appearing on the SAROAD site identification form to eliminate any confusion to persons not familiar with the station.

2 Connect the transfer standard orifice to the inlet of the sampler. Connect the orifice manometer to the orifice pressure tap, as illustrated in Figure 2.10 Make sure there are no leaks between the orifice unit and the sampler.

3. Verify that the flow indicator or recorder is properly connected to the pressure tap on the lower side of the high volume sampler motor housing. Install a clean flow chart in the recorder and adjust the recorder pen to read zero.

4. Operate the sampler for at least 5 minutes to establish thermal equilibrium prior to the calibration

5. Measure and record the barometric pressure (P_2) and ambient temperature (T_2) on the calibration worksheet (Items 1 and 2 on the upper part of the sheet).

6. Adjust the variable resistance of the transfer standard, or if applicable, insert the appropriate resistance plate to achieve the desired flow rate. If samplers have an orifice-type flow indicator downstream of the motor, do not vary the flow rate by adjusting the voltage or power supplied to the sampler

7. Let the sampler run for at least 2 minutes to reestablish the run-temperature conditions Read and record the pressure drop across the transfer standard orifice (ΔH) under Column 1 of the worksheet Read the sampler flow rate indication (I) from the flow recorder and record under column 4 Tap the flow recorder lightly before taking each reading to assure that the pen is not sticking.

8 Calculate $\sqrt{\Delta H\,(P_2/P_{std})\,(298/T_2)}$ and record under column 2.

9 Determine the standard volumetric flow rate (Q_{std}) either graphically from the transfer standard certification curve or by calculating Q_{std} from the least squares slope and intercept of the transfer standard's transposed certification curve

$$Q_{std} = 1/m \left[\sqrt{\Delta H\,(P_2/P_{std})\,(298/T_2)} - b\right]$$

Equation 2-6 (repeated)

Record the value of Q_{std} under Column 3

10. Repeat steps 6 through 9 for at least four additional flow rates distributed over a range that includes 1 1 to 1 7 std m^3/min

11 For each calibration point, calculate a Y value from the appropriate expression selected from Table 2-1 for the flow device being calibrated This should be done whether or not average barometric pressure and seasonal average temperature are to be incorporated into the calibration. Record this value under the appropriate side of Column 5 Calibration Worksheet (Figure 2.8), and mark the box showing which expression was used. For a pressure recorder, use the lower expression for square root function chart paper or middle expression for linear (uniform) chart paper.

12 Determine the calibration relationship by plotting the corresponding values of the Y expression involving I against Q_{std} on a graph similar to that shown in Figure 2.9. The Y expression plotted on the Y axis is from Column 5 of the calibration worksheet; the Q_{std} plotted on the X axis is from Column 3.

13 Draw the sampler calibration curve and/or calculate the linear least squares slope (m), intercept (b), and correlation coefficient of the calibration curve Calibration curves should be readable to 0.02 std m^3/min.

14. After the calibration relationship is determined, recheck each calibration point to determine if it is within the limits of linearity (±5%). This can be done by determining a Y_{cal} for each Q_{std} value recorded under Column 3 of the calibration worksheet. Y_{cal} can be determined from the calibration curve drawn in Figure 2 9 or by using the slope (m) and intercept (b) from the calibration worksheet (Figure 2.8) in the following equation

$$Y_{cal} = m\,Q_{std} + b$$

Equation 2-7

The percent difference for each value (Q_{std}) is determined by comparing each Y_{cal} with the corresponding Y recorded under Column 5 of the worksheet by using the following equation.

$$\%\ \text{difference} = \frac{Y - Y_{cal}}{Y_{cal}} \times 100$$

Equation 2-8

where

Y = Value of appropriate expression as recorded under Column 5 of the calibration worksheet

Y_{cal} = Corresponding Y value for the same Q_{std} as determined from the calibration relationship (Equation 2-7)

Any calibration points that are found to have a greater difference than ±5 percent should be repeated, and a corrected calibration relationship should be recalculated

The use of the calibration relationship determining sampler flow rates and the appropriate expressions to be used are discussed later in Subsection 4.4

2.6.3 *Flow-Controlled Sampler Calibration Procedures* - Samplers equipped with a flow controlling device may be calibrated either by means of a full multipoint calibration of the flow indicator (as described in Subsection 2.6.2 or by a single point calibration of the flow controller, without calibrating the flow indicator.

Multipoint Calibration. The flow controller must be rendered inoperative to allow flow changes to be made during calibration of the flow indicator. Calibration procedures and data forms given in Subsection 2.6.2 can then be used to determine the calibration relationship for the sampler's flow indicator. After calibration, the flow-controlling mechanism should be made operative again and set to a flow near the lower flow limit (1.1 std m^3/min) to allow maximum control range. At this time the sample flow rate should be verified with a clean filter installed. Two or more filters should then be added to the sampler to see if the flow controller maintains a constant flow; this is particularly important at high altitudes where the range of the flow controller may be reduced.

Single-Point Calibration. A flow-controlled sampler may be calibrated solely at its controlled flow rate,

High-Volume Air Sampler Calibration Worksheet

Site location: 114 E. MAIN ST. JONESVILLE OHIO

Date: 4-7-83 (1) Barometric pressure, P_2 mm Hg (or in.): 765

Calibrated by: SONJA FELIX (2) Temperature, T_2 (K): 293

Sampler No: 3 Serial No: 2864

Transfer std type: ORIFICE Serial No: 142

Optional

P_{std} = 760 mm Hg (or 29.92 in.)

Average barometric pressure P_a = _____

Seasonal average temperature T_a = _____

No	1 ΔH Pressure drop across orifice (in) or (cm)	$\sqrt{\Delta H \left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	(X) 3 Q_{std} (from orifice certification std m^3/min	4 I Sampler flow rate indication (arbitrary)	5 (Y) For specific pressure and temperature corrections (see Table 2.1) ☐ I or ☐ $\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$ or ☐ $\sqrt[4]{\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	5 (Y) For incorporation of average pressure and seasonal average temperature (see Table 2.1) ☐ I or ☐ $\sqrt{I\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$ or ☐ $\sqrt[4]{\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$
1	2.2	1.501	0.750	20.0	20.236	
2	3.7	1.946	0.975	28.0	28.330	
3	5.3	2.329	1.155	34.0	34.401	
4	7.1	2.696	1.330	39.0	39.460	
5	8.5	2.950	1.455	43.0	43.507	
6	12.0	3.505	1.725	51.7	52.301	

Least Squares Calculations

Linear regression of Y on X: $Y = mX + b$, Y = appropriate expression from Table 2.1, $X = Q_{std}$

Slope (m) = 32.799 Intercept (b) = 3.951 Correlation Coefficient (r) = 0.9991

To determine subsequent flow rate during use: $X = 1/m\,(Y-b)$ $Q_{std} = 1/m$ ([appropriate expression from Table 4.1 of Section 2.2.4] -b)

Figure 2.8. Example of high volume air sampler calibration worksheet

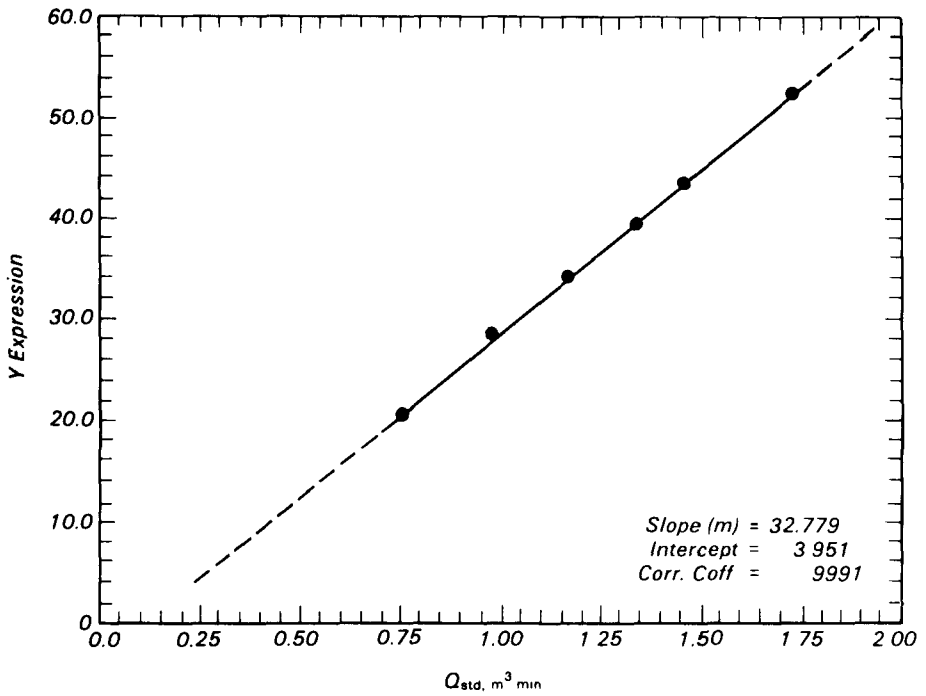


Figure 2.9. *Example of a high-volume sampler calibration relationship.*

provided the previous operating history of the sampler demonstrates that the flow rate is stable and reliable. In this case, the flow indicator may remain uncalibrated, but it should be used to indicate any relative change between initial and final flows, and the sampler should be recalibrated more often to minimize potential loss of samples because of controller malfunction. The following procedures should be used.

1. Set the flow controller for a flow near the lower limit of the flow range (1.1 std m^3/min) to allow maximum control range.
2. Install a clean filter in the sampler and carry out steps 2 through 5 and 7 through 9 of Subsection 2.6.2. No resistance plate should be used with the flow rate transfer standard.
3. Following calibration, add one or two additional clean filters to the sampler, reconnect the transfer standard, and operate the sampler to verify that the controller maintains the same calibrated flow rate; this is particularly important at high altitudes, where the flow control range may be reduced.

2.6.4 *Rotameter Calibration Procedure* - High-volume samplers equipped with rotameters are calibrated by using the same procedures and forms as specified in Subsection 2.6.2. Should adjustment of the rotameter be necessary, the following procedures may be used. (Refer to Figure 2.11, a photographic copy of the rotameter, to identify the working components in this procedural step for adjusting the rotameter.)

1 Attach the rotameter to the high-volume sampler motor.
2. Turn on motor and adjust to selected flow rate.
3 If adjustment is necessary, hold the rotameter vertically and loosen the locking nut by turning it counterclockwise.
4. Turn the adjusting screw to the desired setting (clockwise to lower the ball, or counterclockwise to raise the ball).
5. Be sure the ball continues to read the desired setting after the adjustment is made and as the locking nut is tightened.
6. Seal both the locking nut and the adjustment screw with glue to assure that the setting does not change. Do not cover the exhaust orifice
7. Proceed with calibration of rotameter as specified in Subsection 2.6.2.

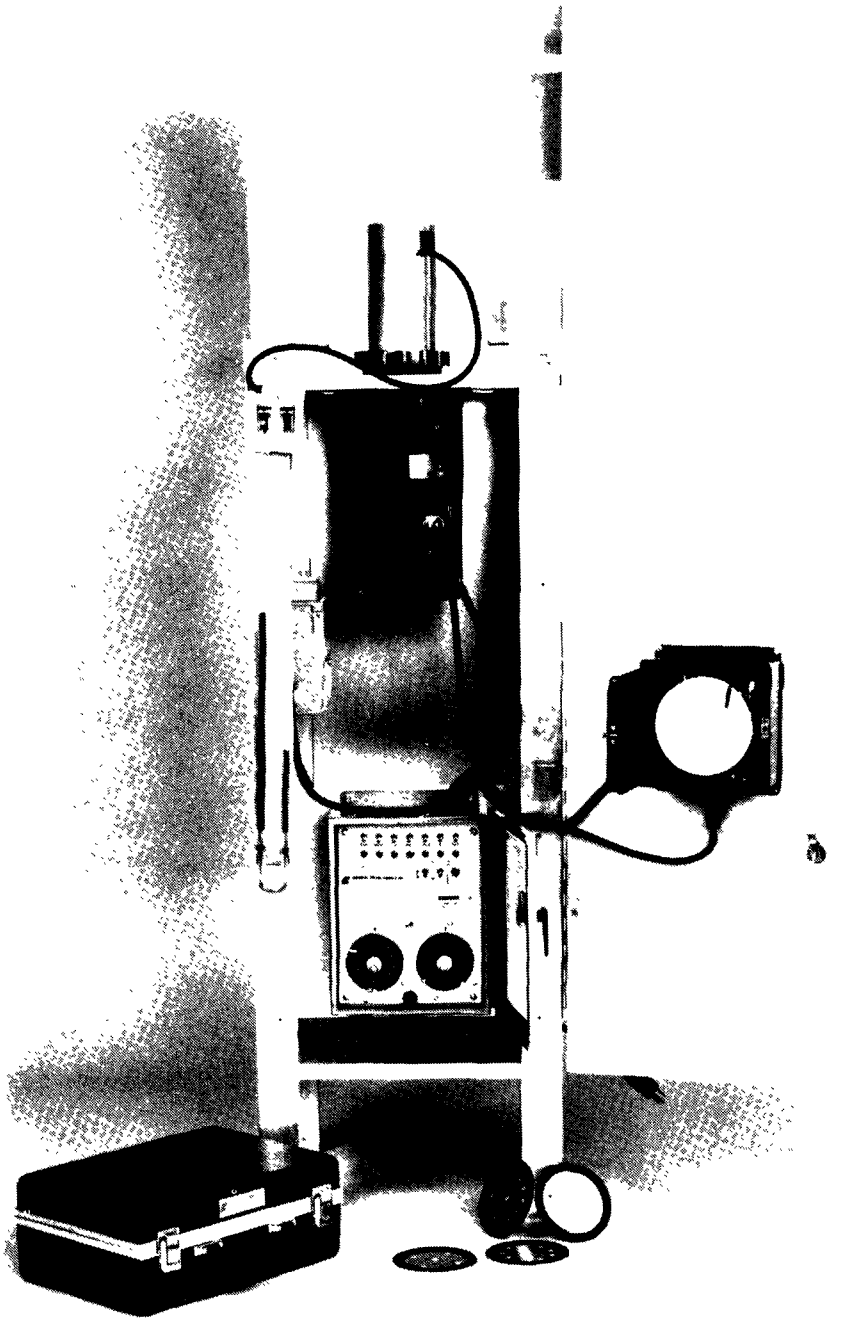


Figure 2.10 *High volume sampler and orifice unit assembled for calibration with flow recorder*

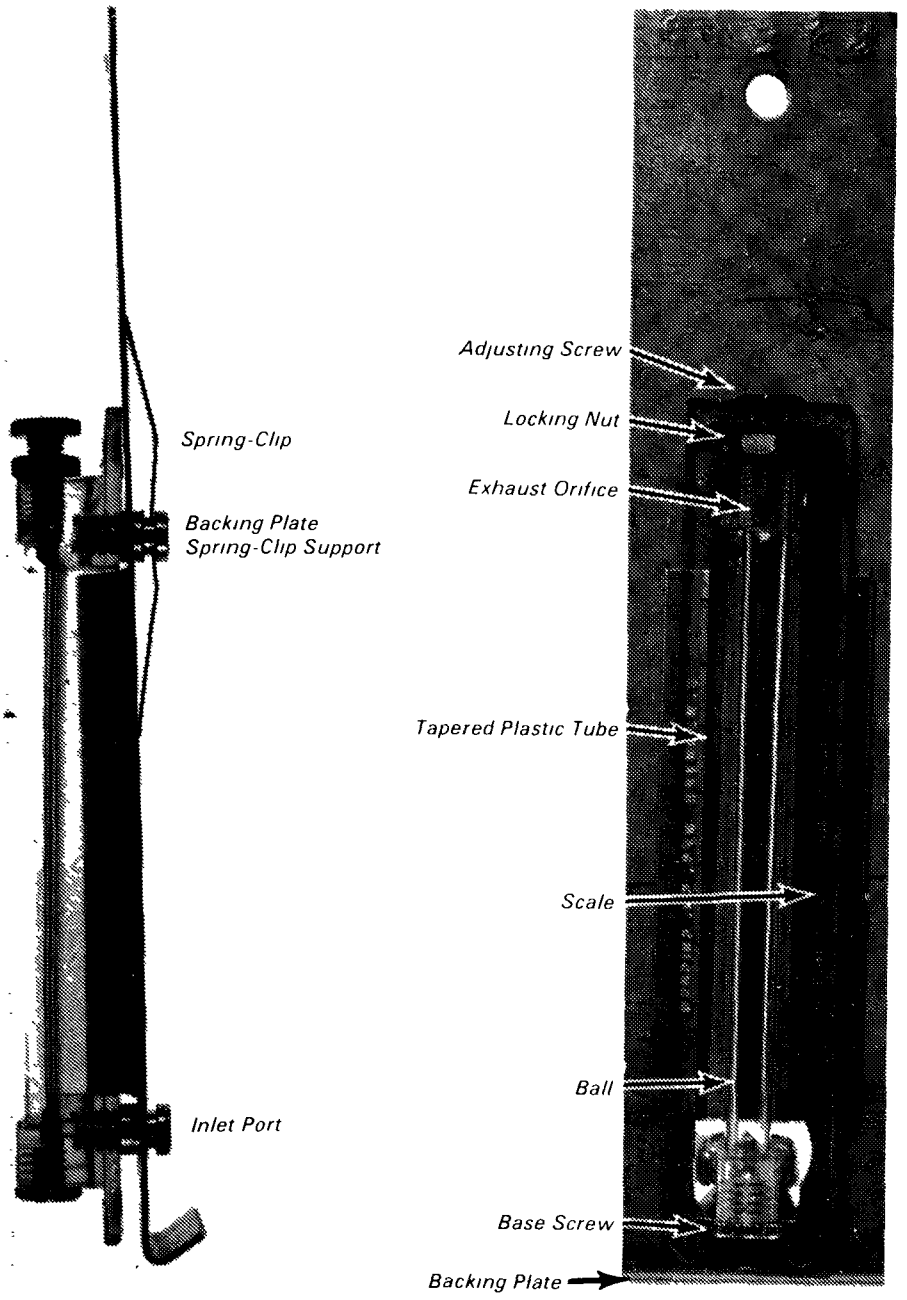


Figure 2.11. *Example of high volume sampler rotameter*

Table 2.2. Activity Matrix for Calibration of Equipment

Equipment	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Analytical balance	Indicated weight = true weight ±0.0005 g	Gravimetvic test-weighing at purchase and during periodic calibration checks; use three to five standard weights covering normal range of filter weights.	Have balance repaired and/or recalibrated
Relative humidity indicator	Indicator reading = psychrometer reading ±6%	Compare with reading of wet bulb/dry bulb psychrometer on receipt and at 6-mo intervals.	Adjust or replace to attain acceptance limits
On-off timer	±30 min/24 h	Check at purchase and quarterly with elapsed-time meter.	Adjust or repair
Elapsed-time meter	±2 min/24 h	Compare with a standard timepiece of known accuracy at receipt and at 6-mo intervals.	Adjust or replace time indicator to attain acceptance limits.
Flow-rate transfer standard	Indicated flow rate (from previous calibration) = actual flow rate ±2%	Check at receipt and at 1-yr intervals against positive-displacement standard volume meter; recalibrate or replace orifice unit if damage is evident.	Adopt new calibration curve.
Sampler	Indicated flow rate = actual individual calibration points ±5% of linearity	Calibrate with certified transfer standard on receipt, after maintenance on sampler, and any time audit deviates more than ±7%.	Recalibrate.

3.0 Filter Selection and Preparation

Suppliers of glass fiber filters for measurement of TSP have two grades of materials—the standard or traditional grade that has been in use for more than 20 years and a spectro-quality grade. Because the spectro-quality grade contains less organic and inorganic contaminants, it is recommended for use where additional chemical analyses are anticipated A filter with low surface alkalinity is preferred to avoid positive interferences from absorption of acid gases while sampling. Ideally, surface alkalinity should be between pH 6 5 and 7 5; however, most commercially available glass fiber filters have a pH of >7.5. Filters having a pH of between 6 to 10 are acceptable. An activity matrix for filter selection and preparation is presented as Table 3.1 at the end of this section.

3.1 Selection

Only filters having a collection efficiency of ≥99 percent for particles of 0.3-μm diameter (as measured by the DOP test ASTM-D2986-71) are to be used. The manufacturer should be required to furnish proof of the collection efficiency of a batch of new filters. The collection efficiency should be recorded in the procurement log, Figure 1.1 of Section 2 2.1.

Each filter should be visually inspected using a light table. Loose fibers should be removed with a soft brush. Discard or return to the supplier the filters with pinholes and other defects such as tears, creases, or lumps

3.2 Identification for Filters Not Numbered by the Supplier

A serial number should be assigned to each filter. The number should be stamped on two diagonally opposite corners—one stamp on each side of the filter Gentle pressure should be used in application to avoid damaging the filter.

3.3 Equilibration

Each filter should be equilibrated in the conditioning environment for 24 h before weighing to minimize errors in the weight; longer periods of equilibration will not affect accuracy. The conditioning environment temperature should be between 15° and 30°C (59° to 86°F) and should not vary more than ±3°C (5°F); the relative humidity (RH) should be <50% and not vary more than ±5%. A convenient working RH is 40%

3.4 Weighing

Clean filters are usually processed in lots—that is, several at one time. Clean filters must not be folded or creased prior to their weighing or use. Before the first filter is weighed, the balance should be checked by weighing a standard Class-S weight of between 3 and 5 g Actual and measured weights, the date, and the operator's initials should be recorded, as shown in Figure 2.1.

If the actual and measured values differ by more than ±0.5 mg (0.0005 g), the values should be reported to the supervisor before proceeding. If the actual and measured values agree within ±0.5 mg, each filter should be weighed to the nearest milligram Each filter should be weighed within 30 seconds after removing it from the equilibration chamber, and the tare weight and the serial number of each filter should be recorded in the laboratory log (Figure 3.1). Section 2.2.13 contains a blank copy of Figure 3.1 for the Handbook user. *Note:* Silicone-treated high volume filters have been found to have a static charge problem. This problem can be eliminated by placing an antistatic device containing a low-level alpha radiation source within the balance chamber. These devices are commercially available

3.5 Handling

A quantity of filters sufficient for a ≥3-mo period for each sampler should be numbered and weighed at one time. Pack the filters in their original container (or a box of similar size) so that each filter is separated by a sheet of 8½-by-11-in. tracing paper. Be sure the filters are stacked in the box in numerical order so that the operator will use the proper filter first.

In addition to the filters, the field operator should be supplied with preaddressed return envelopes to protect the filters during mailing; these can be printed front and back to serve as a sample record data form, as shown in Figure 3.2. Section 2.2.13 contains a blank copy of Figure 3.2 for the Handbook user.

Laboratory Log for Total Suspended Particulate Data

City Name: Notown, Ohio

Site Address: 600 South Street

State | Area | Site: 3 7 1

Project | Time | Year: 7 5

Instrument Last Calibrated: 6/4/75

Sampler Identification No: 0326

Project

The Interval

Total Suspended Particulate

Name Parameter Code

Sampling Date Month	Day	ST NR	Conc µg/m³	Filter Number	Average* CFM	Sampling Time	Air m³ Volume	Cross WCT	Tare WCT	Net WCT	Remarks
01	08	00	797	10004	49.4	14.37	1993.4	3.301	3.142	0.159	

*From Average Flow Determined from Calibration

Laboratory Functions

Filter Preparation

- Filter must be free of pinholes, tears, creases, lumps, etc
- Filter must be properly equilibrated (20 hrs <time<28 hrs, humidity <50%) (Δ Humidity ± 5% Δ Temp ± 3°C)
- Balance must be checked before weighing (STD WGT 3 to 5 g ±0 0005 g)

Sampling Analysis

- Sample must be free or evidence of malfunction, ten or fewer insects in sample
- Filter must be properly equilibrated (see above)
- Balance must be checked before weighing (see above)

All samples were handled in accordance with the above guidelines

A. J. Smith
Signature

Figure 3.1. Laboratory log for total suspended particulate data

Comments _____

_____

_____

_____

_____

_____

Hi-Vol Data Record

Project _____

Station _____

_____

_____

Site and/or Sampler No _____

SAROAD Site Code

Sample Date _____

Filter No _____

Flow Reading initial _____

final _____

Average Flow Rate _____

Running Time Meter initial _____

final _____

Total Sampler Time _____ *min*

Total Air Volume _____ *std m³*

Net TSP Weight _____ *g*

TSP Concentration _____ *μg/std m³*

Optional

	Temperature	*Barometric Pressure*
initial	_____	_____
final	_____	_____
average	_____	_____

Operator _____

Figure 3.2. *Hi-Vol field data form.*

Table 3.1. *Activity Matrix for Filter Selection and Preparation*

Activity	*Acceptance limits*	*Frequency or method of measurement*	*Action if requirements are not met*
Selection and collection efficiency	*Efficiency of >99% in 0.3-µm diameter particle collection*	*Manufacturer's proof of DOP test ASTM-D2986-71*	*Reject shipment or return to supplier*
Integrity	*No pinholes, tears, creases, etc.*	*Visual check of each filter with light table*	*Discard filter*
Identification	*Identification number in accordance with specifications*	*Visual check of each filter*	*Identify properly or discard filter*
Equilbration	*Equilibration in controlled environment for ≥24 h; constant humidity chamber with RH of <50% constant within ±5%, temperature between 15° and 30°C with less than ±3°C variation*	*The room or chamber conditions and the equilibration period are observed for each sample.*	*Repeat equilibration*
Weighing procedure	*Indicated filter weight determined to nearest mg within 30 s after removing from the equilibration chamber.*	*Observation of weighing procedure*	*Reweigh after re-equilibration*
Handling	*Filter in protective folder; envelopes undamaged*	*Visual check of each filter*	*Replace undamaged filters, discard damaged filters*

4.0 Sampling Procedure

The activity matrix presented as Table 4 2 at the end of this section summarizes the sample collection activities and the operational checks

4.1 Filter Installation

Care must be taken to assure that the clean weighed filters are not damaged or soiled prior to installation in the high-volume sampler They should be kept in a protective folder or box and must not be bent or folded The use of filter cassettes (Figure 4 1) that can be loaded and unloaded in the laboratory may be used to minimize damage to the filter Damaged or soiled filters must be discarded

The following procedures are used to install a filter

1 Open the shelter and remove the faceplate of the sampler by loosening the four wingnuts and swinging the bolts outward

2 Wipe all dirt from the support screen and faceplate.

3 Center the filter with the rough side up on the wire screen so that the gasket will form an airtight seal on the outer edge (1 cm) of the filter when the faceplate is in position. When aligned correctly, the edges of the filter will be parallel both to the edges of the screen behind it and to the faceplate gasket above it. Poorly aligned filters show uneven white borders (Figure 4.2) around the filter.

4 Tighten the four wingnuts just enough to prevent leakage when the filter is aligned and the faceplate is in place. Excessive tightening may cause the filter to stick or permanently damage the gasket.

5 Close the shelter and run the sampler for at least 5 min to establish run-temperature conditions.

6. Record the flow indicator reading and, if needed, the barometric pressure ($P_{3\ initial}$) and the ambient temperature ($T_{3\ initial}$), then stop the sampler. *Note.* No onsite pressure or temperature measurements are necessary if the sampler flow indicator does not require pressure or temperature corrections (e g., a mass flowmeter) or if average barometric pressure and seasonal average temperature for the site have been incorporated into the sampler calibration. For individual pressure and temperature corrections, the ambient pressure and temperature at the time of the flow indicator reading can be obtained by onsite measurements or from a nearby weather station. Barometric pressure readings obtained from airports must be station pressure, not corrected to sea level, and may need to be corrected for differences in elevation between the sampler site and the airport. For samplers having flow recorders but not constant flow controllers, the average temperature and pressure at the site *during the sampling period* should be estimated from U S Weather Bureau or other available data.

7. Determine the flow rate from the sampler's calibration relationship (Subsection 4.4) to verify that it is operating within the acceptable range of 1.1 to 1.7 m^3/min (39-60 ft^3/min). If not within this range, use a different filter or adjust the sampler flow rate *Warning:* Substantial flow adjustments may affect the calibration of orifice-type flow indicators and may necessitate their recalibration

8. Record the sample identification information (filter number, site location or identification number, sample date) and the initial flow rate (or flow indicator reading and temperature and barometric pressure if needed) on the Hi-Vol field data form (Figure 4.3). See Subsection 4.7 for proper documentation.

9. Set the timer to start and stop the sampler such that the sampler runs 24 hours, from midnight to midnight local time.

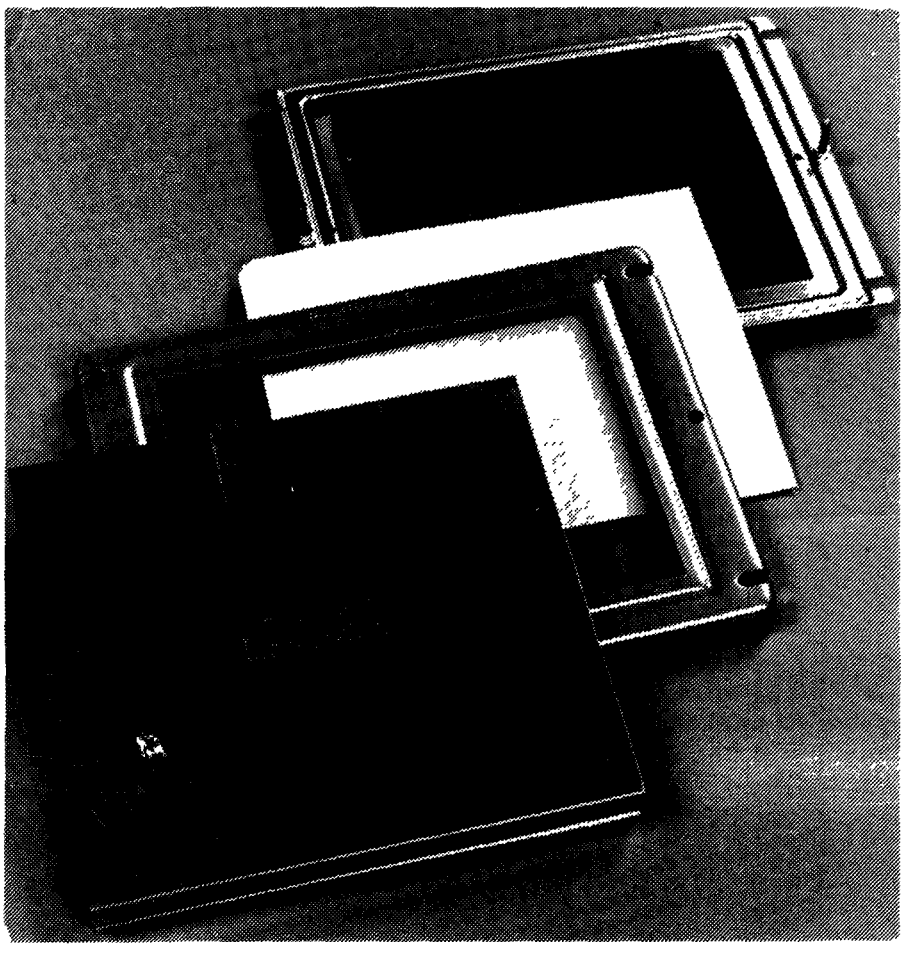


Figure 4.1 *High volume sampler filter cartridge assembly*

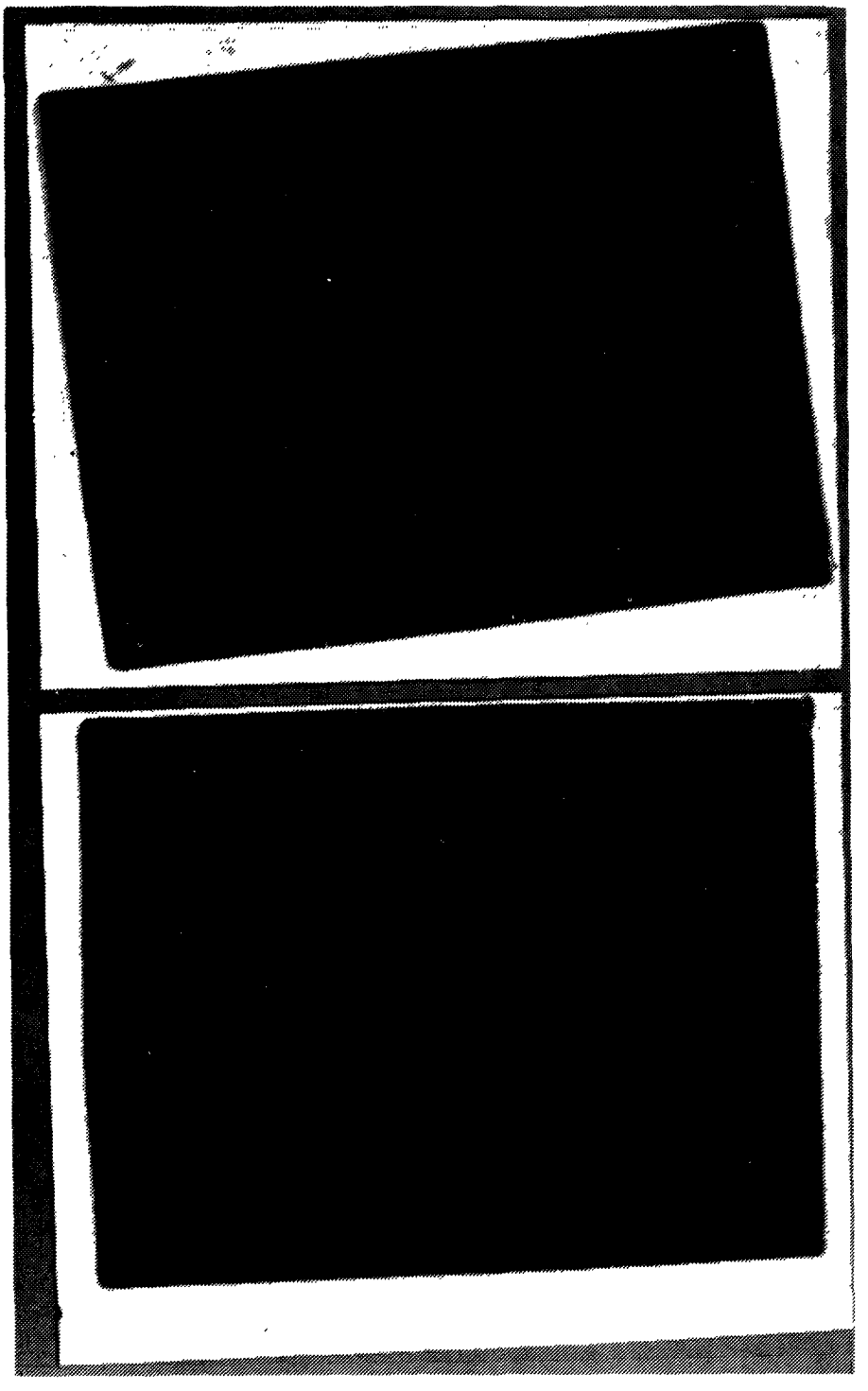


Figure 4.2. Nonuniform borders resulting from poorly aligned filters

4.2 Retrieval of Exposed Filter and Post-Sampling Checks

1. As soon as practical following the sampling period, run the sampler for at least 5 min to reestablish run-temperature conditions.

2. Record the flow indicator reading and, if needed, the barometric pressure ($P_{3\ final}$) and the ambient temperature ($T_{3\ final}$)

3. Stop the sampler, remove the faceplate, and lift the exposed filter from the supporting screen by grasping it gently at the ends, not at the corners.

4. Check the filter for signs of air leakage. Leakage may result from a worn faceplate gasket (Figure 4 4) or from an improperly installed gasket. If signs of leakage are observed, void the sampler, determine the cause, and take corrective actions before starting another sampling period A gasket generally deteriorates slowly; thus the operator can decide well in advance (by the increased fuzziness of the sample outline) when to change the gasket before a total failure results

5. Visually inspect the gasket face to see if glass fibers from the filter are being left behind due to overtightening of the faceplate wingnuts and the consequent cutting of the filter along the gasket interface.

6. Check the exposed filter for physical damage that may have occurred during or after sampling. Physical damage after sampling would not invalidate the sample if all pieces of the filter were put in the folder; however, sample losses due to leakages during the sampling period or losses of loose particulates after sampling (e.g , loss when folding the filter) would invalidate the sample, so mark such samples "void" before forwarding them to the laboratory.

7. Check the appearance of the particulates Any changes from normal color, for example, may indicate new emission sources or construction activity in the area. Note any change on the filter folder along with any obvious reasons for the change.

8. Fold the filter lengthwise at the middle with the exposed side in; if the collected sample is not centered on the filter (i.e , the unexposed border is not uniform around the filter), fold so that only the deposit touches the deposit Results of an improperly folded filter are illustrated in Figure 4 5, where smudge marks from the deposit extend across the borders; this can reduce the value of the sample if the analyses for which the sample was collected need to be divided into equal portions.

9. Place the filter in its numbered folder.

10. Determine the final flow rate from the sampler's calibration relationship (see Subsections 4.3 and 4.4) and record it on the data record along with other pertinent information (see Figure 4.3).

11. Remove the sampler's flow recorder chart and place the chart inside the filter folder with the inked side against the folder and the backside against the filter.

4.3 Flow Readings

4.3.1 *Rotameters* - To obtain a valid measurement, make flow rate

Hi-Vol Data Record

Project SPECIAL STUDY

Station 4278 ELM ST.
SMITHFIELD, CAL

Site and/or Sampler No. 12

SAROAD Site Code

Comments
CITY CONDUCTED STREET
CLEANING ON DAY
SAMPLE WAS COLLECTED.

Sample Date 5-23-73

Filter No 14876

Flow Reading initial 1.32 m^3
final 1.28 m^3

Average Flow Rate 1.30 std m^3

Running Time Meter initial 0000
final 1438

Total Sampler Time 1438 *min*

Total Air Volume 1869.4 *std m³*

Net TSP Weight 0.1402 *g*

TSP Concentration 75 *µg/std m³*

Optional

	Temperature	*Barometric Pressure*
initial		
final		
average (seasonal)	20°C	740 m^3

Operator SONIA FELIX

Figure 4.3. *Example of completed Hi-Vol field data form.*

measurements while the sampler is at normal operating temperature, after a warmup time of ≥5 min.

1. Connect the rotameter to the sampler with the same tubing used during calibration, and place or hold it in a vertical position at eye level.

2. Read the widest part of the float (ball), and use the calibration relationship (see Subsection 4.4) to convert the reading to Q_{std} (m^3/min) and record to the nearest 0.02_{std} m^3/min.

3. Measure the flow rates at the beginning and end of each sampling period. Observe the flow rate for ≥1 min after connecting the rotameter to the sampler before taking a reading. If a gradual change in flow rate is observed, do not take a reading until equilibrium is reached; a gradual change is usually observed when the rotameter is at a substantially different temperature from that of the sampler exhaust air, and thus equilibration may require 2 or 3 min.

4.3.2 *Flow Recorders* - The following procedure is for a high-volume sampler equipped with a flow recorder.

2. Remove any moisture by wiping the inside of the recorder case with a clean cloth. Carefully insert the new chart into the recorder without bending the pen arm beyond its limits of travel. An easy way to do this is to raise the pen head by pushing in on the very top of the pen arm with the right hand while inserting the chart

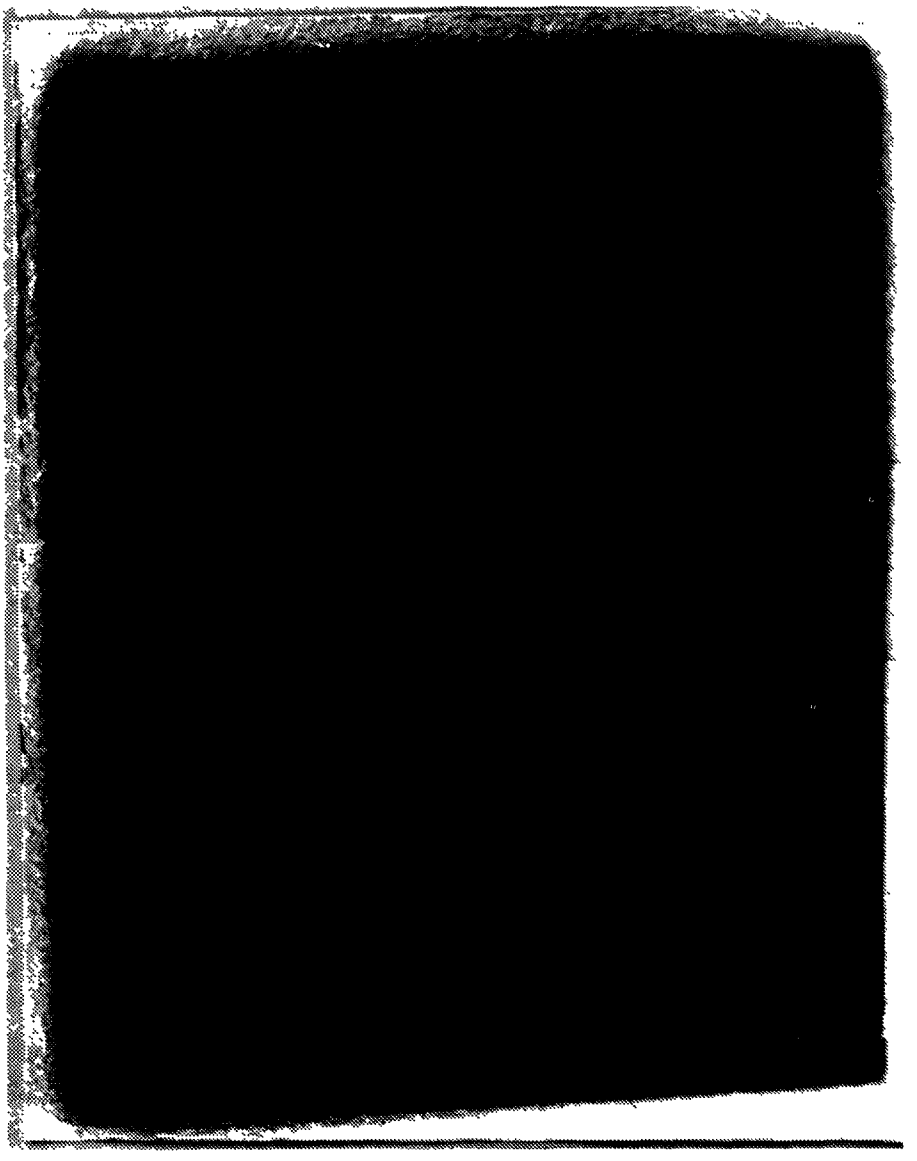


Figure 4.4. Example of air leakage around the filter due to worn faceplate gasket or to improper installation

with the left hand. Be careful not to damage or weaken the center tab on the chart, but be sure the tab is centered on the slotted drive so that the chart will rotate the full 360 degrees in 24 h without binding or slipping. A properly installed chart is shown in Figure 4.6.

3. Check to see that the pen head rests on zero (i.e., the smallest circle diameter on the chart). If not, tap the recorder lightly to make certain that the pen arm is free.

4. Check the time indicated by the pen. If it is in error, rotate the chart clockwise by inserting a screwdriver or coin into the slotted drive in the center of the chart face until the time is correct. If the sampler is started with a timer switch, the correct time is the starting time on the timer (usually midnight).

5. Using an eyedropper, put a small amount of ink into the hole in back of the pen tip. Use of cartridge-type pens will minimize problems with inking.

6. Turn the sampler on (never turn it on until a filter is in place because the transducer and recorder may be damaged), and observe it long enough to know whether the transducer and recorder are operating properly

4.4 Determination of Flow Rates

High-volume sampler flow rate readings must be converted to units of std m^3/min (25°C, 760 mm Hg) for use in calculating TSP concentrations. Expressions for converting sampler flow rate readings (I) to standard conditions are given in Table 4 1 Instructions for the use of this table and the flow measuring device calibration relationships (Figures 2 8 or 2 9) to obtain the sampling flow rate Q_{std} (m^3/min) are given in Subsections 4.4 1 and 4 4 2

No onsite pressure or temperature measurements are necessary if the sampler flow indicator does not require pressure or temperature corrections (e g., a mass flowmeter) of if average barometric pressure and seasonal average temperature for the site have been incorporated into the sampler calibration For individual pressure and temperature corrections, the ambient pressure and temperature at the time of flow indicator reading can be obtained by onsite measurements or from a nearby weather station. Barometric pressure readings obtained from airports must be station pressure, not corrected to sea level, and may need to be corrected for differences in elevation between the sampler site and the airport For samplers having flow recorders but not constant flow controllers, the average temperature and pressure at the site during the sampling period should be established from Weather Bureau or other available data

4.4.1 *Samplers Without Continuous Flow Recorders* - For a sampler without a continuous flow recorder, determine the appropriate expression to be used (from Table 4 1) corresponding to the one used in calibration (from Table 2 1) Using this appropriate expression, determine Q_{std} for the initial flow rate from the sampler calibration curve, either graphically or from the transposed regression equation (see Figure 2 8)·

$$Q_{std} = \frac{1}{m}\left([\text{Appropriate expression from Table 4 1}] - b\right) \qquad \text{Equation 4-1}$$

Similarly, determine Q_{std} from the final flow reading, and calculate the average flow Q_{std} as one-half the sum of the initial and final flow rates.

4.4.2 *Samplers With Continuous Flow Recorders* - For a sampler with a continuous flow recorder, determine the average flow rate reading (I) for the period Determine the appropriate expression from Table 4.1 corresponding to the one used in calibration (from Table 2.1) Then using this expression and the average flow rate reading, determine Q_{std} from the sampler calibration relationship, either graphically or from the

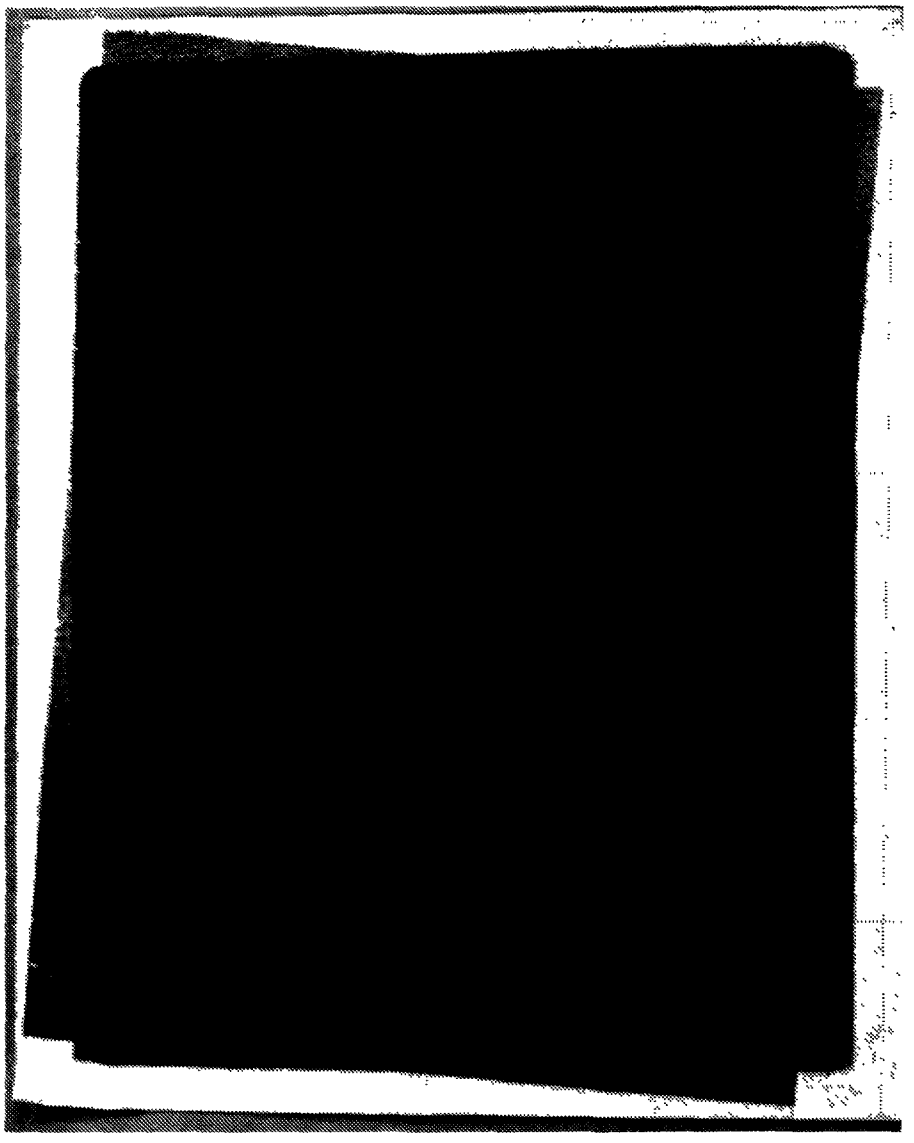


Figure 4.5. Example of smudged filter border resulting from an improperly folded filter.

Table 4.1. Expressions for Determining Flow Rate During Sampler Operation

Type of sampler flow rate measuring device	Expression: For actual pressure and temperature corrections	Expression: For use when geographic average pressure and seasonal average temperature have been incorporated into the sampler calibration
Mass flowmeter	1	1
Orifice and pressure indicator	$\sqrt{1\left(\frac{P_3}{P_{std}}\right)\left(\frac{298}{T_3}\right)}$	$\sqrt{1}$
Rotameter, or orifice and pressure recorder having square root scale*	$1\sqrt{\left(\frac{P_3}{P_{std}}\right)\left(\frac{298}{T_3}\right)}$	1

*This scale is recognizable by its nonuniform divisions and is the most commonly available for high-volume samplers

transposed regression equation (see Figure 2.8 and Equation 4-1 above):

If the trace shows substantial flow change during the sampling period, greater accuracy may be achieved by dividing the sampling period into intervals, calculating an average reading for each interval, determining Q_{std} for each interval, and finally computing the average Q_{std} for the whole sampling period.

Calculate the total air volume sampled by the following equation:

$$V = Q_{std}\, t \quad \text{Equation 4-2}$$

where:

V = total air volume sampled, in standard volume units (std m^3);

Q_{std} = average standard flow rate, std m^3/min;

t = sampling time, min.

4.5 Sampling Flow Rate Checks

The two types of sampling flow rate checks recommended are discussed in the following Subsections (4.5.1 and 4.5.2).

4.5.1 *Initial Flow Rate Check* - Initial flow rate measurements should be monitored for each sampler to determine whether corrective action is needed.

1. Record the initial and final flow rates for each sample in the log book maintained with the sampler. A sampler equipped with a continuous recorder should be observed for at least 5 min. before the initial flow rate is recorded.

2. Average the initial flow rate measurements for the first four samples after each calibration. Check future initial flow rates that deviate more than ±10% from this average for samplers on which a manometer or a flow recorder is used and ±15 percent for samplers on which a rotameter is used. If the change has been gradual over time, recalibrate. If large deviations occur between successive samples, repeat the flow reading after 5 minutes. If the second reading is within the above limits, continue normal operations; if not, check the line voltage and/or replace the filter

3. Perform a calibration check if neither of the above checks identifies the trouble. If the calibration check is satisfactory, continue normal operations; if not, perform a complete calibration

4.5.2 *Operational Flow Rate Check* - It is recommended that a one-point operational flow check be made on each sampler at least once every 2 weeks. The purpose of this check is to

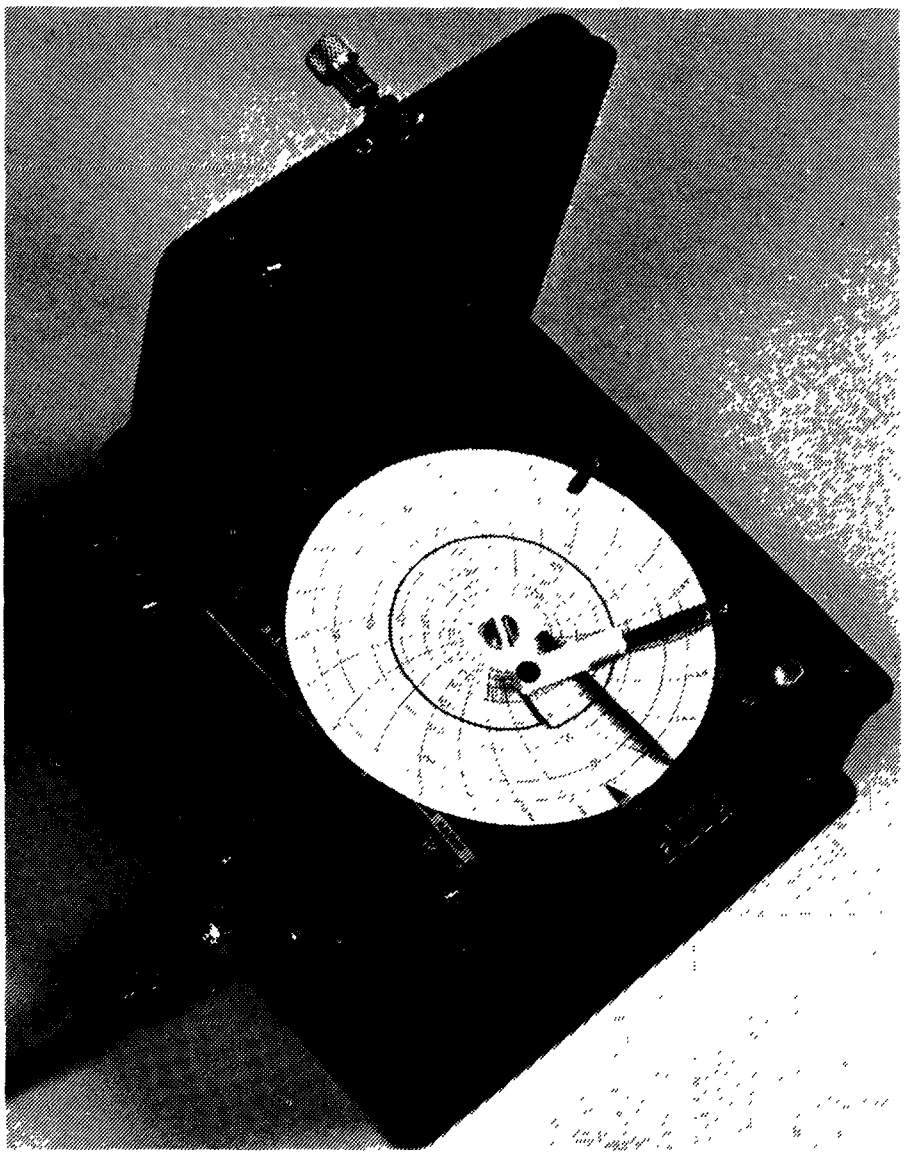


Figure 4 6 Flow rate recorder with chart installed

track the in-control conditions of the sampler calibration The same flow rate transfer standard used to calibrate the high-volume sampler may be used for the operational flow check

1 Operate the sampler at its normal flow rate with flow check device in place Determine Q_{std} for the check point from the calibration of the flow check device, and determine the measured flow rate from the sampler's calibration (see Subsections 4 3 and 4 4) Use the following procedure for plotting the check data

2 Calculate the percentage difference (% D) between the known check flow measurement and the flow measured by the sampler's normal flow indicator (Equation 4-1) Let Q_a represent the known flow rate and Q_m the measured flow rate for the flow check

$$\% D = \left(\frac{Q_m - Q_a}{Q_a}\right) 100$$

Equation 4-3

Thus if Q_m = 1.48 m^3/min and Q_a = 1 42 m^3/mm then

$$\% D = \left(\frac{1.48 - 1\ 42}{1.42}\right) 100 = +4\%$$

If the % D is not within ±7 percent for any one check, recalibrate before resuming the sampling

3 Record the Q_m, the Q_a, and the % D on an $\bar{X}$-and-R chart (Figure 4 7) under "Measurement Result, Items 1 and 2 " Record the % D in the cells preceded by the "Range R " The % D can be positive or negative, so retain the sign of the difference, since it may indicate trends and/or consistent biases More information on the construction of a quality control chart and the interpretation of the results are in Appendix H, Volume I of this Handbook [2]

4. Repeat the above for each operational flow rate check, plot all points on the chart, and connect the points by drawing connecting lines Tentative limits are ±4 7 percent (warning lines) and ±7 percent (out-of-control lines) Out-of-control points indicate possible problems in calibration or instrument errors When out-of-control results are obtained, recalibrate the sampler prior to further sampling After 15 to 20 points are plotted, new control and warning limits may be derived, as described in Appendix H of Volume I of this Handbook.[2] Do not increase the control and warning limits, however, more stringent limits may be established

5 Forward the $\bar{X}$-and-R chart to the QA supervisor for review

4.6 Time Measurements

Start and stop times for samplers not equipped with a timer switch or an elapsed-time meter are recorded by the operator who starts and stops the sampler If more than one operator is involved, each should set his/her watch to a common reference to achieve accurate times, such a reference could be an office clock that is checked daily or the local telephone company, which gives the time of day The time measurement procedure is as follows

1 Take the start and stop times for samplers equipped with timer switches from the timers' start and stop settings

2 Check the timer clock, and set it, if necessary, for the correct times at each filter change

3 Use an elapsed-time meter to determine the number of minutes sampled because timers cannot be set or read to within less than ±30 min

4.7 Documentation

The following information should be recorded on the filter folder or on a field data record form (Figure 4 3) by the persons indicated, and it should be verified with a signature

4.7.1 *The Operator Who Starts the Sample*

1 Station location
2 Project number
3 Site number
4 Sampler ID number
5 Filter number

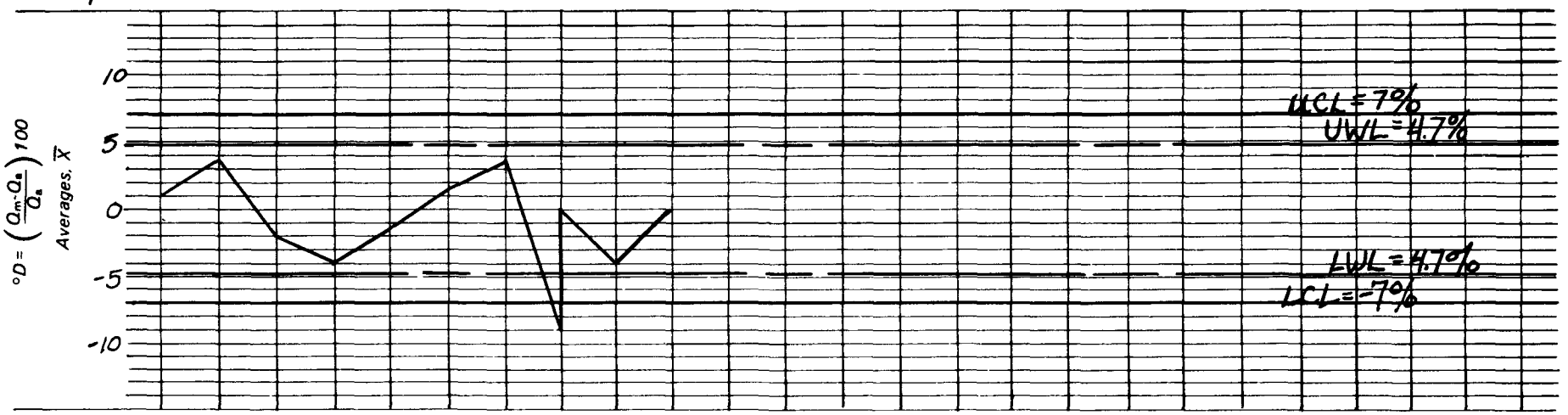
Project Name: Operational Flow Rate Check

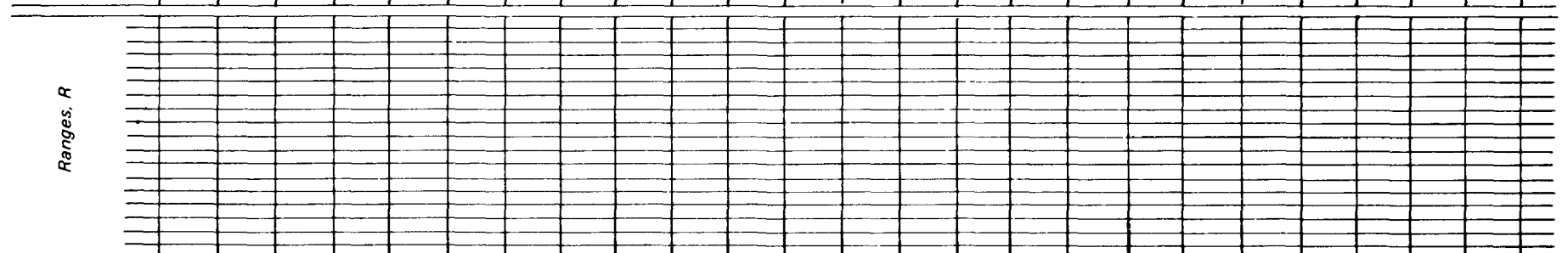
Measurement: $\bar{X}$, %D=100(Qm-Qa)/Qa

Performed: % accuracy in routine and audited measurements

Measurement Units: Qm, Qa in cfm,

		Date	2/4	2/26	3/10	3/25	4/7	4/22	5/6	5/29	6/9	6/30		
Measured Actual Measurement	Code	1												
		2												
		3												
	Result	1	60	55	54	54	58	60	56	50	53	56		Qm
		2	59	53	55	56	59	59	54	55	55	56		Qa
		3												
Sum														
Average, $\bar{X}$														
Range, R		%D	1.7	3.8	-1.8	-3.6	-1.7	1.7	3.7	-9.1	-3.6	0		





Comments (Correct Action, etc.)								Recalibration done																		

Figure 4.7. Quality control chart for operational flow check

6 Sample date
7 Initial flow reading (if using rotameter) and/or initial temperature and barometric pressure if required
8. Unusual conditions that may affect the results (e.g., subjective evaluation of pollution that day, construction activity, meteorology)
9 Signature.

4.7.2 *The Operator Who Removes the Sample*
1 Elapsed time
2. Final flow reading (or be sure that the flow rate chart accompanies the sample) and final temperature and barometric pressure if required
3. Existing conditions that may affect the results
4. Signature

4.7.3 *The Operator Who Transfers the Sample to the Laboratory Record*
1. Receiving date initialed
2. Shipping date initialed

Table 4.2. *Activity Matrix for Sampling Procedure*

Activity	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Filter installation	*Filter rough side up, centered on screen, edges parallel to edges of screen and to faceplate gasket, gasket tightened to prevent leakage*	*Visually check each exposed filter.*	*Void the filter; install substitute filter*
Flow checks	*1) Sampler flow rate within acceptable range of 1 1 to 1.7 m^3/min (39-60 ft^3/min) 2) Stabilized initial flow rate = established initial flow rate ±10% for pressure transducer or ±15% for rotameter*	*Check flow rate at each filter change*	*1) Determine cause of flow problem and correct; measure line voltage, change the filter, check calibration and calibrate sampler.*
Elapsed time	*3) Sampling time 24 ±1 h*	*Check on and off settings of timers*	*Reset timer*
Sample handling	*No evidence of malfunction in post-sampling check*	*Visually check each sample for tears, missing pieces, or leakage*	*Void the sample; correct the cause of malfunction.*
Documentation	*Names, sampling dates, times; sample, filter, and station numbers; unusual conditions, flow rates, and handling dates recorded on sample envelope*	*Visually check each sample data record*	*Complete or correct the documentation; if unavailable, void the sample.*

5.0 Analysis of Samples

A matrix summarizing the major quality assurance activities for sample analyses is presented as Table 5.1 at the end of this section.

5.1 Sample Documentation and Inspection

Upon receipt of the sample from the field the following procedure should be followed:

1. Remove the filter folder from its shipping envelope and examine the Hi-vol Field Data Record (Figure 4.3) to determine whether all data needed to verify the sample and to calculate the concentration have been provided. Void the sample if data are missing and unobtainable from the field operator or if a sampler malfunction (e.g., faceplate gasket leakage) is evident.
2. Record the filter number on the Hi-vol Field Data Record and on the Laboratory Data Log (Figure 3.1).
3. Examine the shipping envelope. If sample material has been dislodged from the filter, recover as much as possible by brushing it from the envelope onto the deposit on the filter with a soft camel's-hair brush.
4. Examine the filter. If insects are embedded in the sample deposit, remove them with Teflon-tipped tweezers, but disturb as little of the sample deposit as possible. If more than 10 insects are observed, refer the sample to the supervisor for a decision to accept or reject it
5. Record the data verification, the sample inspection, and removal of insects under "Remarks" in the Laboratory Data Log

5.2 Filter Equilibration

The following procedure should be used to equilibrate the exposed filters in a conditioning environment for 24 h; up to 48 h may be needed for very damp filters.

1 Use an eqilibration chamber with a desiccant or an environmentally controlled weighing room to maintain an RH of <50 percent at 15° and 30°C (59° to 86°F) An air-conditioned room may be used for equilibration if it can be maintained at an RH of <50% that is constant within ±5% and an air temperature between 15° and 30°C that is constant within ±3°C (5°F) while the filters are equilibrating A convenient working RH is 40 percent. Keep a hygrometer in the room

2. Check the RH daily

3 Record the hygrometer readings and any equilibration chamber malfunctions, discrepancies, or maintenance in the Laboratory Data Log.

5.3 Gravimetric Analysis

A balance check should be performed as specified in Subsection 2 1

1 Weigh the exposed filters to the nearest milligram (mg) on the analytical balance.

2 Weigh the filters in the conditioning environment if practical; if not, be sure that the analytical balance is as close as possible to the conditioning chamber where it is relatively free of air currents and where it is at or near the temperature of the chamber. Weighing should take place within 30 seconds after removing filters from the equilibration chamber

3. Record the weight in the Laboratory Data Log and on the High Volume Field Data Record.

Table 5.1. *Activity Matrix for Analysis of Samples*

Activity	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Documentation verification and sample inspection	*Complete documentation; no evidence of malfunction or sample loss; ≤10 insects in sample*	*Visually check all samples and documentation.*	*Void the sample*
Filter equilibration	*Controlled environment for ≥24 h; RH <50% within ±5%; temperature constant within ±3°C at 15° to 30°C (59° to 86°F)*	*For each sample, observe room or chamber conditions and equilibration period.*	*Repeat equilibration for 24 h at properly controlled conditions*
Gravimetric analysis	*Indicated weight obtained to nearest milligram within 30 s after removal from equilibration chamber*	*Observe filter weighing*	*Report to supervisor; reweigh after equilibration for 24 h at controlled conditions.*

6.0 Calculations of TSP Concentrations and Data Reporting

A matrix summarizing the quality control activities for the calculations and the data-reporting requirements is presented in Table 6 1

6.1 TSP Concentration

Equation 6-1 should be used to calculate the total air volume sampled

$$V = Q_{std}\, t \quad \text{Equation 6-1}$$

where

V = Total air volume sampled, in standard volume units, std m^3;

Q_{std} = average standard flow rate, std m^3/min;

t = sampling time, min

Equation 6-2 should be used to calculate the TSP sample concentration.

$$TSP = \frac{(W_f - W_i)10^6}{V} \quad \text{Equation 6-2}$$

where

TSP = concentration of TSP, $\mu g/std\ m^3$,

W_f = weight of exposed filter, g

W_i = tare weight of filter, g

All original calculations should be recorded in the Laboratory Data Log (Figure 3.1).

6.2 Data Documentation and Reporting

All daily concentration levels should be recorded in micrograms per standard cubic meter ($\mu g/std\ m^3$), with the required identifying information, on the SAROAD Daily Data form (Figure 6.1). See AEROS User's Manual, OAQPS No. 1.2-039, for detailed instructions.

Table 6.1. *Activity Matrix for Calculations and Data Reporting*

Activity	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Sample volume and concentration	*All needed data available*	*Visually check data records for each sample.*	*Void the sample.*
Data documentation and reporting	*Complete documentation for calculation of concentration; all sample and data identification numbers matched; no evidence of malfunction or sample loss; all needed data available*	*Visually check data record and data log for each sample.*	*Void the sample.*

24-Hour or Greater Sampling Interval

[2] Smelter Town Pollution Control
1 Agency

Smelter Town
City Name

400 North Street
Site Address

TSP 24 hour
Project Time Interval

State	Area	Site
46	09000	01
2 3	4 5 6 7 8	9 10

Agency	Project	Time	Year	Month
P	02	7	76	02
11	12 13	14	15 16	17 18

Name PARAMETER Code	Name PARAMETER Code	Name PARAMETER Code	Name PARAMETER Code
TSP			
11101			
23 24 25 26 27	37 38 39 40 41	51 52 53 54 55	65 66 67 68 69

Day	St Hr			
01	01	0		
28 29	30 31	32	42 43 44 45 46	56 57 58 59 60	70 71 72 73 74

19 20	21 22	33 34 35 36	47 48 49 50	61 62 63 64	75 76 77 78
	00	0078			
	00	0095			
DP→	4 3 2 1 0	4 3 2 1 0	4 3 2 1 0	4 3 2 1 0

Figure 6.1. SAROAD daily data form.

7.0 Maintenance

Scheduled or preventive maintenance of the sampling equipment reduces voided samples, downtime, and remedial maintenance Because the sampling equipment is operated only intermittently, the frequency of maintenance is a function of the actual hours of use. Normally, two or three preventive maintenance activities are required each year When possible, maintenance is best performed in the laboratory rather than in the field. Motors on which maintenance has been performed can then be carried to the field for installation and calibration. Table 7 1 at the end of this section summarizes the quality assurance activities of major maintenance checks. All maintenance activities should be recorded in a log book

7.1 Sampler Motor

Motor brushes usually require replacement after 400 to 500 h of operation at normal line voltage (115 V) The procedure is as follows.

1. Replace the brushes before they are worn to the point that damage can occur to the commutator of the Hi-Vol motor The optimum replacement interval must be determined from experience
2. Follow the manufacturer's instructions for replacing the brushes.
3. Recalibrate the high-volume sampler after the brushes are replaced Do not recalibrate the motor until after an initial break-in period for the proper seating of the brushes against the armature; this period usually requires running the sampler for several hours against a resistance equivalent to a clean filter or a No. 18 calibration plate.
4. Refer to the flow diagram in Figure 7.1 for the various steps required for motor maintenance
5. Record all sampler maintenance operations (with dates performed and the operator's initials) in the sampler log book and on a gummed label (Figure 7 2) attached to the sampler

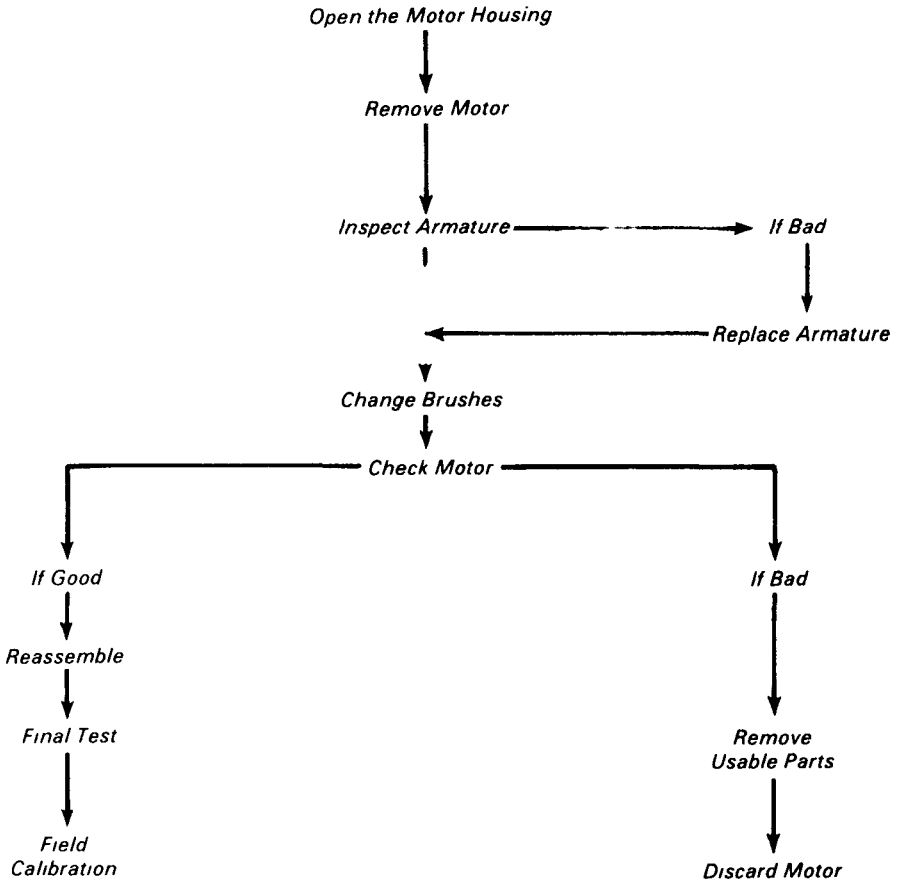


Figure 7.1. Flow diagram for high volume sampler motor maintenance

7.2 Faceplate Gasket

A worn faceplate gasket is characterized by a gradual blending of the interface between the collected particulates and the clean filter border Any decrease in the sharpness of this interface indicates the need for a new gasket.

1 Remove the old gasket with a knife.

2. Clean the surface properly.

3 Seal a new gasket to the faceplate with rubber cement or double-sided adhesive tape.

Hi-vol motor number _____

Site location _____

Last maintenance _____

Last calibration _____

Checked by _____

Next maintenance due _____

Next calibration due _____

Figure 7.2. Example of a gummed label for a high-volume sampler.

4. Record all gasket replacements with dates and operator's initials in the sampler log book

7.3 Rotameter

1. Clean and recalibrate the rotameter of a sampler when the float behaves erratically or when moisture or foreign matter is detected in the rotameter.
2. Clean the rotameter prior to routine calibration (alcohol is a satisfactory cleaning solvent).
3. Refer to the flow diagram (Figure 7.3) for the required maintenance steps.

7.4 Sampling Head

Leaks in the sampling head occur infrequently. The welded seams and the condition of the guide pins on the top surface of the head should be visually checked initially. Should a

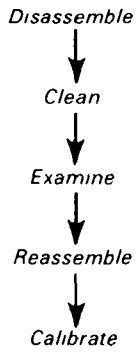


Figure 7.3. Maintenance sequence for rotameter

defect be suspected, the following procedure should be followed:

1. Assemble the sampling head to the motor
2. Install a filter for resistance
3. Apply a soap solution to the suspect problem area
4. Disassemble the sampling head.
5. Examine the inside of the head for soap bubbles
6. Repair or discard the sampling head if a leak is indicated by soap solution being inside of the head

7.5 Motor Gaskets

Two gaskets are used with each sampler motor The top rubber gasket is approximately 3/16-in. thick and the bottom foam rubber gasket is approximately 3/4-in. thick

1. Inspect both gaskets for wear or deterioration
2. Replace if necessary.

7.6 Flow Transducer and Recorder

Routine maintenance is not required for this device. Should a malfunction occur, replace the old recorder with a new one.

Table 7.1. Activity Matrix for Maintenance

Equipment	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Sampler motor	*400-500 h of motor brush operation; no malfunction*	*Visually check upon receipt and after each 400 h of operation.*	*Replace motor brushes; perform other maintenance as indicated.*
Faceplate gasket	*No leaks at the filter seal*	*Visually check after each sampling period.*	*Replace the gasket.*
Rotameter	*No foreign materials; stable operation*	*Visually check at each reading.*	*Clean; replace if damaged.*
Motor gaskets	*Leak-free fit*	*Visually check after each 400 h of operation.*	*Replace gaskets.*
Sampling head	*No leaks*	*Visually check after each 400 h of operation.*	*Replace sampling head.*

8.0 Auditing Procedure

An audit is an independent assessment of the accuracy of data *Independence is achieved by having the audit made by an operator other than the one conducting the routine measurements and by using audit standards and equipment different from those routinely used in monitoring.* The audit should be a true assessment of the accuracy of the measurement process under normal operation—that is, without any special preparation or adjustment of the system Routine quality assurance checks by the operator are necessary for obtaining good quality data, but they are not part of the auditing procedure.

Three performance audits and one systems audit are detailed in Subsections 8.1 and 8.2. These audits are summarized in Table 8 2 at the end of this section. See Sections 2.0.11 and 2 0 12 of this volume for detailed procedures for systems audits and performance audits, respectively

Proper implementation of an auditing program serves a two-fold purpose: to ensure the integrity of the data and to assess the accuracy of the data A technique for estimating the accuracy of the data is given in section 2.0 8 of this volume

8.1 Performance Audits

Performance audits conducted by another operator/analyst provide a quantitative evaluation of the quality of the data produced by the total measurement system (sample collection, sample analysis, and data processing). Performance audits of three individual portions of the total measurement system are recommended

1. Flow rate calibration
2. Exposed filter reweighing
3. Data processing.

8.1.1 *Audit of Flow Rate Calibration* - The frequency of audits of the flow rate depends on the use of the data (e.g., for PSD[3] air monitoring or for SLAMS[4]). It is recommended that the flow rate of each high-volume sampler be audited each quarter. Any type flow-rate transfer device acceptable for use in calibration of high-volume samplers may be used as the audit flow-rate reference standard, however, the audit standard must be different from the standard used to calibrate the high-volume samplers. The audit standard must be calibrated with a positive-displacement standard volume meter (i.e , Roots meter) traceable to the National Bureau of Standards See Subsection 2 2 for procedures used to certify flow rate transfer standards

With the audit device in place, the high-volume sampler should be operated at its normal flow rate The differences in flow rate (in std m^3/min) between the audit flow measurement (X) and the flow indicated by the sampler's normal flow indicator (Y) are used to calculate accuracy as described in Section 2 0 8 of this volume

Great care must be taken in auditing high-volume samplers having flow regulators because the introduction of the audit device can cause abnormal flow patterns at the point of flow sensing. For this reason, the orifice of the flow audit device must be used with a normal glass fiber filter in place (and without resistance plates) in auditing flow-regulated high-volume samplers, or other steps should be taken to assure that flow patterns are not disturbed at the point of flow sensing

Detailed procedures and forms used to perform flow rate audits are given in Section 2 0.12 of this volume

8.1.2 *Audit of Exposed Filter Reweighing* - To avoid possible loss of volatile components, exposed filters should be weighed, including any necessary reweighing, as soon after collection and equilibration as practical. Thus, it may be impossible to have lot sizes of more than 10 or 20 exposed filters. The procedure is as follows.

1 Select randomly and reweigh four re-equilibrated filters out of every group of 50 or less. (This would mean 100 percent checking if four or fewer exposed filters were weighed at one time). For groups of 50 to 100, reweigh 7 from each group These suggested starting frequencies may be altered, based on experience and data quality Decrease the frequency if past experience indicates that the data are of good quality, or increase it if the data are of poor quality. It is more important to be sure that the sample is representative of the various conditions that may influence data quality than to adhere to a fixed frequency

2 Reweigh all filters in a lot if any audit weight differs by more than ±5 0 mg from the original weight.

3 Accept the lot with no change if all audits are within ±5 0 mg of the originals

4 Record the original and the audit weights in milligrams (mg) on an $\bar{X}$-and-R chart (Figure 8 1). Plot the difference (d), defined as

$$d = \text{original weight} - \text{audit weight}. \quad \text{Equation 8-1}$$

Tentative warning and control limits of ±3 3 and ±5 0 mg, respectively, are recommended until sufficient data are obtained to support an alteration of these limits Out-of-control points indicate the need for recalibration of the balance and/or improved operator technique Do not increase the limits, however, more stringent limits may be established if experience warrants

5 Forward the $\bar{X}$-and-R chart to the supervisor for review

6. Reweigh all of the remaining exposed filters in the lot if the balance requires recalibration or the operation technique is changed

8.1.3 *Audit of Data Processing* - For convenience, the data processing should be audited soon after the original calculations have been performed This allows corrections to be made immediately. This also allows for possible retrieval of additional explanatory data from field personnel when necessary The procedure is as follows

1. Use the audit rate of Subsection 8 1 2
2. Starting with the raw data on the data form or on the flow rate recorder chart, independently compute the concentration (in μg TSP/m^3) and compare it with the corresponding concentration reported on the SAROAD form. If the mass concentration computed by the audit check (μg TSP/m^3)$_a$ does not agree (within round-off error) with the original

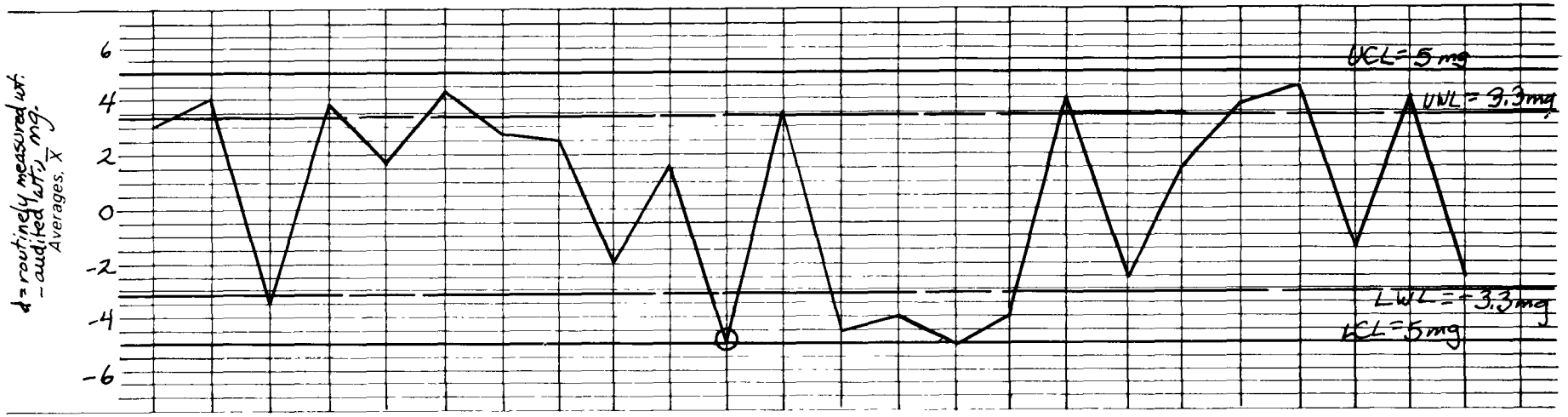
$\overline{X}$ and R Chart

Project Name: Audits of weights of exposed filters

Measurement Performed: d = routinely measured weight − audited weight (mg)

Measurement Units: mg

Data	1/1	1/8	1/15	1/22	1/29	2/5	2/12	2/19	2/26	3/4	3/11	3/18	3/25	4/1	4/8	4/15	4/22	4/29	5/6	5/13	5/20	5/27	6/3	6/10
Code 1	LOT 1 →								LOT 2 →								LOT 3 →							
Code 2																								
Code 3																								
Measurement Result 1 (original weight)	3872.7	3710.2	3873.9	3744.7	3971.5	3804.0	3867.0	3740.7	3903.0	3763.6	3798.6	4253.7	4089.9	3868.0	3709.8	3962.9	3799.9	4275.4	4225.2	3905.9	3755.1	3982.4	3788.2	4255.1
Measurement Result 2 (audit weight)	3875.5	3706.4	3877.7	3741.0	3969.7	3799.6	3864.1	3738.0	3905.1	3762.0	3804.6	4257.3	4094.3	3864.0	3704.9	3946.7	3795.6	4279.2	4223.9	3902.2	3750.4	3983.9	3784.0	4258.2
Measurement Result 3																								
Sum																								
Average, $\overline{X}$																								
d ~~Range, R~~	3.2	3.8	-3.8	3.7	1.8	4.4	2.9	2.7	-2.1	1.6	-5.4	3.6	-4.4	4.0	4.9	-3.9	4.3	-2.8	1.3	3.7	4.5	-1.5	4.2	-3.1



Ranges, R

Comments (Correct Action etc.): Reweigh all filters in LOT 2

Figure 8.1 Quality control chart for audit of weights of exposed filters.

value (μg TSP/m^3)$_m$, recheck all samples in the lot and correct them as necessary.

3. Record the audit values in the data log, and report them along with the original values to the supervisor for review. The audit value is always given as the correct value, based on the assumption that a discrepancy between the two values is always double-checked by the auditor.

8.2 Systems Audit

A systems audit is an on-site inspection and review of the quality of the total measurement system (sample collection, sample analysis, data processing, etc.), and it is normally a qualitative appraisal The procedure is as follows

1 Conduct a systems audit on receipt of a new monitoring system and as appropriate thereafter to audit possible degradation or significant changes in system operation

2 Use the preliminary checklist given in Figure 8.2 Check the questions for applicability to the particular local, State, or Federal agency.

See Sections 2.0.11 and 2.0 12 of this volume for detailed procedures and forms for systems audits and performance audits, respectively.

Table 8.2. *Activity Matrix for Auditing Procedure*

Audit	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Flow rate	*Percentage difference,* $d = \frac{Y - X}{X} 100$ *within* $^{3}7\%$	*Once each quarter*	*Recalibrate before resuming sampling.*
Exposed filter reweighing	*Audit weight = original weight* $^{3}5$ *mg*	*Perform 7 audits/100 filters, or 4 audits/≤50 filters; use analytical balance, condition filters for 24 h before weighing.*	*Reweigh all filters in the lot*
Data processing	*Audit concentration agrees with original reported concentration within round-off error*	*Independently repeat calculation of TSP concentration from data record for 7 samples per 100 (minimum of 4 per lot)*	*Recheck all calculations.*
Systems	*Method described in this section of the Handbook*	*At beginning of a new monitoring system and periodically as appropriate, observe procedures and use checklist.*	*Initiate improved methods and/or training programs.*

Checklist for Use by Auditor for Hi-Vol Method

1 *What type of hi-vol samplers are used in the network?* _____

_____

2 *How often are the samplers run? (a) daily (b) once every 6 days (c) once every 12 days (d) other* _____

3 *What type of filter and how many are being used?* _____

_____

4 *Are there any preexposure checks for pin holes or imperfections run on the filters?* _____

5 *What is the collection efficiency for your filters?* _____

6 *What is the calibration procedure for the hi-vol sampler?* _____

_____

7 *Which statement most closely estimates the frequency of flow rate calibration? (a) once when purchased (b) once when purchased, then after every sampler modification (c) when purchased, then at regular intervals thereafter* _____

8 *Are flow rates measured before and after the sampling period?*

Yes _____ *No* _____

9 *Is there a log book for each sampler for recording flows and times? Yes* _____ *No* _____

10 *Are filters conditioned before initial and final weighings?* _____ *If so, for how long?* _____ *At what percentage humidity?* _____

11 *Is the balance checked periodically?* _____ *If so, how often?* _____ *With which standard weights?* _____

12 *How often are the hi-vol filters weighed?* _____

How are the data from these weighings handled? _____

_____

13 *Are all weighings and serial numbers of filters kept in a log book at the laboratory?* _____

14 *What is the approximate time delay between sample collection and the final weighing?* _____ *days*

Figure 8.2. *Example of simplified checklist for use by auditor for hi-vol method*

9.0 Assessment of Monitoring Data for Precision and Accuracy

9.1 Precision

For each monitoring network, collocate an additional sampler at a minimum of one site (two sites are required for SLAMS[4]) as follows

1. Select a site with the highest expected geometric mean concentrations.
2. Locate the two high volume samplers within 4 m of each other, but at least 2 m apart to preclude air flow interference.
3. Identify one of the two samplers at the time of installation as the sampler for normal routine monitoring, identify the other as the duplicate sampler
4. Be sure that the calibration, sampling, and analysis procedure are the same for the collocated sampler as for all other samplers in the network
5. Operate a collocated sampler whenever its associated routine sampler is operated.
6. Use the differences in the concentrations (+g TSP/std m^3) between the routine and duplicate samplers to calculate the precision as described in Section 2 0 8 of this Handbook.

Based on the results of a collaborative test,[5] percent difference (Equation 8-1 of Section 2 0 8) should not exceed ³15% * An example calculation is given in Section 2.0 8 of this Handbook

9.2 Accuracy

The accuracy of the high-volume method for measurement of TSP is assessed by auditing certain portions of the measurement process, as described in Section 2.2.8 The calculation procedure for single instrument accuracy is given in Section 2.0 8 of this volume of the Handbook

*This ³15% is calculated at the 99 7 probability interval This means that if the two samplers do agree, chances are less than 3 out of 1000 that a difference larger than 15% will be observed

10.0 Recommended Standards for Establishing Traceability

For data of the desired quality to be achieved, two considerations are essential: (1) the measurement process must be in a state of statistical control at the time of the measurement, and (2) the combination of systematic errors and random variation (measurement errors) must yield a suitably small uncertainty. Evidence of good-quality data requires the performance of quality control checks and independent audits of the measurement process; documentation of the data on a quality control chart; and the use of materials, instruments, and measurement procedures that can be traced to an appropriate performance standard

Data must be routinely obtained by repeating measurements of Standard Reference samples (primary, secondary, and/or working standards), and a condition of process control must be established. The working calibration standards should be traceable to standards of higher accuracy, such as those listed here.

10.1 Recommended Standards for Establishing Traceability

1 Class-S weights of NBS specifications are recommended for the analytical balance calibration. See Subsection 2.1 for details on balance calibration checks.

2. A positive displacement rootsmeter is recommended for calibrating the flow rate transfer standard that is used to calibrate the high-volume sampler. See Subsection 2.6 for details on high-volume sampler calibration.

3. A positive displacement rootsmeter (including a resistance plate) is recommended for calibrating the device used to audit the high-volume-sampler flow-rate calibration. See Subsection 8.1 for details on flow-rate calibration audits.

4. The elapsed-time meter, checked semiannually against an accurate timepiece, must be within ±2 min/day.

11.0 Reference Method*

Appendix B—Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method)

1.0 Applicability.

1.1 This method provides a measurement of the mass concentration of total suspended particulate matter (TSP) in ambient air for determining compliance with the primary and secondary national ambient air quality standards for particulate matter as specified in § 50 6 and § 50.7 of this chapter. The measurement process is nondestructive, and the size of the sample collected is usually adequate for subsequent chemical analysis Quality assurance procedures and guidance are provided in Part 58, Appendixes A and B, of this chapter and in References 1 and 2

2.0 Principle.

2.1 An air sampler, properly located at the measurement site, draws a measured quantity of ambient air into a covered housing and through a filter during a 24-hr (nominal) sampling period The sampler flow rate and the geometry of the shelter favor the collection of particles up to 25-50 +m (aerodynamic diameter), depending on wind speed and direction (3) The filters used are specified to have a minimum collection efficiency of 99 percent for 0 3 +m (DOP) particles (see Section 7 1 4)

2.2 The filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain The total volume of air sampled, corrected to EPA standard conditions (25°C, 760 mm Hg [101 kPa]), is determined from the measured flow rate and the sampling time. The concentration of total suspended particulate matter in the ambient air is computed as the mass of collected particles divided by the volume of air sampled, corrected to standard conditions, and is expressed in micrograms per standard cubic meter (+g/std m^3) For samples collected at temperatures and pressures significantly different than standard conditions, these corrected concentrations may differ substantially from actual concentrations (micrograms per actual cubic meter), particularly at high elevations The actual particulate matter concentration can be calculated from the corrected concentration using the actual temperature and pressure during the sampling period

3.0 Range.

3.1 The approximate concentration range of the method is 2 to 750 +g/std m^3 The upper limit is determined by the point at which the sampler can no longer maintain the specified flow rate due to the increased pressure drop of the loaded filter This point is affected by particle size distribution, moisture content of the collected particles, and variability from filter to filter, among other things The lower limit is determined by the sensitivity of the balance (see Section 7 10) and by inherent sources of error (see Section 6)

3.2 At wind speeds between 1 3 and 4 5 m/sec (3 and 10 mph), the high-volume air sampler has been found to collect particles up to 25 to 50 +m, depending on wind speed and direction (3) For the filter specified in Section 7 1, there is effectively no lower limit on the particle size collected

4.0 Precision.

4.1 Based upon collaborative testing the relative standard deviation (coefficient of variation) for single analyst precision (repeatability) of the method is 3 0 percent. The corresponding value for interlaboratory precision (reproducibility) is 3 7 percent. (4)

5.0 Accuracy.

5.1 The absolute accuracy of the method is undefined because of the complex nature of atmospheric particulate matter and the difficulty in determining the "true" particulate matter concentration This method provides a measure of particulate matter concentration suitable for the purpose specified under Section 1 0. Applicability.

6.0 Inherent Sources of Error.

6.1 *Airflow variation.* The weight of material collected on the filter represents the (integrated) sum of the product of the instantaneous flow rate times the instantaneous particle concentration Therefore, dividing this weight by the average flow rate over the sampling period yields the true particulate matter concentration only when the flow rate is constant over the period The error resulting from a nonconstant flow rate depends on the magnitude of the instantaneous changes in the flow rate and in the particulate matter concentration Normally, such errors are not large, but they can be greatly reduced by equipping the sampler with an automatic flow controlling mechanism that maintains constant flow during the sampling period Use of a constant flow controller is recommended *

6.2 *Air volume measurement* If the flow rate changes substantially or nonuniformly during the sampling period, appreciable error in the estimated air volume may result from using the average of the presampling and postsampling flow rates Greater air volume measurement accuracy may be achieved by (1) equipping the sampler with a flow controlling mechanism that maintains constant air flow during the sampling period,* (2) using a calibrated, continuous flow rate recording device to record the actual flow rate during the sampling period and integrating the flow rate over the period, or (3) any other means that will accurately measure the total air volume sampled during the sampling period. Use of a continuous flow recorder is recommended, particularly if the sampler is not equipped with a constant flow controller

6.3 *Loss of volatiles.* Volatile particles collected on the filter may be lost during subsequent sampling or during shipment and/or storage of the filter prior to the postsampling weighing (5) Although such losses are largely unavoidable, the filter should be reweighed as soon after sampling as practical.

6.4 *Artifact particulate matter.* Artifact particulate matter can be

*Reproduced from 40 CFR 50, Appendix B, as amended, December 6, 1982 (47 FR 54912)

formed on the surface of alkaline glass fiber filters by oxidation of acid gases in the sample air, resulting in a higher than true TSP determination. (6, 7) This effect usually occurs early in the sample period and is a function of the filter pH and the presence of acid gases It is generally believed to account for only a small percentage of the filter weight gain, but the effect may become more significant where relatively small particulate weights are collected.

6.5 *Humidity.* Glass fiber filters are comparatively insensitive to changes in relative humidity, but collected particulate matter can be hygroscopic. (8) The moisture conditioning procedure minimizes but may not completely eliminate error due to moisture.

6.6 *Filter handling.* Careful handling of the filter between the presampling and postsampling weighings is necessary to avoid errors due to loss of fibers or particles from the filter. A filter paper cartridge or cassette used to protect the filter can minimize handling errors. (See Reference 2, Section 2).

6.7 *Nonsampled particulate matter.* Particulate matter may be deposited on the filter by wind during periods when the sampler is inoperative. (9) It is recommended that errors from this source be minimized by an automatic mechanical device that keeps the filter covered during nonsampling periods, or by timely installation and retrieval of filters to minimize the nonsampling periods prior to and following operation.

6.8 *Timing errors.* Samplers are normally controlled by clock timers set to start and stop the sampler at midnight. Errors in the nominal 1,440-min sampling period may result from a power interruption during the sampling period or from a discrepancy between the start or stop time recorded on the filter information record and the actual start or stop time of the sampler. Such discrepancies may be caused by (1) poor resolution of the timer set-points, (2) timer error due to power interruption, (3) missetting of the timer, or (4) timer malfunction. In general, digital electronic timers have much better set-point resolution than mechanical timers, but require a battery backup system to maintain continuity of operation after a power interruption. A continuous flow recorder or elapsed time meter provides an indication of the sampler run-time, as well as indication of any power interruption during the sampling period and is therefore recommended.

6.9 *Recirculation of sampler exhaust.* Under stagnant wind conditions, sampler exhaust air can be resampled. This effect does not appear to affect the TSP measurement substantially, but may result in increased carbon and copper in the collected sample. (10) This problem can be reduced by ducting the exhaust air well away, preferably downwind, from the sampler.

7.0 Apparatus.

(See References 1 and 2 for quality assurance information.)

Note.—Samplers purchased prior to the effective date of this amendment are not subject to specifications preceded by (†).

7.1 *Filter.* (Filters supplied by the Environmental Protection Agency can be assumed to meet the following criteria. Additional specifications are required if the sample is to be analyzed chemically.)

7.1.1 Size. 20.3 ± 0 2 x 25.4 ± 0.2 cm (nominal 8 x10 in).

7.1.2 Nominal exposed area: 406.5 cm^3 (63 in^2).

7.1.3 Material Glass fiber or other relatively inert, nonhygroscopic material. (8)

7.1.4 Collection efficiency: 99 percent minimum as measured by the DOP test (ASTM-2986) for particles of 0.3 μm diameter.

7.1.5 Recommended pressure drop range· 42-54 mm Hg (5.6-7.2 kPa) at a flow rate of 1.5 std m^3/min through the nominal exposed area.

7.1.6 pH: 6 to 10. (11)

7.1.7 Integrity: 2.4 mg maximum weight loss. (11)

7.1.8 Pinholes: None.

7.1.9 Tear strength: 500 g minimum for 20 mm wide strip cut from filter in weakest dimension. (See ASTM Test D828-60).

7.1.10 Brittleness: No cracks or material separations after single lengthwise crease.

7.2 *Sampler.* The air sampler shall provide means for drawing the air sample, via reduced pressure, through the filter at a uniform face velocity.

7.2.1 The sampler shall have suitable means to:

a. Hold and seal the filter to the sampler housing.
b. Allow the filter to be changed conveniently.
c. Preclude leaks that would cause error in the measurement of the air volume passing through the filter.
d. (†)Manually adjust the flow rate to accommodate variations in filter pressure drop and site line voltage and altitude The adjustment may be accomplished by an automatic flow controller or by a manual flow adjustment device Any manual adjustment device must be designed with positive detents or other means to avoid unintentional changes in the setting.

7.2.2 Minimum sample flow rate, heavily loaded filter: 1.1 m^3/min (39 ft^3/min).††

7.2.3 Maximum sample flow rate, clean filter: 1.7 m^3/min (60 ft^3/min).††

7.2.4 Blower Motor: The motor must be capable of continuous operation for 24-hr periods.

7.3 *Sampler shelter.*

7.3.1 The sampler shelter shall·

a. Maintain the filter in a horizontal position at least 1 m above the sampler supporting surface so that sample air is drawn downward through the filter.
b. Be rectangular in shape with a gabled roof, similar to the design shown in Figure 1.
c. Cover and protect the filter and sampler from precipitation and other weather.
d. Discharge exhaust air at least 40 cm from the sample air inlet.
e. Be designed to minimize the collection of dust from the supporting surface by incorporating a baffle between the exhaust outlet and the supporting surface.

*At elevated altitudes, the effectiveness of automatic flow controllers may be reduced because of a reduction in the maximum sampler flow

(†) See note at beginning of Section 7

††These specifications are in actual air volume units to convert to EPA standard air volume units, multiply the specifications by (P_b/P_{std}) (298/T) where P_b and T are the barometric pressure in mm Hg (or kPa) and the temperature in K at the sampler, and P_{std} is 760 mm Hg (or 101 kPa)

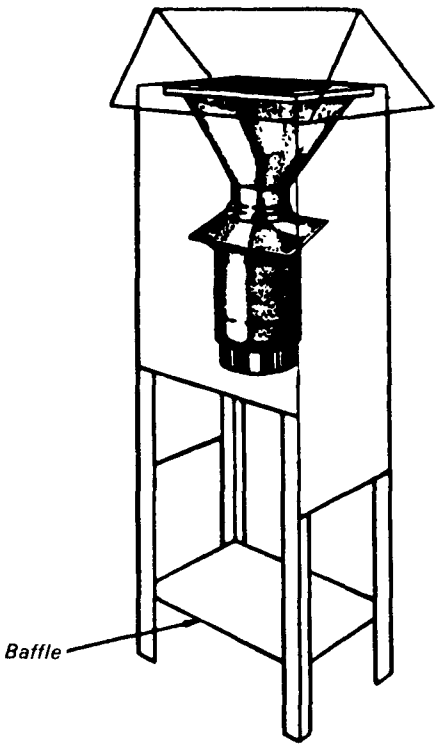


Figure 1. High-volume sampler in shelter

7.3.2 The sampler cover or roof shall overhang the sampler housing somewhat, as shown in Figure 1, and shall be mounted so as to form an air inlet gap between the cover and the sampler housing walls †This sample air inlet should be approximately uniform on all sides of the sampler. †The area of the sample air inlet must be sized to provide an effective particle capture air velocity of between 20 and 35 cm/sec at the recommended operational flow rate. The capture velocity is the sample air flow rate divided by the inlet area measured in a horizontal plane at the lower edge of the cover. †Ideally, the inlet area and operational flow rate should be selected to obtain a capture air velocity of 25 ±2 cm/sec

7.4 *Flow rate measurement devices.*

7.4.1 The sampler shall incorporate a flow rate measurement device capable of indicating the total sampler flow rate. Two common types of flow indicators covered in the calibration procedure are (1) an electronic mass flowmeter and (2) an orifice or orifices located in the sample air stream together with a suitable pressure indicator such as a manometer, or aneroid pressure gauge. A pressure recorder may be used with an orifice to provide a continuous record of the flow Other types of flow indicators (including rotameters) having comparable precision and accuracy are also acceptable.

7.4.2 †The flow rate measurement device must be capable of being calibrated and read in units corresponding to a flow rate which is readable to the nearest 0.02 std m^3/min over the range 1.0 to 1.8 std m^3/min

7.5 *Thermometer,* to indicate the approximate air temperature at the flow rate measurement orifice, when temperature corrections are used.

7.5.1 *Range:* -40° to +50°C (223-323 K).

7.5.2 *Resolution:* 2° C (2 K).

7.6 *Barometer,* to indicate barometric pressure at the flow rate measurement orifice, when pressure corrections are used

7.6.1 *Range:* 500 to 800 mm Hg (66-106 kPa).

7.6.2 *Resolution:* ±5 mm Hg (0.67 kPa).

7.7 *Timing/control device.*

7.7.1 The timing device must be capable of starting and stopping the sampler to obtain an elapsed run-time of 24 hr ±1 hr (1,440 ±60 min).

7.7.2 *Accuracy of time setting:* ±30 min, or better. (See Section 6 8).

7.8 *Flow rate transfer standard,* traceable to a primary standard. (See Section 9.2).

7.8.1 *Approximate range:* 1.0 to 1.8 m^3/min.

7.8.2 *Resolution:* 0.02 m^3/min.

7.8.3 *Reproducibility:* ±2 percent (2 times coefficient of variation) over normal ranges of ambient temperature and pressure for the stated flow rate range. (See Reference 2, Section 2.)

7.8.4 Maximum pressure drop at 1.7 std m^3/min; 50 cm H_2O (5 kPa).

7.8.5 The flow rate transfer standard must connect without leaks to the inlet of the sampler and measure the flow rate of the total air sample

[Corrected by 48 FR 17355, April 22, 1983]

7.8.6 The flow rate transfer standard must include a means to vary the sampler flow rate over the range of 1.0 to 1.8 m^3/min (35-64 ft^3/min) by introducing various levels of flow resistance between the sampler and the transfer standard inlet.

7.8.7 The Conventional type of flow transfer standard consists of: An orifice unit with adapter that connects to the inlet of the sampler, a manometer or other device to measure orifice pressure drop, a means to vary the flow through the sampler unit, a thermometer to measure the ambient temperature, and a barometer to measure ambient pressure Two such devices are shown in Figures 2a and 2b. Figure 2a shows multiple fixed resistance plates, which necessitate disassembly of the unit each time the flow resistance is changed. A preferable design, illustrated in Figure 2b, has a variable flow restriction that can be adjusted externally without disassembly of the unit. Use of conventional, orifice-type transfer standard is assumed in the calibration procedure (Section 9). However, the use of other types of transfer standards meeting the above specifications, such as the one shown in Figure 2c, may be approved; see the note following Section 9.1.

7.9 *Filter conditioning environment*

7.9.1 *Controlled temperature:* between 15° and 30° C with less than ±3° C variation during equilibration period.
[Corrected by 48 FR 17355, April 22, 1983]

7.9.2 *Controlled humidity:* Less than 50 percent relative humidity, constant within ±5 percent.

7.10 *Analytical balance.*

7.10.1 *Sensitivity:* 0.1 mg.

7.10.2 Weighing chamber designed to accept an unfolded 20.3 x 25.4 cm (8 x 10 in) filter.

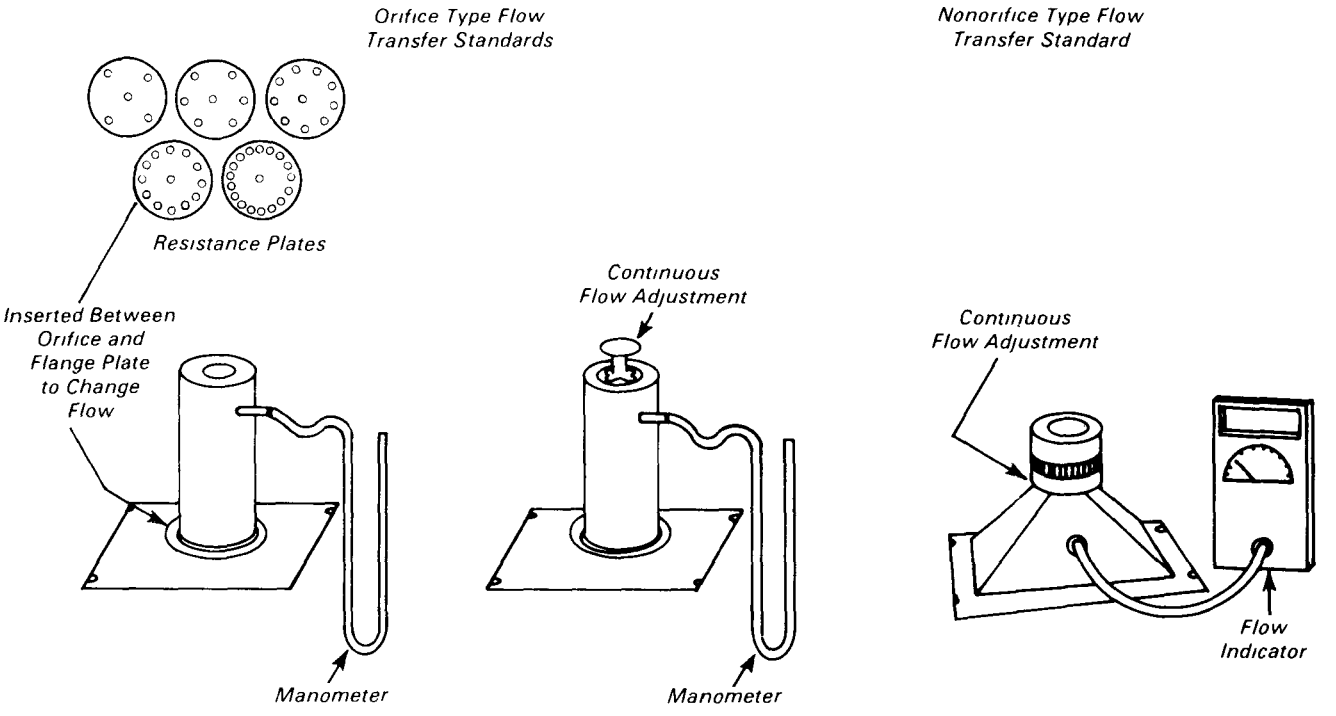
7.11 *Area light source,* similar to X-ray film viewer, to backlight filters for visual inspection.

7.12 *Numbering device,* capable of printing identification numbers on the filters before they are placed in the filter conditioning environment, if not numbered by the supplier.

8.0 Procedure.

(See References 1 and 2 for quality assurance information.)

8.1 Number each filter, if not already numbered, near its edge with a unique identification number.



2a Orifice Unit Using Fixed Resistance Plates

2b Preferable Orifice Unit with Externally Adjustable Resistance.

2c Electronic Flowmeter with Externally Adjustable Resistance.

Figure 2. *Various types of flow transfer standards Note that all devices are designed to mount to the filter inlet area of the sampler*

8.2 Backlight each filter and inspect for pinholes, particles, and other imperfections; filters with visible imperfections must not be used.

8.3 Equilibrate each filter in the conditioning environment for at least 24-hr

8.4 Following equilibration, weigh each filter to the nearest milligram and record this tare weight (W_i) with the filter identification number

8.5 Do not bend or fold the filter before collection of the sample

8.6 Open the shelter and install a numbered, preweighted filter in the sampler, following the sampler manufacturer's instructions During inclement weather, precautions must be taken while changing filters to prevent damage to the clean filter and loss of sample from or damage to the exposed filter Filter cassettes that can be loaded and unloaded in the laboratory may be used to minimize this problem (See Section 6.6). [Corrected by 48 FR 17355, April 22, 1983]

8.7 Close the shelter and run the sampler for at least 5 min to establish run-temperature conditions.

8.8 Record the flow indicator reading and, if needed, the barometric pressure (P_3) and the ambient temperature (T_a) see NOTE following step 8 12). Stop the sampler Determine the sampler flow rate (see Section 10 1); if it is outside the acceptable range (1.1 to 1.7 m^3/min [39-60 ft^3/min]), use a different filter, or adjust the sampler flow rate Warning Substantial flow adjustments may affect the calibration of the orifice-type flow indicators and may necessitate recalibration.

8.9 Record the sampler identification information (filter number, site location or identification number, sample date, and starting time)

8.10 Set the timer to start and stop the sampler such that the sampler runs 24-hrs from midnight to midnight (local time).

8.11 As soon as practical following the sampling period, run the sampler for at least 5 min to again establish run-temperature conditions.

8.12 Record the flow indicator reading and, if needed, the barometric Pressure (P_a) and the ambient temperature (T_a).

Note.—No onsite pressure or temperature measurements are necessary if the sampler flow indicator does not require pressure or temperature corrections (e.g., a mass flowmeter) or if average barometric pressure and seasonal average temperature for the site are incorporated into the sampler calibration (see step 9.3.9). For individual pressure and temperature corrections, the ambient pressure and temperature can be obtained by onsite measurements or from a nearby weather station. Barometric pressure readings obtained from airports must be station pressure, not corrected to sea level, and may need to be corrected for differences in elevation between the sampler site and the airport. For samplers having flow recorders but not constant flow controllers, the average temperature and pressure at the site during the sampling period should be estimated from weather bureau or other available data.

8.13 Stop the sampler and carefully remove the filter, following the sampler manufacturer's instructions.

Touch only the outer edges of the filter. See the precautions in step 8.6.

8.14 Fold the filter in half lengthwise so that only surfaces with collected particulate matter are in contact and place it in the filter holder (glassine envelope or manila folder).

8.15 Record the ending time or elapsed time on the filter information record, either from the stop set-point time, from an elapsed time indicator, or from a continuous flow record. The sample period must be 1,440 ± 60 min. for a valid sample.

8.16 Record on the filter information record any other factors, such as meteorological conditions, construction activity, fires or dust storms, etc., that might be pertinent to the measurement. If the sample is known to be defective, void it at this time.

8.17 Equilibrate the exposed filter in the conditioning environment for at least 24-hrs.

8.18 Immediately after equilibration, reweigh the filter to the nearest milligram and record the gross weight with the filter identification number. See Section 10 for TSP concentration calculations.

9.0 Calibration.

9.1 Calibration of the high volume sampler's flow indicating or control device is necessary to establish traceability of the field measurement to a primary standard via a flow rate transfer standard. Figure 3a illustrates the certification of the flow rate transfer standard and Figure 3b illustrates its use in calibrating a sampler flow indicator. Determination of the corrected flow rate from the sampler flow indicator, illustrated in Figure 3c, is addressed in Section 10.1.

Note.—The following calibration procedure applies to a conventional orifice-type flow transfer standard and an orifice-type flow indicator in the sampler (the most common types). For samplers using a pressure recorder having a square-root scale, 3 other acceptable calibration procedures are provided in Reference 12. Other types of transfer standards may be used if the manufacturer or user provides an appropriately modified calibration procedure that has been approved by EPA under Section 2.8 of Appendix C to Part 58 of this chapter.

9.2 *Certification of the flow rate transfer standard.*

9.2.1 *Equipment required:* Positive displacement standard volume meter traceable to the National Bureau of Standards (such as a Roots meter or equivalent), stop-watch, manometer, thermometer, and barometer

9.2.2 Connect the flow rate transfer standard to the inlet of the standard volume meter. Connect the manometer to measure the pressure at the inlet of the standard volume meter. Connect the orifice manometer to the pressure tap on the transfer standard. Connect a high-volume air pump (such as a high-volume sampler blower) to the outlet side of the standard volume meter. See Figure 3a.

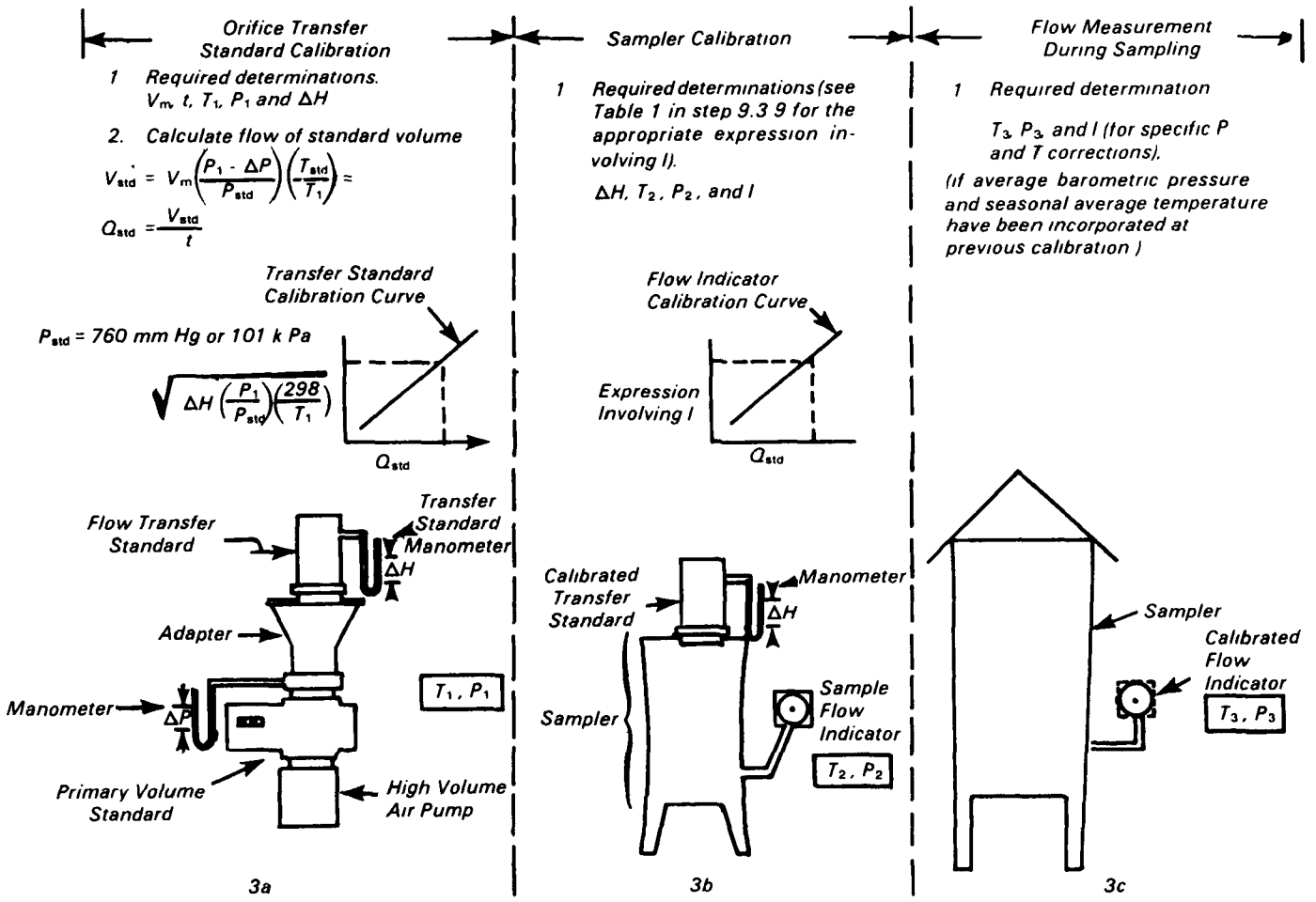


Figure 3. *Illustration of the 3 steps in the flow measurement process.*

9.2.3 Check for leaks by temporarily clamping both manometer lines (to avoid fluid loss) and blocking the orifice with a large-diameter rubber stopper, wide cellophane tape, or other suitable means. Start the high-volume air pump and note any change in the standard volume meter reading. The reading should remain constant. If the reading changes, locate any leaks by listening for a whistling sound and/or retightening all connections, making sure that all gaskets are properly installed.

9.2.4 After satisfactorily completing the leak check as described above, unclamp both manometer lines and zero both manometers.

9.2.5. Achieve the appropriate flow rate through the system, either by means of the variable flow resistance in the transfer standard or by varying the voltage to the air pump. (Use of resistance plates as shown in Figure 1a is discouraged because the above leak check must be repeated each time a new resistance plate is installed.) At least five different but constant flow rates, even distributed, with at least three in the specified flow rate interval (1.1 to 1.7 m^3/min [39-60 ft^3/min]), are required.

9.2.6 Measure and record the certification data on a form similar to the one illustrated in Figure 4 according to the following steps.

9.2.7 Observe the barometric pressure and record as P_1 (item 8 in Figure 4).

9.2.8 Read the ambient temperature in the vicinity of the standard volume meter and record it as T_1 (item 9 in Figure 4).

9.2.9 Start the blower motor, adjust the flow, and allow the system to run for at least 1 min for a constant motor speed to be attained.

9.2.10 Observe the standard volume meter reading and simultaneously start a stopwatch. Record the initial meter reading (V_i) in column 1 of Figure 4.

9.2.11 Maintain this constant flow rate until at least 3 m^3 of air have passed through the standard volume meter. Record the standard volume meter inlet pressure manometer reading as ΔP (column 5 in Figure 4), and the orifice manometer reading as ΔH (column 7 in Figure 4). Be sure to indicate the correct units of measurement.

9.2.12 After at least 3 m^3 of air have passed through the system, observe the standard volume meter reading while simultaneously stopping the stopwatch. Record the final meter reading (V_f) in column 2 and the elapsed time (t) in column 3 of Figure 4.

9.2.13 Calculate the volume measured by the standard volume meter at meter conditions of temperature and pressures as $V_m = V_f - V_i$. Record in column 4 of Figure 4.

9.2.14 Correct this volume to standard volume (std m^3) as follows:

$$V_{std} = V_m \frac{P_1 - \Delta P}{P_{std}} \frac{T_{std}}{T_1}$$

where:

V_{std} = standard volume, std m^2;
V_m = actual volume measured by the standard volume meter;
P_1 = barometric pressure during calibration, mm Hg or kPa;
ΔP = differential pressure at inlet to volume meter, mm Hg or kPa;
P_{std} = 760 mm Hg or 101 kPa;
T_{std} = 298 K;
T_1 = ambient temperature during calibration, K.

Calculate the standard flow rate (std m^3/min) as follows:

$$Q_{std} = \frac{V_{std}}{t}$$

where:

Q_{std} = standard volumetric flow rate, std m^3/min
t = elapsed time, minutes.

Record Q_{std} to the nearest 0.01 std m^3/min in column 6 of Figure 4.

9.2.15 Repeat steps 9.2.9 through 9.2.14 for at least four additional constant flow rates, evenly spaced over the approximate range of 1.0 to 1.8 std m^3/min (35-64 ft^3/min).

9.2.16 For each flow, compute

$$\sqrt{\Delta H\,(P_1/P_{std})\,(298/T_1)}$$

(column 7a of Figure 4) and plot these values against Q_{std} as shown in Figure 3a. Be sure to use consistent units (mm Hg or kPa) for barometric pressure. Draw the orifice transfer standard certification curve or calculate the linear least squares slope (m) and intercept (b) of the certification curve:

$$\sqrt{\Delta H\,(P_1/P_{std})\,(298/T_1)} = m\,Q_{std} + b.$$

See Figures 3 and 4. A certification graph should be readable to 0.02 std m^3/min.

9.2.17 Recalibrate the transfer standard annually or as required by applicable quality control procedures. (See Reference 2.)

9.3 Calibration of sampler flow indicator.

Note.—For samplers equipped with a flow controlling device, the flow controller must be disabled to allow flow changes during calibration of the sampler's flow indicator, or the alternate calibration of the flow controller given in 9.4 may be used. For samplers using an orifice-type flow indicator downstream of the motor, do not vary the flow rate by adjusting the voltage or power supplied to the sampler.

9.3.1 A form similar to the one illustrated in Figure 5 should be used to record the calibration data

9.3.2 Connect the transfer standard to the inlet of the sampler. Connect the orifice manometer to the orifice pressure tap, as illustrated in Figure 3b. Make sure there are no leaks between the orifice unit and the sampler.

9.3.3 Operate the sampler for at least 5 minutes to establish thermal equilibrium prior to the calibration.

9.3.4 Measure and record the ambient temperature, T_2, and the barometric pressure, P_2, during calibration.

9.3.5 Adjust the variable resistance or, if applicable, insert the appropriate resistance plate (or no plate) to achieve the desired flow rate.

9.3.6 Let the sampler run for at least 2 min to re-establish the run-temperature conditions. Read and record the pressure drop across the orifice (ΔH) and the sampler flow rate indication (I) in the appropriate columns of Figure 5.

9.3.7 Calculate

$$\sqrt{\Delta H(P_2/P_{std})\,(298/T_2)}$$

and determine the flow rate at standard conditions (Q_{std}) either graphically from the certification curve or by calculating Q_{std} from the least square slope and intercept of the transfer standard's transposed certification curve:

$$Q_{std} = 1/m \sqrt{\Delta H(P_2/P_{std})\,(298/T_2)} - b.$$

Record the value of Q_{std} on Figure 5. [Corrected by 48 FR 17355, April 22, 1983]

9.3.8 Repeat steps 9.3.5, 9.3.6, and 9.3.7 for several additional flow rates distributed over a range that includes 1.1 to 1.7 std m^3/min.

9.3.9 Determine the calibration curve by plotting values of the

Orifice Transfer Standard Certification Worksheet

Run No	1	2	3	4	5	6	7	7a
	Meter reading start V_i (m^3)	Meter reading stop V_f (m^3)	Elapsed time t (min)	Volume measured V_m (m^3)	Differential pressure (at inlet to volume meter) ΔP (mm Hg or in)	(X) Flow rate Q_{std} (std m^3 min)	Pressure drop across orifice ΔH ☐ (in) or ☐ (cm) of water	$\Delta H \left(\frac{(Y)\ P_1}{P_{std}}\right) \frac{298}{T_1}$
1								
2								
3								
4								
5								
6								

Recorded Calibration Data

Standard volume meter No _____

Transfer standard type ☐ orifice ☐ other

Model No _____ Serial No _____

(8) P_1 _____ mm Hg (or in) (10) P_{std} 760 mm Hg (or 29 92 in)

(9) T_1 _____ K (11) T_{std} 298 K

By _____

Date _____

Calculation Equations

(1) $V_m = V_f - V_i$

(2) $V_{std} = V_m \left(\frac{P_1 - \Delta P}{P_{std}}\right)\left(\frac{T_{std}}{T_1}\right)$

(3) $Q_{std} = \frac{V_{std}}{t}$

Least Squares Calculations

linear ($Y = mX + b$) regression equation of $Y = \sqrt{\Delta H\,(P_1/P_{std})\,(298/T_1)}$ on $X = Q_{std}$ for Orifice Calibration Unit (i e , $\sqrt{\Delta H(P_1/P_{std})\,(298/T_1)} = mQ_{std} + b$)

Slope (m) = _____ Intercept (b) = _____ Correlation coefficient (r) = _____

To use for subsequent calibration $X = \frac{1}{m}(Y - b)$,

$$Q_{std} = \frac{1}{m}\left[\sqrt{\Delta H\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)} - b\right]$$

Figure 4. Example of orifice transfer standard certification worksheet

High-Volume Air Sampler Calibration Worksheet

Site location: _____

Date: _____ *(1) Barometric pressure, P_2 mm Hg (or in.)* _____

Calibrated by: _____ *(2) Temperature, T_2 (K)* _____

Sampler No. _____ *Serial No.* _____

Transfer std. type _____ *Serial No* _____

Optional. P_{std} = 760 mm Hg (or 29.92 in.) Average barometric pressure P_a = _____ Seasonal average temperature T_a = _____					5 (Y)	
					For specific pressure and temperature corrections (see Table 2.1)	For incorporation of average pressure and seasonal average temperature (see Table 2.1)
No	1 ΔH Pressure drop across orifice (in) or (cm)	$\sqrt{\Delta H \left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	(X) 3 Q_{std} (from orifice certification std m^3/min	4 I Sampler flow rate indication (arbitrary)	☐ I or ☐ $\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$ or ☐ $I\sqrt{\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	☐ I or ☐ $\sqrt{I\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$ or ☐ $I\sqrt{\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$
1	2.2	1.501	0.750	20.0	20.236	
2	3.7	1.946	0.975	28.0	28.330	
3	5.3	2.329	1.155	34.0	34.401	
4	7.1	2.696	1.330	39.0	39.460	
5	8.5	2.950	1.455	43.0	43.507	
6	12.0	3.505	1.725	51.7	52.301	

Least Aquares Calculations

Linear regression of Y on X Y = mX + b, Y = appropriate expression from Table 2.1, X = Q_{std}

Slope (m) = _____ *Intercept (b) =* _____ *Correlation Coefficient (r) =* _____

To determine subsequent flow rate during use X = 1/m (Y-b) Q_{std} = 1/m ([appropriate expression from Table 2] - b)

Figure 5. *Example of high-volume air sampler calibration worksheet.*

appropriate expression involving I, selected from Table 1, against Q_{std}. The choice of expression from Table 1 depends on the flow rate measurement device used (see Section 7.4.1) and also on whether the calibration curve is to incorporate geographic average barometric pressure (P_a) and seasonal average temperature (T_a) for the site to approximate actual pressure and temperature. Where P_a and T_a can be determined for a site for a seasonal period such that the actual barometric pressure and temperature at the site do not vary by more than ±60 mm Hg (8 kPa) from P_a or ±15° C from T_a respectively, then using P_a and T_a avoids the need for subsequent pressure and temperature calculation when the sampler is used. The geographic average barometric pressure (P_a) may be estimated from an altitude-pressure table or by making an (approximate) elevation correction of — 26 mm Hg (— 3.46 kPa) for each 305 m (1,000 ft) above sea level (760 mm Hg or 101 kPa). The seasonal average temperature (T_a) may be estimated from weather station or other records. Be sure to use consistent units (mm Hg or kPa) for barometric pressure.
[Corrected by 48 FR 17355, April 22, 1983]

9.3.10 Draw the sampler calibration curve or calculate the linear least squares slope (m), intercept (b), and correlation coefficient of the calibration curve: [Expression from Table 1] = m Q_{std} + b. See Figures 3 and 5. Calibration curves should be readable to 0.02 std m^3/min

9.3.11 For a sampler equipped with a flow controller, the flow controlling mechanism should be re-enabled and set to a flow near the lower flow limit to allow maximum control range. The sample flow rate should be verified at this time with a clean filter installed. Then add two or more filters to the sampler to see if the flow controller maintains a constant flow; this is particularly important at high altitudes where the range of the flow controller may be reduced

9.4 Alternate calibration of flow-controlled samplers. A flow-controlled sampler may be calibrated solely at its controlled flow rate, provided that previous operating history of the sampler demonstrates that the flow rate is stable and reliable In this case, the flow indicator may remain uncalibrated but should be used to indicate any relative change between initial and final flows, and the sampler should be recalibrated more often to minimize potential loss of samples because of controller malfunction

9.4.1 Set the flow controller for a flow near the lower limit of the flow range to allow maximum control range

9.4.2 Install a clean filter in the sampler and carry out steps 9.3.2, 9.3.3, 9.3.4, 9.3.6, and 9 3.7.

9.4.3 Following calibration, add one or two additional clean filters to the sampler, reconnect the transfer standard, and operate the sampler to verify that the controller maintains the same calibrated flow rate; this is particularly important at high altitudes where the flow control range may be reduced

10.0 Calculations of TSP Concentration

10.1 Determine the average sampler flow rate during the sampling period according to either 10.1.1 or 10 1 2 below.

10.1.1 For a sampler without a continuous flow recorder, determine the appropriate expression to be used from Table 2 corresponding to the one from Table 1 used in step 9.3 9 Using this appropriate expression, determine Q_{std} for the initial flow rate from the sampler calibration curve either graphically or from the transposed regression equation

$Q_{std} = \frac{1}{m}$ ([Appropriate expression from Table 2]—b)

Similarly, determine Q_{std} from the final flow reading and calculate the average flow Q_{std} as one-half the sum of the initial and final flow rates.

10.1.2 For a sampler with a continuous flow recorder, determine the average flow rate device reading, I, for the period. Determine the appropriate expression from Table 2 corresponding to the one from Table 1 used in step 9.3.9 Then using this expression and the average flow rate reading, determine Q_{std} from the sampler calibration curve, either graphically or from the transposed regression equation

$Q_{std} = \frac{1}{m}$ ([Appropriate expression from Table 2]—b)

If the trace shows substantial flow change during the sampling period, greater accuracy may be achieved by dividing the sampling period into intervals and calculating an average reading before determining Q_{std}.

10.2 Calculate the total air volume sampled as.

$$V\text{-}Q_{std} \times t$$

where:

V = total air volume sampled, in standard volume units, std m^3/;

Q_{std} = average standard flow rate, std m^3/min,

t = sampling time, min.

[Corrected by 48 FR 17355, April 22, 1983]

10.3 Calculate and report the particulate matter concentration as:

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

where:

TSP = mass concentration of total suspended particulate matter, μg/std m^3;

W_i = initial weight of clean filter, g;

W_f = final weight of exposed filter, g

V = air volume sampled, converted to standard conditions, std m^3

10^6 = conversion of g to μg

10.4 If desired, the actual particulate matter concentration (see Section 2.2) can be calculated as follows:

$$(TSP)_a = TSP\ (P_3/P_{std})\ (298/T_3)$$

Table 1. *Expressions for Plotting Sampler Calibration Curves*

Type of sampler flow rate measuring device	*Expression: For actual pressure and temperature corrections*	*Expression: For incorporation of geographic average pressure and seasonal average temperature*
Mass flowmeter	I	I
*Orifice and *pressure indicator*	$\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$\sqrt{I\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$
Rotameter, or orifice and pressure recorder having square root scale[a]	$I\sqrt{\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$I\sqrt{\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$

**This scale is recognizable by its nonuniform divisions and is the most commonly available for high-volume samplers.*

Table 2. Expressions for Determining Flow Rate During Sampler Operation

Type of sampler flow rate measuring device	Expression: For actual pressure and temperature corrections	Expression: For use when geographic average pressure and seasonal average temperature have been incorporated into the sampler calibration
Mass flowmeter	1	1
Orifice and pressure indicator	$\sqrt{1\left(\frac{P_3}{P_{std}}\right)\left(\frac{298}{T_3}\right)}$	1
Rotameter, or orifice and pressure recorder having square root scale*	$1\sqrt{\left(\frac{P_3}{P_{std}}\right)\left(\frac{298}{T_3}\right)}$	1

*This scale is recognizable by its nonuniform divisions and is the most commonly available for high-volume samplers.

where

$(TSP)_a$ = actual concentration at field conditions, $\mu g/m^3$;

TSP = concentration at standard conditions, $\mu g/std\ m^3$;

P_3 = average barometric pressure during sampling period, mm Hg;

P_{std} = 760 mm Hg (or 101 kPa);

T_3 = average ambient temperature during sampling period, K.

11.0 References.

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12.0 References

1. 40 CFR 50, Appendix B, as amended December 6, 1982 (47 FR 54912).
2. Quality Assurance Handbook for Air Pollution Measurement Systems - Volume I, Principles. EPA-600/9-76-005, March 1976.
3. 40 CFR 58, Appendix B.
4. 40 CFR 58, Appendix A.
5. McKee, H.C., et al. Collaborative Study of Reference Method for the Determination of Suspended Particulates in the Atmosphere (Hi-Vol Method). PB 205-891, June 1971.

13.0 Data Forms

Blank data forms are provided on the following pages for the convenience of the Handbook user Each blank form has the customary descriptive title centered at the top of the page, but the usual section-page documentation in the top right-hand corner of each page has been replaced with a number in the lower right-hand corner that will enable the user to identify and refer to a similar filled-in form in a text section For example, Form TSP-1 1 indicates that the form is Figure 1.1 of the TSP method description. Any future revisions of these forms can be documented as 1.1A, 1.1B, etc The following data forms are included in this section·

Form	Title
1.1	Procurement Log
2.3	Timer Calibration Log
2.4	Orifice Transfer Standard Certification Work Sheet
2 8	High-Volume Sampler Calibration Work Sheet
3.1	Laboratory Log for Total Suspended Particulate Data
3.2	Hi-Vol Field Data Form
4.6	Quality Control Chart
6.1	SAROAD Daily Data Form
8.2	Checklist for Use by Auditor for Hi-Vol Method

Procurement Log

Item description	Quantity	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ordered	Received			

Time Calibration Log

Site location number	Timer number	Date		Elapsed-time indicator serial number	Test period	Elapsed-time indicator reading	Accuracy	Technician (signature)
		Start	Stop					

Orifice Transfer Standard Certification Worksheet

	1	2	3	4	5	6	7	7a
Run No	Meter reading start V_i (m^3)	Meter reading stop V_f (m^3)	Elapsed time t (min)	Volume measured V_m (m^3)	Differential pressure (at inlet to volume meter) ΔP (mm Hg or in)	(X) Flow rate Q_{std} (std m^3 min)	Pressure drop across orifice ΔH ☐ (in) or ☐ (cm) of water	$\Delta H \left(\frac{P_1}{P_{std}}\right)^{(Y)} \frac{298}{T_1}$
1								
2								
3								
4								
5								
6								

Recorded Calibration Data

Standard volume meter No _____

Transfer standard type ☐ orifice ☐ other

Model No _____ Serial No _____

(8) P_1 _____ mm Hg (or in) (10) P_{std} 760 mm Hg (or 29 92 in)

(9) T_1 _____ K (11) T_{std} 298 K

By. _____

Date _____

Calculation Equations

(1) $V_m = V_f - V_i$

(2) $V_{std} = V_m \left(\frac{P_1 - \Delta P}{P_{std}}\right)\left(\frac{T_{std}}{T_1}\right)$

(3) $Q_{std} = \frac{V_{std}}{t}$

Least Squares Calculations

linear ($Y = mX + b$) regression equation of $Y = \sqrt{\Delta H (P_1/P_{std}) (298/T_1)}$ on $X = Q_{std}$ for Orifice Calibration Unit (i e , $\sqrt{\Delta H (P_1/P_{std}) (298/T_1)} = mQ_{std} + b$)

Slope (m) = _____ Intercept (b) = _____ Correlation coefficient (r) = _____

To use for subsequent calibration $X = \frac{1}{m}(Y-b)$,

$$Q_{std} = \frac{1}{m}\left[\sqrt{\Delta H \left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)} - b\right]$$

High-Volume Air Sampler Calibration Worksheet

Site location: _____

Date: _____ *(1) Barometric pressure, P_2 mm Hg (or in.)* _____

Calibrated by _____ *(2) Temperature, T_2 (K)* _____

Sampler No. _____ *Serial No.* _____

Transfer std. type. _____ *Serial No.* _____

Optional: P_{std} = 760 mm Hg (or 29.92 in.)

Average barometric pressure: P_a = _____

Seasonal average temperature: T_a = _____

No	1 ΔH Pressure drop across orifice (in) or (cm)	$\sqrt{\Delta H \left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	(X) 3 Q_{std} (from orifice certification std m^3/min	4 I Sampler flow rate indication (arbitrary)	5 (Y) For specific pressure and temperature corrections (see Table 2 1) ☐ I or ☐ $\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$ or ☐ $I\sqrt{\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	5 (Y) For incorporation of average pressure and seasonal average temperature (see Table 2 1) ☐ I or ☐ $\sqrt{I\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$ or ☐ $I\sqrt{\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$
1						
2						
3						
4						
5						
6						

Least Aquares Calculations

Linear regression of Y on X: Y = mX + b, Y = appropriate expression from Table 2 1, X = Q_{std}

Slope (m) = _____ *Intercept (b) =* _____ *Correlation Coefficient (r) =* _____

To determine subsequent flow rate during use: X = 1/m (Y-b)

Q_{std} = 1/m [appropriate expression from Table 2] - b]

Laboratory Log for Total Suspended Particulate Data

City Name

Site Address

State Area Site

Project The Interval

Project Time Year

Instrument Last Calibrated

Sampler Identification No

Total Suspended Particulate

Name Parameter Code

Sampling Date Month	Day	ST NR	Conc µg/m³	Filter Number	Average* CFM	Sampling Time	Air m³ Volume	Cross WCT	Tare WCT	Net WCT.	Remarks

*From Average Flow Determined from Calibration

Laboratory Functions

Filter Preparation

- Filter must be free of pinholes, tears, creases, lumps, etc
- Filter must be properly equilibrated (20 hrs <time<28 hrs, humidity <50%)
  (Δ Humidity ± 5% Δ Temp ± 3°C)
- Balance must be checked before weighing (STD. WGT 3 to 5 g ±0 0005 g)

Sampling Analysis

- Sample must be free or evidence of malfunction, ten or fewer insects in sample
- Filter must be properly equilibrated (see above)
- Balance must be checked before weighing (see above)

All samples were handled in accordance with the above guidelines

Signature

Comments _____

_____

_____

_____

_____

_____

Hi-Vol Data Record

Project _____

Station _____

_____

_____

Site and/or Sampler No _____

Saroad Site Code

Sample Date _____

Filter No. _____

Flow Reading initial _____

final _____

Average Flow Rate _____

Running Time Meter initial _____

final _____

Total Sampler Time _____ *min*

Total Air Volume _____ *std m³*

Net TSP Weight _____ *g*

TSP Concentration _____ *µg/std m³*

Optional

	Temperature	*Barometric Pressure*
initial	_____	_____
final	_____	_____
average	_____	_____

Operator _____

$\overline{X}$ and R Chart

Project Name _____ Measurement _____ Measurement Units _____

Performed _____

Data	Measurement									
	Code			Result						
	1	2	3	1	2	3				

SAROAD Daily Data Form

24-Hour or Greater Sampling Interval

2

1 Agency

City Name

Site Address

Project Time Interval

State Area Site

2 3 4 5 6 7 8 9 10

Agency Project Time Year Month

11 12 13 14 15 16 17 18

Name PARAMETER Code

23 24 25 26 27

Name PARAMETER Code

37 38 39 40 41

Name PARAMETER Code

51 52 53 54 55

Name PARAMETER Code

65 66 67 68 69

Day St Hr 28 29 30 31 32

42 43 44 45 46

56 57 58 59 60

70 71 72 73 74

19 20 21 22 33 34 35 36 47 48 49 50 61 62 63 64 75 76 77 78

DP→ 4 3 2 1 0 4 3 2 1 0 4 3 2 1 0 4 3 2 1 0

Checklist for Use by Auditor for Hi-Vol Method

1 *What type of hi-vol samplers are used in the network?* _____

_____

2 *How often are the samplers run? (a) daily (b) once every 6 days (c) once every 12 days (d) other* _____

3 *What type of filter and how many are being used?* _____

_____

4 *Are there any preexposure checks for pin holes or imperfections run on the filters?* _____

5 *What is the collection efficiency for your filters?* _____

6. *What is the calibration procedure for the hi-vol sampler?* _____

_____

7. *Which statement most closely estimates the frequency of flow rate calibration? (a) once when purchased (b) once when purchased, then after every sampler modification (c) when purchased, then at regular intervals thereafter* _____

8. *Are flow rates measured before and after the sampling period?*

Yes _____ *No* _____

9. *Is there a log book for each sampler for recording flows and times? Yes* _____ *No* _____

10 *Are filters conditioned before initial and final weighings?* _____ *If so, for how long?* _____ *At what percentage humidity?* _____

11 *Is the balance checked periodically?* _____ *If so, how often?* _____ *With which standard weights?*

12 *How often are the hi-vol filters weighed?* _____

How are the data from these weighings handled? _____

_____

13 *Are all weighings and serial numbers of filters kept in a log book at the laboratory?* _____

14. *What is the approximate time delay between sample collection and the final weighing?* _____ *days*

United States
Environmental Protection
Agency

Environmental Monitoring Systems
Laboratory
Research Triangle Park NC 27711

Research and Development

EPA-600/4-77-027a

EPA

Test Method
Section 2.6
Reference Method for the Determination of Carbon Monoxide in the Atmosphere (Nondispersive Infrared Photometry)

Outline

Section	Documentation	Number of pages
Summary	2.6	1
Method Highlights	2 6	1
Method Description		
1. Procurement of Equipment and Supplies	2.6.1	4
2. Calibration of Equipment	2.6.2	6
3. Operation and Procedure	2.6.3	6
4. Data Reduction, Validation, and Reporting	2.6.4	3
5. Maintenance	2.6 5	2
6. Auditing Procedure	2.6.6	4
7. Assessment of Monitoring Data for Precision and Accuracy	2.6.7	1
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9. Reference Method	2.6 9	3
10. References	2.6.10	1
11. Data Forms	2.6.11	12

Summary

Measurements of carbon monoxide (CO) in ambient air are based on the absorption of infrared radiation by CO in a nondispersive photometer. Infrared energy from a source is passed through a cell containing the gas sample to be analyzed, and the quantitative absorption of energy by CO in the sample cell is measured by a suitable detector. The photometer is sensitized to CO by employing CO gas in either the detector or in a filter cell in the optical path, thereby limiting the measured absorption to one or more of the characteristic wavelengths at which CO strongly absorbs. Optical filters or other means may also be used to limit sensitivity of the photometer to a narrow band of interest. Various schemes may be used to provide a suitable zero

reference for the photometer. The measured absorption is converted to an electrical output signal, which is related to the concentration of CO in the measurement cell.

An analyzer based on this principle will be considered a Reference Method only if it has been designated as a Reference Method in accordance with 40 CFR 53.

A current list of all designated Reference and Equivalent Methods is maintained by EPA and updated whenever a new method is designated This list may be obtained from any EPA Regional Office or from the Environmental Monitoring Systems Laboratory, Department E, MD-77, Research Triangle Park, North Carolina 27711 Moreover, any analyzer offered for sale as a Reference or Equivalent Method after April 16, 1976, must bear a label or sticker indicating that the EPA has so designated it. Further discussion of the concepts of Reference and Equivalent Methods appears in Section 2.0.4 of this Handbook.

Quality assurance procedures for measuring CO with a nondispersive, infrared radiation, automated sampler are not instrument specific; therefore, the following quality assurance functions are applicable to all CO analyzers designated as EPA Reference Methods.

Method Highlights

This section presents procedures for the Carbon Monoxide (CO) Reference Method (Nondispersive Infrared Photometry), which are intended to serve as guidelines for the development of agency quality assurance programs. Because recordkeeping is critical in quality assurance activities, example data forms are included to aid in data documentation. The blank data forms (Section 2.6.11) may be used as they are, or they may serve as a basis for the preparation of forms more appropriate to the individual agency; the partially filled-in forms are interspersed throughout the method description to illustrate their uses. Activity matrices at the end of pertinent sections provide quick reviews of the method description. The CO method is summarized briefly in the remainder of this section.

1. *Procurement of Equipment and Supplies*

Section 2.6.1 gives the specifications, criteria, and design features of the equipment and the supplies needed for the operation of and quality assurance checks on a continuous CO analyzer Selection of the correct equipment and supplies is a prerequisite of a quality assurance program. This section provides a guide for the procurement and the initial checks of equipment and supplies.

2. *Calibration of Equipment*

Section 2.6.2 provides procedures and forms to be used in performing a multipoint calibration, and in evaluating the calibration data. Subsection 2 1 deals primarily with minimum acceptable requirements for standards to be applied to the generation of CO concentrations. Subsection 2.2 provides step-by-step recommended calibration procedures for a nondispersive infrared (NDIR) CO analyzer, along with example calculations The data form (Figures 2.1 and 2 2) is to be used in the documentation of calibration data. Dynamic instrument calibration is essential for quality control

3. *Operation and Procedure*

Section 2.6 3 outlines the protocol to be followed by the operator during each site visit. To provide documentation and accountability of activities, the operator should compile and fill out a checklist, similar to the example in Figure 3 1 of Section 2.6.3, as each activity is completed. Checks should include visual inspection of the shelter, the sample introduction system, the analyzer, and the recorder Level 1 zero and span checks must be carried out at least once every 2 weeks; Level 2 checks should be conducted between the Level 1 checks at a frequency established by the user. Span concentrations for both levels should be between 70 and 90 percent of the measurement range. A one-point precision check should be made every 2 weeks at a CO concentration between 8 and 10 ppm. Data forms similar to Figures 3.2 and 3 3 of Section 2.6.3 should be used to document the analyzer performance checks. Routinely scheduled checks to verify the operational status of the monitoring system are essential in a quality assurance program

4. *Data Reduction, Validation, and Reporting*

Section 2.6.4 describes procedures to be used for editing strip charts and for data validation and reduction. Data collected on strip charts serve no useful function until they are converted into meaningful units ($\mu g/m^3$, ppm) applying to a specific time period (e.g., hourly) through the use of the calibration relationship. These data must be transcribed into an appropriate format such as that of the SAROAD hourly data form.

5. *Maintenance*

Section 2.6.5 addresses the recordkeeping and the scheduled activities pertinent to preventive and corrective maintenance A sample maintenance log is shown in Figure 5.1. Preventive and corrective maintenance are necessary to minimize loss of air quality data due to analyzer malfunctions and out-of-control conditions.

6. *Assessment of Data for Accuracy and Precision*

Section 2.6.6 discusses procedures and forms for system and performance audits. Multipoint performance audits to be used to assess the accuracy of the data collection are discussed in Subsection 6.1.1; audit procedures are given in Subsection 6.1.2; a data reduction audit is discussed in Subsection 6.1.3; and a system audit is discussed in Subsection 6.2. Figure 6.1 presents examples of audit summary and audit calculation forms. Figure 6.2 is an example checklist to be used by the auditor.

Section 2.6.7 describes the techniques for assessment of data for accuracy and precision.

7. *Reference Information*

Section 2 6.8 discusses the traceability of standards to established standards of higher accuracy, a prerequisite for obtaining accurate data.

Sections 2 6.9 and 2.6.10 contain the Reference Method and pertinent references.

1.0 Procurement of Equipment and Supplies

Measurement of carbon monoxide (CO) in ambient air requires basic sampling equipment and peripheral supplies; these include, but are not limited to, the following:

1. Reference method CO analyzer (NDIR) (Subsection 1 1 provides information on obtaining an up-to-date list of analyzers)
2. Strip chart recorder or data logging system
3. Sampling lines
4. Sampling manifold
5. Calibration equipment
6. NBS-SRM or commercial CRM calibration standard
7. Working calibration and audit gases traceable to NBS or CRM standard
8. Zero-air source
9. Spare parts and expendable supplies
10. Record forms
11. Independent audit system

The person responsible for purchasing materials should maintain a log to record vendor names, part numbers, prices, dates, and other pertinent information. An example log is shown in Figure 1 1. The log will serve as a reference for future procurement needs and as a tool for planning budgets for future monitoring programs. Quality assurance activities for procurement of equipment and supplies are summarized in Table 1.2 at the end of this section

1.1 The CO Analyzer (NDIR)

As stated in the Code of Federal Regulations,[1] each method for measuring CO shall be either a Reference or Equivalent Method when the purpose is to determine compliance with the National Ambient Air Quality Standards (NAAQS). For carbon monoxide, the Reference Method is Nondispersive Infrared Photometry (NDIR)

Although the NDIR analyzers currently available for measuring CO in ambient air are competitively priced, price differences become apparent when options to the basic package are ordered. The buyer should consult the list of designated Reference and Equivalent Methods for approved options. An up-to-date list of analyzers designated as reference or Equivalent methods for CO is available by writing to:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Department E, MD-77
Research Triangle Park, North Carolina 27711

Available options include automatic zero and span systems and complete telemetry systems for transmitting daily zero and span checks and real-time data from the site to a central location. For certain CO analyzers, the automatic zero and span systems are required to meet the EPA Reference Method designation. Although options can add convenience and flexibility, their necessity and desirability must be dictated by the availability of field personnel, accessibility of the site, and limitations of the budget.

When purchasing, the buyer should request that the manufacturer supply documented proof that the specific analyzer performs within specifications (Table 4 1, Section 2.0 4). The best proof is a strip chart recording showing the specific analyzer's zero drift, span drift, electronic noise, risetime, falltime, and lagtime. Acceptance of the analyzer should be based on these performance tests; once accepted, the Reference and Equivalent analyzers are warranted by the manufacturer to operate within the required performance limits for 1 year. The strip chart will also serve as a reference to determine whether the performance of the analyzer has deteriorated at a later date. The user should reverify the performance characteristics either during the initial calibration or by using abbreviated forms of the test procedures in the ambient air monitoring Reference and Equivalent Methods Regulations [2]

1.2 Strip Chart Recorder

Recorders are commercially available at a wide variety of prices and specifications. Factors to be considered in the purchase of a recorder are:

1. Compatibility with the output signal of the analyzer
2. A minimum chart width of 15 cm (6 in.) for the desired accuracy in data reduction
3. A minimum chart speed of at least 2.5 cm/h (1 in./h)
4. Response time
5. Precision and reliability
6. Flexibility of operating variables (speed, range)
7. Maintenance requirements.

1.3 Sampling Lines and Manifold

Wherever possible, sampling lines and manifolds should be constructed of Teflon or glass to minimize degradation of the sample; however, because of the relative inertness of CO, other types of materials (polypropylene, stainless steel) will suffice if only CO is being measured Sample residence time should be minimized The use of a particle filter on the sample inlet line of an NDIR CO analyzer is optional on some analyzers, and left to the discretion of the user or the manufacturer. Use of the filter should depend on the analyzer's susceptibility to interference, malfunction, or damage due to particles.

1.4 Calibration Equipment and Standards

The two acceptable methods for dynamic multipoint calibration of CO analyzers are:[3]

1. The use of individual certified standard cylinders of CO for each concentration needed.
2. The use of one certified standard cylinder of CO, diluted as necessary with zero-air, to obtain the various calibration concentrations needed.

Both methods require the following:

1. Pressure regulator(s) for CO cylinder(s)
2. Flow controller
3. Flow meter
4. Mixing chamber (dynamic dilution only)
5. Output manifold
6. Zero-air source
7. Calibration standard.

The equipment needed for calibration can be purchased commercially, or it can be assembled by the user. When a calibrator or its components are being purchased, certain factors must be considered:

1. Traceability of the certified calibration gases to an NBS-SRM[4] or an NBS/EPA-approved commercially available Certified Reference Material (CRM).
2. Accuracy of the flow-measuring device (rotameter, mass flow meter, bubble meter).

Item description	Quantity	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ordered	Received			
NDIR CO Analyzer	1	01580	Beckman	3-8-79	3-30-79	$6230		OK
Recorder	1	01581	Leeds & Northrup	3-8-79	3-22-79	$1343		OK

Figure 1.1. Example of a procurement log.

3. Maximum and minimum flows of dilution air and calibration gases.
4. Ease of transporting the calibration equipment from site to site.

1.4.1 *Pressure Regulator* —
A pressure regulator will be required for the CO calibration standard cylinder If individual cylinders are to be used for individual calibration points, it is advisable to procure regulators for each cylinder Regulators must have a nonreactive diaphragm and suitable delivery pressure. A two-stage regulator with inlet and delivery pressure gauges is recommended. The supplier from which the CO cylinders are to be obtained should be consulted as to the correct cylinder fitting size required for the regulator

1.4.2 *Flow Controller* —
The flow controller can be any device (valve) capable of adjusting and regulating the flow from the calibration standard If the dilution method is to be used for calibration, a second device will be required for the zero-air. For dilution, the controllers must be capable of regulating the flow to ±1 percent

1.4.3 *Flow Meter* —
A calibrated flow meter capable of measuring and monitoring the calibration standard flow rate will be required. If the dilution method is used, a second flow meter will be required for the zero-air flow. For dilution, the flow meters must be capable of measuring the flow with an accuracy of ±2 percent

1.4.4 *Mixing Chamber* —
A mixing chamber is required only if the calibrator concentrations are generated by dynamic dilution of a CO standard. The chamber should be designed to provide thorough mixing of CO and zero-air

1.4.5 *Output Manifold* —
The output manifold should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold

1.4.6 *Zero-Air Source* —
A source of dry zero-air that is verified to be free of contaminants that could cause detectable responses from the CO analyzer will be needed. Zero-air containing <0 1 ppm CO may be purchased in high-pressure cylinders or generated with commercially available clean air systems The zero-air must contain <0 1 ppm CO; some air cylinders sold as ultrapure may actually contain 1 to 2 ppm CO The use of a catalytic oxidizing agent such as Hopcalite on any zero-air source would be prudent

1.4.7 *Calibration Standard* —
Both methods require CO standards to be traceable to a National Bureau of Standards Standard Reference Material (NBS-SRM) or an NBS/EPA-approved commercially available Certified Reference Material (CRM) (Section 2 6 8)

The CO standards must be in air unless the dilution method is used. For dilution, CO in nitrogen may be used if the zero-air dilution ratio is not less than 100 1 An acceptable protocol for demonstrating the traceability of commercial cylinder gas to an NBS-SRM or CRM cylinder gas is described in Section 2 0 7 of this volume of the Handbook Table 1 1 lists these NBS-SRM's available for CO monitoring

A list of gas manufacturers who have approved CRM is available by writing to

U S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory (MD-77)
Research Triangle Park, North Carolina 27711
ATTN: List of CRM Manufacturers

1.5 Verification of Calibration Equipment and Gases

The user should reanalyze all working standards used for calibrations at least once every 6 months, as specified in Section 2 0 7 of this volume of the Handbook (particularly Subsections 7 1 2 and 7 1 5 on analysis and reanalysis of cylinder gases) Flow-measuring devices should be recalibrated by following the procedures and schedules in Section 2 1 2

1.6 Audit Equipment

All audit gas standards must be traceable to an NBS-SRM or a commercially available CRM, as described by the protocol in Sections 2 6 2 and 2 0.7. All flow rates should be measured by use of a calibrated soap bubble meter or an equivalently accurate device Personnel, equipment, and reference materials used in audits must be independent from those normally used in calibrations and operations

1.7 Spare Parts and Expendable Supplies

In addition to the basic equipment just discussed, an inventory of spare parts and expendable supplies must be maintained The manufacturer's manual contains a maintenance section describing the parts that require periodic replacement and the frequency of this replacement. Based on these requirements, the manager of the monitoring network can determine which parts and the quantity of each that should be available at all times. Typical spare parts and expendable supplies for CO monitors are listed below; for more specific requirements refer to the manufacturer's manual

1 Particulate filters
2 Sampling lines
3 Pump diaphragms
4 Recorder chart paper
5 Recorder ink or pens
6 Record forms
7. Calibration gas
8 Spare fittings

1.8 Record Forms

Recordkeeping is a critical part of all quality assurance programs. Standard forms similar to those in this manual should be developed for each individual program Three things to consider in the development of record forms are

1 Does the form serve a necessary function?
2 Is the documentation complete?
3 Will the forms be filed in such a manner that they can easily be retrieved when needed?

Table 1.1. *NBS-SRM's for CO Monitors*

SRM	*Type*	*Vol/unit, liters at STP*	*Nominal CO concentration, ppm*
1680b	*CO in nitrogen*	*870*	*500*
1681b	*CO in nitrogen*	*870*	*1000*
2613	*CO in air*	*870*	*18.1*
2614	*CO in air*	*870*	*43.0*

Table 1.2. Activity Matrix for Procurement of Equipment and Supplies

Equipment and supplies	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
NDIR analyzer	*Performance according to specifications in Table 4.1, Sec. 2 0 4*	*Manufacturer strip chart recording of analyzer's performance*	*Have the manufacturer adjust and rerun the performance checks*
Strip chart recorder	*Compatible with output signal of analyzer, recommended chart width of 15 cm (6 in)*	*Visually observe upon receipt*	*Return to supplier*
Sampling lines and manifold	*Constructed of Teflon or glass*	*Visually observe upon receipt*	*Other types of materials may be acceptable for CO sampling*
Calibration gases	*Traceable to an NBS-SRM or a commercially available CRM; ±2.0% of rated concentration*	*Upon receipt and monthly thereafter for first 3 mo; if concentration remains stable, verify every 6th month*	*Return to supplier*
Audit gases	*Traceable to an NBS-SRM or commercially available CRM; ±2 0% of rated concentration*	*As above*	*As above*
Zero-air	*<0.1 ppm CO*	*Check against analyzer internal zero or another source of zero-air known to to be CO-free*	*As above*

2.0 Calibration of Equipment

The accuracy and validity of measurement data recorded by air monitoring equipment depend on the quality assurance procedures used The primary procedure is dynamic calibration, which determines the relationship between the observed and the actual values of the variable being measured.

In dynamic multipoint calibration, gas samples of known concentrations are introduced to an instrument to derive a calibration relationship or to adjust the instrument to a predetermined sensitivity The relationship is derived from the instrumental responses to the successive samples of known concentrations A minimum of four reference points and a zero point are recommended to derive the relationship. The "true" value of each calibration gas must be traceable to an NBS-SRM or a commercially available CRM (Section 2 0 7)

Most present-day monitoring systems are subject to drift and variability of internal parameters, and they cannot be expected to maintain calibrations over long periods of time Therefore, it is necessary that the calibration relationship be dynamically checked on a predetermined schedule. Precision is determined by a one-point check performed at least once every 2 weeks Network accuracy is determined by a three-point audit performed at least once each quarter. Zero and span checks must be made to document in-control conditions; these checks are also used in data reduction and validation.

Table 2.1 at the end of this section summarizes the quality assurance activities for calibration procedures

2.1 Calibration Gases

2.1.1 *CO Standard —*

The CO standards must be in air unless the dilution method is used. For dilution, CO in nitrogen may be used if the zero-air dilution ratio is not less than 100:1. All calibration gas mixtures must be referenced against an NBS-SRM or a commercially available CRM (Section 2 0.7). The steps required for comparing the concentration of a commercial working calibration standard to the concentration of an NBS-SRM or a CRM are described in Subsection 7.1 of Section 2.0.7. Subsections 7 1 4 and 7 1.5 describe the procedures for verification and reanalysis of cylinder gases The CO gas cylinders should be recertified every 6 months The use of aluminum cylinders will provide better stability of CO standards

2.1.2 *Dilution Gases —*

Zero-air, verified to be free of contaminants that would cause detectable responses in the CO analyzer, may be purchased in high-pressure cylinders or generated with commercially available clean air systems Care must be exercised to ensure that <0 1 ppm CO is present in the zero air; some air cylinders sold as ultrapure may actually contain 1 to 2 ppm CO Any zero air source used must be verified to contain <0 1 ppm CO. The use of a catalytic oxidizing agent such as Hopcalite on any zero-air source would be prudent Any zero air passing through a catalytic oxidizer must be free of water vapor

2.2 Calibration

The procedure for dynamically calibrating the NDIR analyzer may be found in 40 CFR 50,[3] and in the manufacturer's manual Essentially, the procedure involves challenging the analyzer with a minimum of four CO concentrations and defining the relationship between the concentration and the analyzer response Forms for recording operational and calculation data have been developed to aid in the documentation of calibrations and quality assurance checks Documentation of all data on the station, instrument, calibrator, reference standard, and calibration activity is of prime importance because the validity of the data collected by the monitor depends on its calibration

2.2.1 *Calibration Procedure —*

The following calibration procedure is based on dynamically diluting a high CO concentration with zero-air. An alternative procedure is to use individual cylinders containing the desired CO concentrations, which eliminates the necessity of dilution

Any dynamic dilution system used for calibration must be capable of measuring and controlling flow rates to within ±2 percent of the required flow. Flow meters must be calibrated under the conditions of use against a reliable standard, such as a soap bubble meter or a wet test meter All volumetric flow rates should be corrected to 25°C (77°F) and 760 mm (29 92 in) Hg If both the CO and the zero-air flow rates are measured with the same device under the same conditions of temperature and pressure, the STP correction factor in the calibration equations can be disregarded

The following step-by-step procedure uses a data form (Figure 2 1) to aid in the collection and documentation of calibration data The calibration equations in Figure 2 1, the CO calibration and linearity check table, and the calibration relationship plot in Figure 2 2 are given to facilitate the systematic recording of data derived during the calibration of the NDIR CO analyzer. The user should consult the manufacturer's manual before beginning the calibration because the zero and calibration procedures and adjustments differ from analyzer to analyzer

1 Record the official name and address of the individual station. *Note:* Where appropriate, the station name, address, and SAROAD ID should be the same as that on the hourly average data form (Figure 4 1 of Section 2.6.4) to help eliminate confusion on the part of persons not familiar with the station

2 Identify the analyzer being calibrated by recording the manufacturer's name, model, and serial number

3 Identify the person performing the calibration and give the date of calibration

4 Identify the calibrator or dilution system used If the system was purchased, record the manufacturer's name, model, and serial number, if the system was assembled by the user, assign it an identification number so that calibrations can be referenced to that particular apparatus

5 Identify, by supplier and cylinder number, the reference standard used; record the concentration of calibration gases determined by the user and the cylinder pressure, provide a record of NBS-SRM or CRM traceability for any cylinder used in a calibration, and include the date and the name of the person who conducted the traceability test *Note* Cylinders with pressures of

Calibration Summary

1. *Station* Downtown
1470 North Street

2 *Analyzer* ACME
Model 120
S/N 14677

3 *Calibration by* JOE SMITH
Date 11-10-79

4 *Calibrator mfr* ACME
Model 022
S/N 14780

5 *CO standard* Cal gas cylinder 832
Concentration 250 ppm
Verified against NBS-SRM Co cylinder CC 1247
Cylinder pressure 500 psi
By JOE SMITH
Date 9-15-79

6 *Flow-measuring device* Mass flow meter
Traceability bubble meter 208

7. *Barometric pressure* 740 mm Hg
Shelter temperature 25°C

8 *Analyzer's sample flow rate* 1 lpm

9 *Zero knob setting* 24.6
Span knob setting 28.1

Calibration Equations

Equation 2-1

F_D or F_{CO} = F (STP correction factor)

Equation 2-2

$$\text{STP Correction factor} = \frac{BP}{760} \times \frac{298}{AT+273}$$

Equation 2-3

$$[CO]_{OUT} = \frac{[CO]_{STD} \times F_{CO}}{F_D + F_{CO}}$$

Equation 2-4

$$\%\ scale = \frac{[CO]_{OUT} \times 100}{URL} + Z_{CO}$$

F = uncorrected flow rate for dilution air or CO standard gas, l/min

F_D = flow rate of dilution air corrected to 25°C and 760 mm Hg, l/min

F_{CO} = flow rate of CO standard corrected to 25°C and 760 mm Hg, l/min

BP = barometric pressure, mm Hg

AT = temperature of gas being measured, °C

$[CO]_{OUT}$ = concentration at the output manifold, ppm

$[CO]_{STD}$ = concentration of the undiluted standard, ppm

Z_{CO} = recorder response to zero air

Figure 2.1. *Example of calibration data form*

<200 psig should not be used for calibration because gases in cylinders may become unstable for some concentrations at low pressures (Section 2.0.7).

6. Identify the flow-measuring device used, and document the traceability of its accuracy.

7. Record the barometric pressure and the shelter temperature before the calibration.

8. Record the analyzer's sample flow rate.

9. Record the zero and span knob settings after the calibration so that these settings can be used later to determine changes in instrument performance.

Figure 2.2 contains a CO calibration and linearity check table and a graph to facilitate the plotting of the calibration data. The equations at the bottom of Figure 2 1 are to be used to obtain the entries in the table in Figure 2.2. The detailed steps of the calibration procedure are given below. Analyzer responses in these steps refer to recorder responses. The manufacturer's instrument manual should be consulted for analyzer-specific calibration procedures.

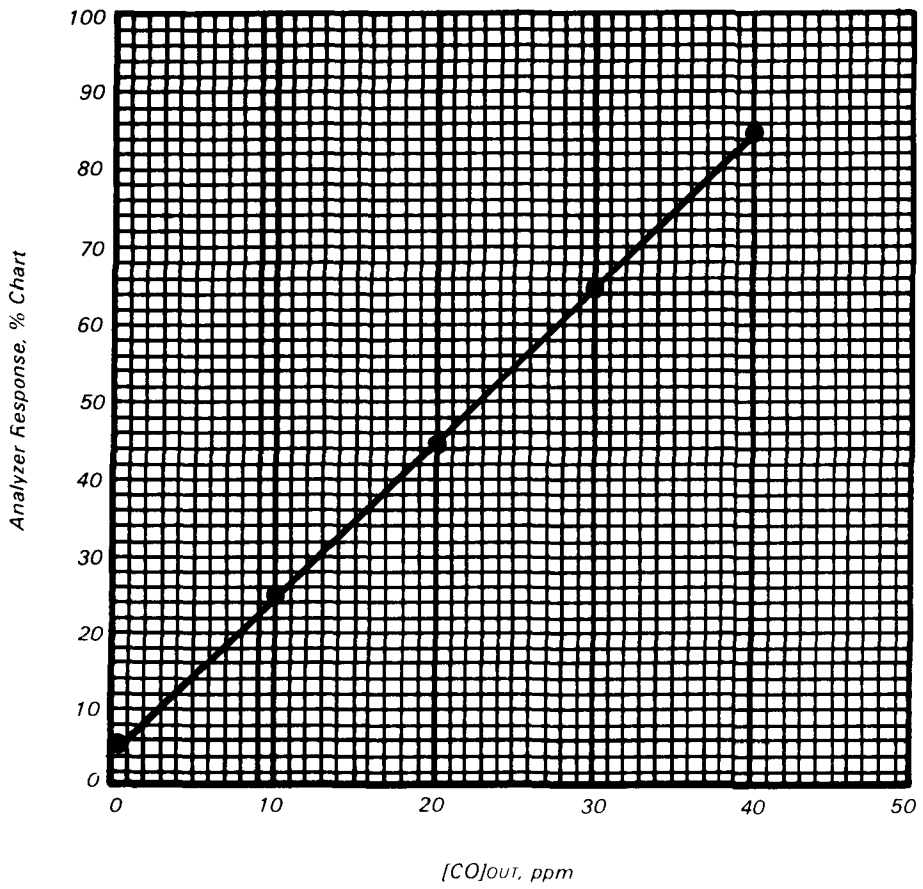
1. Select the operating range of the analyzer to be calibrated by referring to the manufacturer's manual for the ranges over which the analyzer is considered to be a reference method.

2. Connect the recorder output cable(s) of the analyzer to the input terminals of the strip chart recorder(s). All adjustments to the analyzer should be based on the appropriate strip chart readings. *Note:* When data acquisition systems are used to store and/or transmit data to a base station, some provision must be made to verify the accuracy of the transmitted data. In these cases, a voltmeter or recorder can be used to take readings and to make adjustments onsite A comparison check must then be made between signal outputs from the analyzer and data received at the base locations.

3. Adjust the zero-air flow to the

Calibration points	1 F_{CO} l/min (Eq 2-1 & 2-2)[a]	2 F_D l/min (Eq 2-1 & 2-2)	3 $[CO]_{OUT}$, ppm (Eq 2-3)	4 % scale (Eq 2-4)
Zero			0	5%
80% URL	0.500	2.625	40	85%
1	0.500	3.667	30	65%
2	0.500	5.750	20	45%
3	0.500	12.000	10	25%

[a]Equations 2-1 through 2-4 are given in Figure 2 1 and in the text



Slope (b) of calibration relationship 2.0

Intercept (a) of calibration relationship 5%

Figure 2.2. *Example of calibration data form. (Linearity Check and Calibration Relationship)*

analyzer; the flow must exceed the total demand of the analyzer connected to the output manifold to ensure that no ambient air is pulled into the manifold vent.

4. Allow the analyzer to sample the zero air until a stable response is obtained; adjust the analyzer zero control to within ±0.5 ppm of zero base line, and record the stable zero-air response (% scale) under column 4 of the calibration table in Figure 2.2. *Note:* Offsetting the analyzer zero adjustment to +5% of scale is recommended to facilitate observing negative zero drift On most analyzers, this should be done by offsetting the recorder zero

5. Determine the 80 percent upper range limit (URL) of the analyzer *Example:* For an analyzer with an operating range of 0 to 50 ppm, the 80 percent URL value would be 0.80 x 50, or 40 ppm

6 Adjust the CO flow from the standard CO cylinder to generate a CO concentration of approximately 80 percent of the URL. Measure the CO flow, correct it to STP, and record under column 1 (F_{CO}), on the 80 percent URL line.

$$F_{CO} = F \times (\text{STP correction factor})$$
Equation 2-1

$$\text{STP correction factor} = \frac{BP}{760} \times \frac{298}{AT + 273}$$
Equation 2-2

where
F_{CO} = flow rate of CO standard corrected to STP, l/min
F = uncorrected flow rate, l/min
BP = barometric pressure, mm Hg
AT = temperature of gas being measured, °C

Note: If wet test meter or bubble meter is used for flow measurement, the vapor pressure of water at the temperature of the meter must be subtracted from the barometric pressure.

Measure the dilution air flow, correct it to STP, and record under column 2 (F_D).

$$F_D = F \times (\text{STP correction factor})$$

7. Calculate the CO concentration $[CO]_{OUT}$ using Equation 2-3.

$$[CO]_{OUT} = \frac{[CO]_{STD} \times F_{CO}}{F_D + F_{CO}}$$
Equation 2-3

Record this value on the 80% URL line under column 3.

8. Calculate the required recorder response for span adjust (80% URL) using Equation 2-4.

$$\%\ \text{scale} = \left(\frac{[CO]_{OUT}}{URL} \times 100\right) + Z_{CO}$$
Equation 2-4

Allow the analyzer to sample until the response is stable; adjust the analyzer span until the required response is obtained, and record the CO recorder response on 80 percent URL line under column 4. *Note.* If substantial adjustments of the span control are necessary, recheck the zero and span adjustments by repeating steps 4 and 8.

9. After the zero and 80 percent URL points have been set, without further adjusting the instrument, generate three approximately evenly spaced points between zero and 80 percent URL by increasing the dilution flow (F_D,) or by decreasing the CO flow (F_{CO}). For each concentration generated, calculate the CO concentrations (using Equation 2-3) and record the results for each point under the appropriate column in the table in Figure 2.2.

10. On the blank graph of Figure 2.2, plot the analyzer responses expressed in percent scale at the recorder (y-axis) versus the corresponding calculated concentrations (x-axis) to obtain the calibration relationship. Determine the straight line of best fit by the method of least squares (Volume I, Appendix J of this Handbook) using a programmed calculator or the calculation data form (Figure 2.3). *Note:* Because manual calculations (using the data form) require considerably more time than the use of a programmed calculator, it is suggested that the latter be used when possible.

11. After determining the slope (b) and the intercept (a) where the line crosses the y-axis, draw the fitted line as follows: On the y-axis, plot the y intercept, a, use the equation Y = a + bx to calculate the predicted Y value using the 80 percent URL concentration for the x value as the second point on the graph. Draw a straight line through these two points to give a best-fit line, as shown in Figure 2.4

12. After drawing the best-fit line, determine if the analyzer response is linear, that is, no calibration point varies from the best-fit line by more than 2 percent of full scale. Make a simple test for linearity by plotting a point 2 percent of scale above and 2 percent of scale below the point where the best-fit line crosses the 40-ppm level and the 10-ppm level, and then draw a straight line through the +2 percent points and one through the -2 percent points (Figure 2.4). The two lines (above and below the best-fit line) define the limits between which the calibration points can fall for the calibration curve to be considered linear. Points outside these limits should be repeated to check for calibration point errors; if the repeated points still fall outside the limits, consult the manufacturer's manual to determine and correct the problem.

2.2.2 *Calibration Frequency* —
To ensure accurate measurements of the CO concentrations, calibrate the analyzer at the time of installation, and then recalibrate it as specified in the instrument manual or·

1. No later than 3 months after the most recent calibration or performance audit. If performance audit results are satisfactory, recalibration must be performed immediately.
2. After an interruption of more than a few days in analyzer operation, after any repairs that might affect its calibration, after physical relocation of the analyzer, or after any other indication (including excessive zero or span drift) of possible significant inaccuracy of the analyzer. Following any of these activities, a Level 1 zero and span check should be made to determine if recalibration is necessary If the zero and span drifts do not exceed the limits (Table 9 1, Section 2.0.9, Subsection 9.1.3), a calibration need not be performed. If either the zero or the span drift exceeds its limit, investigate the cause of the drift, take corrective action, and calibrate the analyzer

Calibration point	Concentration, ppm x	x^2	Recorder reading, % scale y	y^2	xy
Zero	0	0	5	25	0
80% URL	40	1600	85	7225	3400
1	30	900	65	4225	1950
2	20	400	45	2025	900
3	10	100	25	625	250

$\Sigma x =$ 100, $\Sigma x^2 =$ 3000, $\Sigma y =$ 225, $\Sigma y^2 =$ 14125, $\Sigma xy =$ 6500, $x = \Sigma x/n =$ 20, $y = \Sigma y/n =$ 45, and n = number of calibration points.

The equation of the line fitted to the data is written as.

$Y = \bar{y} + b(x-\bar{x}) = (\bar{y}-b\bar{x}) + bx = a + bx$

where Y = predicted mean response for corresponding x

b = slope of the fitted line

a = intercept where the line crosses the y-axis

$$b = \frac{\Sigma xy - \frac{(\Sigma x)(\Sigma y)}{n}}{\Sigma x^2 - \frac{(\Sigma x)^2}{n}} = \frac{6500 - \frac{(100)(225)}{5}}{3000 - \frac{(100)^2}{5}} = 2.0$$

$a = \bar{y} - b\bar{x} =$ 5.0

Figure 2.3. *Calculation form for the method of least squares.*

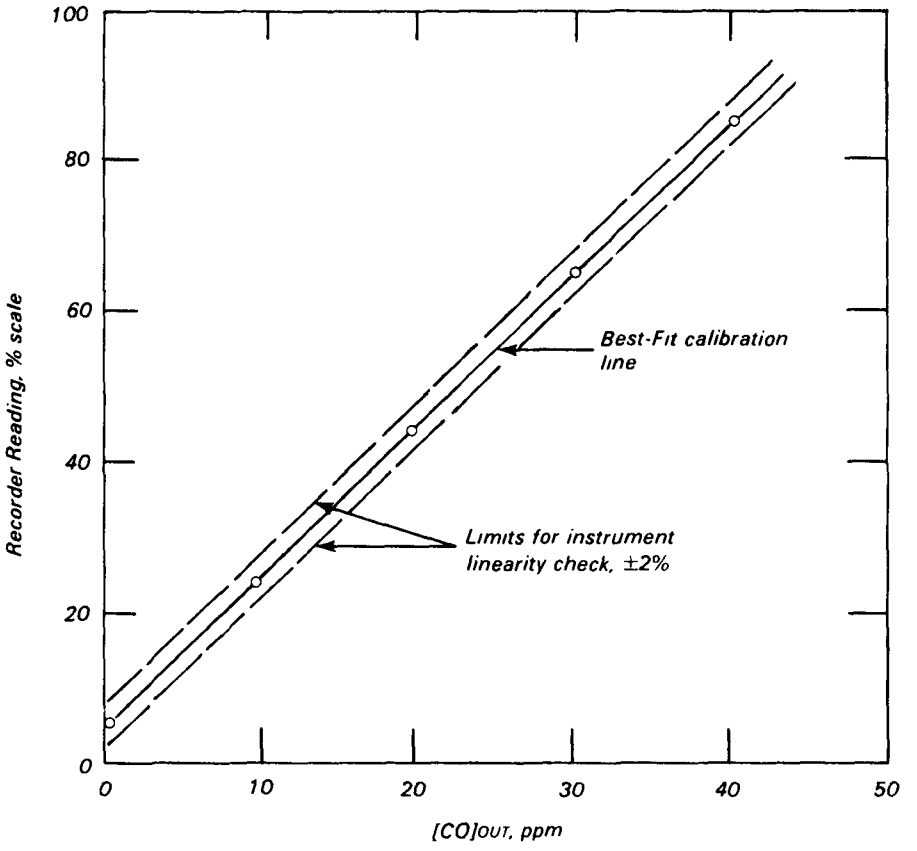


Figure 2.4. *Example of a CO calibration relationship*

Table 2.1. *Activity Matrix for Calibration Procedures*

Calibration activities	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Dilution gas	*Zero-air free of contaminants (Sec. 2.0.7, Subsec. 7.1)*	*Compare the new zero-air against source known to be free of contaminants*	*Return to supplier, or take corrective action with generation system as appropriate*
Span gases	*Cylinder gases certified to NBS or CRM standard; cylinder pressure >200 psig*	*Assay against an NBS-SRM or CRM semiannually (Sec. 2.0.7)*	*Working gas standard unstable, and/or measurment method out of control; take corrective action, e.g., obtain new span gases*
Multipoint calibration	*According to calibration procedure (Subsec. 2.2) and data recorded (Figs 2.1 and 2.2)*	*Calibrate at least once, quarterly; anytime a Level 1 span check indicates discrepancy; after maintenance that may affect the calibration (Subsec. 2.2)*	*Repeat the calibration*

3.0 Operation and Procedure

A routinely scheduled series of checks to verify the operational status of the monitoring system is an essential part of the quality assurance program. The operator should visit the site at least once each week, and he/she must make a Level 1 zero and span check on the analyzer at least once every 2 weeks. The user may decide on the frequency of any Level 2 zero and span checks. In addition, an independent precision check between 8.0 and 10.0 ppm must be carried out at least once every 2 weeks.

Table 3.1 at the end of this section summarizes the quality assurance activities for routine operations discussed in the following subsections. To provide documentation and accountability of activities, the field operator should compile and fill out a checklist as each activity is completed; Figure 3.1 is an example checklist.

In Subsections 3.1 and 3 2, reference is made to the sampling shelter and sample inlet system. The design and construction of these components of the sampling system are not within the scope of this document, but an in-depth study of these is provided in Reference 5.

3.1 Shelter

The shelter's role in quality assurance is to provide a temperature-controlled environment in which the sampling equipment can operate at optimum levels of performance. The mean shelter temperature should be between 22° and 28°C (72° and 82°F). A thermograph should be installed at the shelter so that daily temperature fluctuations can be continuously recorded. Fluctuations greater than ±2°C (4°F) may cause the electronic components of the analyzer to drift and introduce error into the data; thus, fluctuations outside of the specifications should be identified, and the data for the affected time period should be flagged to indicate possible discrepancies. Excess vibrations will cause analyzer fluctuations and should be minimized where possible.

3.2 Sample Introduction System

The sample introduction system consists of an intake port, particulate and moisture traps, a sampling manifold, a blower, and a sampling line to the analyzer As part of the quality assurance program, the field operator should inspect each of these components for breakage, leaks, and buildup of particulate matter or other foreign materials, check for moisture depostion in the sampling line or manifold; and check the connection between the sampling line and the manifold Any component that is not within tolerance should be cleaned or replaced immediately (Section 2.0.2).

3.3 Recorder

During each visit to the monitoring site, the field operator should check the recorder against the following list:

1. Legibility of the ink trace
2. Ink supply in the reservoir
3. Chart paper supply
4. Chart speed control setting
5. Signal input range setting
6. Time synchronization Mark chart with correct time and date

Any operational parameter that is not within tolerance must be corrected immediately.

3.4 Analyzer

The user should read thoroughly the specific instructions in the manufacturer's manual before attempting to operate the analyzer As part of the quality assurance program, each site visit should include a visual inspection of the external parameters of the analyzer, the zero and span checks, and a biweekly precision point check.

3.4.1 *Visual Inspection* —

The field operator should inspect the external operating parameters of the analyzer; these will vary from instrument to instrument, but they generally will include the following

1. Correct setting of flow meter and regulators
2. Cycling of temperature control indicators
3. Verification that the analyzer is in the sampling mode rather than in the zero or calibration modes
4. Zero and span potentiometers set and locked at proper values.

3.4.2 *Zero and Span Checks* —

Interim zero and span checks on the responses of the instrument to known concentrations must be used to document within-control conditions. If a response is outside of the prescribed limits, the analyzer is considered out of control, and the cause must be determined and corrected. A quality control chart can be used to check the analyzer visually for within-control conditions

Level 1 and Level 2 span checks must be conducted in accordance with the specific guidance given in Subsection 9.1 of Section 2.0.9. If permitted by the associated operation or instruction manual, a CO analyzer may temporarily operate during the zero and span checks at reduced vent or purge flows, or the test atmosphere may enter the analyzer at a point other than the normal sample inlet if the analyzer's response is not likely to be altered by these deviations from the normal operational mode. Because variability information may not be uncovered by checking only part of the analyzer's sample-handling system, however, it is recommended that these operational deviations be used only for Level 2 checks

Level 1 zero and span checks must be conducted every 2 weeks, Level 2 checks should be conducted in between the Level 1 checks at a frequency decided on by the user. Span concentrations for both levels should be between 70 and 90 percent of the measurement range. The data should be recorded on a zero and span checks form such as that shown in Figure 3 2.

Level 1 zero and span data are used for the following:

1. To adjust the analyzer for zero and span drifts
2. To decide when to calibrate the analyzer
3. To decide when to invalidate monitoring data

Items 1 and 2 are detailed in Subsection 9.1.3 of Section 2.0.9; Item 3, in Subsection 9 1.4 of the same section.

When the response from a span check is outside of the control limits, the cause for the extreme drift must be determined and corrective action taken. Some of the causes for drift are listed below:

1. Lack of preventive maintenance
2. Fluctuations in electrical power supply
3. Fluctuations in flow
4. Change in zero-air source

Site identification 001 Date 3-1-79

Site location Municipal Incinerator Technician C. JONES

Site address 3336 Jefferson Avenue

✓ 1 Inspect thermograph for temperature variations greater than ±2°C (4°F); identify time frame of any temperature level out of tolerance

Comments. Temp. w/in tolerance levels

✓ 2 Inspect sample introduction system for moisture, particulate buildup, foreign material, breakage, leaks

Comments Accumulation of particulate in trap. Trap removed and cleaned.

✓ 3 Is sample line connected to manifold?

Comments Okay

✓ 4 Inspect data recording system

	OK	Corrective action taken
● Legibility of trace	✓	
● Ink supply		✓
● Paper supply	✓	
● Chart speed	✓	
● Signal range	✓	
● Time synchronization		✓

Comments:

✓ 5 Inspect analyzer operational parameters

	OK	Corrective action taken
● Sample flow rate	✓	
● Oven temp light flashing	✓	
● Analyzer in sampling mode	✓	
● Zero and span potentiometers locked at correct settings	✓	

Comments. none

✓ 6 Zero the analyzer

✓ 7 Is unadjusted zero within tolerance?

Comments: zero okay at 4.5%

✓ 8 Span the analyzer

✓ 9. Is unadjusted span within tolerance?

Comments span okay at 80%

✓ 10 Enter zero and span values on data form, Figure 3 2

✓ 11 Return to sampling mode

✓ 12 Record pressures of zero and span cylinders

Zero air 1300 PSI Span air 1600 PSI

___ 13 Close valve on zero and span cylinders

Signature of technician Collin Jones

Figure 3.1. Example of an operational checklist.

Site identification 2013 Pollutant CO

Location Downtown Analyzer ACME MODEL 120

Address 1470 North Street Serial number 14677

Adjusted zero 5 Adjusted span 75

Date	Operator	Unadjusted zero, % chart	Span concentration, ppm	Unadjusted analyzer response,		Difference, ppm
				% chart	ppm	
11-15-79	J.S.	5.0	35 ppm	757	35	0

Figure 3.2. Example of a Level 1 zero and span check data form

5 Change in span gas concentration
6 Degradation of detector
7. Electronic and physical components not within manufacturer's specifications
Corrective actions for the above can be found in the manufacturer's instruction/operations manual

3.4.3 *Precision Check* —
A periodic precision check is used to assess the data A one-point check on each analyzer must be carried out at least once every 2 weeks at a CO concentration between 8 and 10 ppm The analyzer must be operated in its normal sampling mode, and the precision test gas must pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling. If permitted by the associated operation or instruction manual, a CO analyzer may temporarily operate during the precision check at reduced vent or purge flows, or the test atmosphere may enter the analyzer at a point other than the normal sample inlet if the analyzer's response is not likely to be altered by these deviations from the normal operational mode The standards from which the precision check test concentrations are obtained must be traceable to an NBS-SRM or a commercially available CRM, the standards used for calibration may be used for the precision check.

The precision check procedure is as follows:

1. Connect the analyzer's sample inlet line to a precision gas source that has a concentration between 8 and 10 ppm CO and that is traceable to an NBS-SRM or a CRM. If a precision check is made in conjunction with a zero/span check, it must be made prior to any zero and span adjustments.
2. Allow the analyzer to sample the precision gas for at least 5 min or until a stable recorder trace is obtained.
3. Record this value on a precision check data form (Figure 3.3), and mark the chart as "unadjusted" precision check.

The biweekly check generates data for assessing the precision of the monitoring data; Section 2.0.8 of this volume of the Handbook presents procedures for calculating and reporting precision.

3.4.4 *Special Instructions for Precision Checks on Beckman Model 866 Ambient Carbon Monoxide Analyzer* — Because of the operational nature of the Beckman Model 866 CO analyzer, the following slightly modified procedures for precision checks and audits of this analyzer model are generally necessary to obtain accurate quality assessment of the ambient readings

The Model 866 uses a dynamic, flowing reference cell as part of its compensation for variable environmental factors such as water vapor and carbon dioxide (CO_2) This mechanism responds rather slowly to changes in water vapor concentration. Although the system is entirely adequate to follow natural environmental moisture changes, it does not respond instantly to rapid changes in moisture level that occur when the analyzer is switched from ambient air to dry concentration standards used for precision checks and audits. Most concentration standards obtained from compressed gas cylinders or diluted from high-concentration gas cylinders have a very low moisture level, whereas ambient air normally contains much higher levels of water vapor During the period immediately following a switch from ambient sampling to a concentration standard, the analyzer is operating in a nonequilibrated mode, which causes a significant offset (up to 1 to 2 ppm) in the analyzer's readings Accordingly, the precision check or audit response will be inaccurate unless suitable compensatory measures are taken. (This effect is accounted for in the calibration and automatic standardization procedures in the operation manual, accurate calibration and automatic standardization will be obtained if these procedures are followed explicitly)

Either of two methods may be used to avoid errors from this effect during precision checks and audits The first is simply to allow sufficient time for the analyzer to reestablish equilibrium at the concentration-gas moisture level. Equilibrium is established when the analyzer response to this concentration standard stabilizes at a new reading somewhat different than the original reading. (The original reading may be stable for 10 to 20 minutes after introduction of the dry gas before the offset occurs.) Unfortunately, the analyzer may require as much as 1 to 2 hours to reach moisture equilibrium at the dry-gas condition.

The second method takes advantage of the temporary stable period immediately after dry gas is introduced, and it must be completed before the offset occurs. Prior to the precision check or audit, dry zero gas is introduced into the analyzer just long enough to establish a temporary, nonequilibrated zero baseline. The precision or audit concentration standard(s) is then introduced, and interpretation of the reading(s) is based on the net response referenced to this temporary zero baseline rather than the equilibrated zero baseline; i e., the net difference between the response to the standard and the temporary baseline is used with the calibration curve to determine the response in concentration units. Finally, dry zero gas is reintroduced to verify that the offset has not yet occurred and that the temporary zero baseline has not shifted If the temporary zero baseline has changed significantly, the second method is not valid and the precision check or audit must be repeated by using the first method.

Site ID 2013 Pollutant CO

Location DOWNTOWN Analyzer ACME 14677

Address 1470 NORTH STREET Serial number 14780

Date	Operator	Precision test gas concentration, ppm	Analyzer response		Difference, ppm
			% chart	ppm	
12-20-79	J.S.	10 ppm	26	10.5	0.5

Figure 3.3. *Example of precision check form*

Table 3.1. *Daily Activity Matrix*

Characteristic	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Shelter temperature	*Mean between 22° and 28°C (72° and 82°F); daily fluctuations not greater than ±2°C (4°F)*	*Edit thermograph chart daily for variations ≤2°C (4°F)*	*Mark the strip chart for the affected time period, repair or adjust the temperature control system.*
Sample introduction system	*No moisture, foreign materials, leaks, or obstructions, sampling line connected to manifold*	*Weekly visual inspection*	*Clean, repair, or replace as needed.*
Recorder	*Adequate supply of ink and chart paper; legible ink traces, correct setting of chart speed and range switches; and correct time*	*Weekly visual inspection*	*Replenish the ink and chart paper supplies; adjust the recorder time to agree with clock, and note the time on on the chart*
Analyzer operational settings	*Flow and regulator indicators at proper settings, analyzer in sampling mode, and zero and span controls locked at proper settings*	*Weekly visual inspection*	*Adjust or repair as needed.*
Analyzer operational check	*Zero and span within tolerance limits (Subsec 9 1 3, Sec. 2.0 9)*	*Level 1 zero and span checks every 2 weeks; Level 2 checks between Level 1 checks at frequency decided by user*	*Isolate the source of error, and then repair; after corrective action, recalibrate the analyzer*
Precision checks	*Precision assessed (Subsec 3 4 3)*	*Every 2 weeks (Subsec. 3.4.3)*	*Calculate and report the precision (Sec. 2.0.8)*

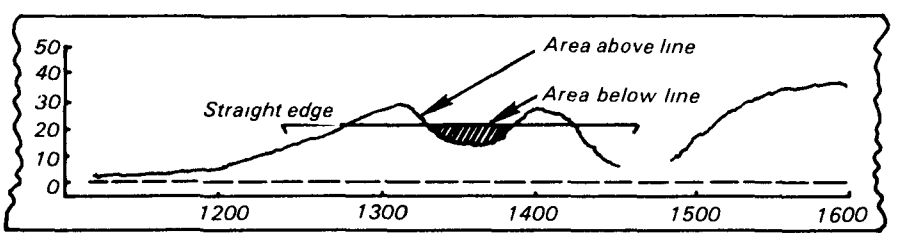
4.0 Data Reduction, Validation, and Reporting

Quality assurance activities for data reduction, validation, and reporting are summarized in Table 4.1 at the end of this section.

4.1 Data Reduction

Hourly average concentrations from a strip chart record may be obtained by the following procedure:

1. Make sure the strip chart record has a zero trace at the beginning and end of the sampling period.
2. Fill in the identification data called for at the top of the hourly average data form (Figure 4.1)
3. Draw a line from the zero baseline at the start of the sampling period to the zero baseline at the end of the sampling period by using a straight edge.
4. Read the zero baseline (% chart) at the midpoint of each hourly interval, and record the value on the data form.
5. Determine the hourly averages by placing a transparent straight edge parallel to the horizontal chart division lines. Adjust the straight edge between the lowest and highest points of the trace in the interval between two vertical hour lines of interest so that the area above the straight edge and bounded by the trace and the hour lines is approximately equal to the area below the straight edge and bounded by the trace and hour lines, as shown below.



Read the deflection (% chart) for all of the hourly intervals for which data have not been marked invalid, and record all values on the hourly average data form in the column headed Reading - Original (Orig).

6. Subtract the zero baseline value from the reading value, and record the difference.
7. Add the percentage of zero offset, +5 percent, to each difference.
8. Convert reading values (% chart) to concentrations (ppm) by using the most recent calibration curve, and record the CO concentrations in the last column of an hourly averages form such as that shown in Figure 4.1.

An alternative method of converting % chart to ppm is to eliminate steps 6, 7, and 8 and to use Equation 4-1:

$$\text{ppm} = \frac{Y - Y_z}{\text{Slope}} \qquad \text{Equation 4-1}$$

where

Y_z = zero baseline from step 4, % scale

Y = recorder reading from step 5, % scale

Slope = slope of calibration relationship from Section 2.6.2

4.2 Data Validation

Data of poor quality can be worse than no data. Data validation to screen for possible errors or anomalies is one activity of a quality assurance program. Statistical screening procedures should be applied to identify gross anomalies in air quality data.[6] Subsections 4.2.1 and 4.2.2 recommend two data validation checks.

4.2.1 *Span Drift Check* — The first level of data validation for accepting or rejecting the monitoring data should be based on routine periodic checks of the analyzer. Results from the Level 1 span checks (Section 2.6.3) should be used as the first Level of data validation. Thus, up to 2 weeks of monitoring data may be invalidated if the span drift for a Level 1 span check is >25 percent. For this reason, it may be desirable to perform Level 1 checks more often than the recommended 2-week frequency

4.2.2 *Edit of Strip Chart* — The strip chart should be edited to detect signs of monitoring system malfunctions that result in traces that do not represent "real" data. In a review of a strip chart, typical points to watch for are:

1. A straight trace (other than minimum detectable) for several hours.
2. A wide solid trace indicating excessive noise or spikes that are sharper than is possible with the normal instrument response time and are indicative of erratic behavior. Noisy outputs usually result when analyzers are exposed to vibration sources.
3. A long, steady increase or decrease in deflection.
4. A cyclic trace pattern within a definite time period, which indicates a sensitivity to changes in temperature or parameters other than CO concentration.
5. A trace that drops below the zero baseline during certain periods; this may indicate a larger-than-normal drop in the ambient room temperature or the power line voltage. This may also indicate CO in the zero-air.

Void any data for any time interval for which a malfunction of the sampling system is detected.

4.3 Data Reporting

Information and data from the hourly average form should be transcribed to a SAROAD hourly data form (see Section 2.0.3 of this volume of the Handbook for details and instructions for filling out the SAROAD). If the data are to be placed in the National Aerometric Data Bank, further instructions can be obtained from the SAROAD Users Manual.[7]

City Dayton, Ohio Site number 361660019

Site location 2100 TIMBERLANE Pollutant CO

Checker T. Johnson Operator B Fleagin

Calibration curve: Slope (b) = 2 Intercept (a) = 5 x = (y-a)/b

Date	Hour	Reading		Zero baseline		Difference		y, Add + 5		x, ppm	
		Orig	Check	Orig	Check	Orig	Check	Orig	Check	Orig	Check
6-15	00	21		6		15		20		8	
6-15	01	23		6		17		22		9	

Figure 4.1. *Sample data form for recording hourly averages*

Table 4.1. Activity Matrix for Data Reduction

Activity	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Data reduction	*Stepwise procedure for data reduction (Subsec. 4.1)*	*Follow method Subsec. 4.1 for each strip chart.*	*Review data reduction procedure.*
Span drift check	*Level 1 span check <25% (Sec. 2.6.3)*	*Perform Level 1 check at least every 2 weeks. (Sec 2.6.3)*	*Invalidate data; take corrective action; increase frequency of Level 1 checks until data are acceptable.*
Editing of strip chart	*No sign of malfunction*	*Visually edit each strip chart. (Subsec. 4.2)*	*Void data for time interval for which malfunction of sampling system detected.*
Data reporting	*Data transcribed to SAROAD hourly data form*	*Visual checks*	*Review data transcription procedure.*

5.0 Maintenance

The quality assurance activities for maintenance are described briefly

5.1 Preventive Maintenance

Maintenance requirements vary from instrument to instrument, therefore, the supervisor should refer to the manufacturer's manual for a thorough discussion of maintenance requirements for a specific analyzer After becoming familiar with the requirements, the supervisor should develop a suitable preventive maintenance schedule.

5.2 Corrective Maintenance

Corrective maintenance is any unscheduled maintenance activity that becomes necessary because of system malfunctions; for example, replacement of a damaged pump diaphragm, cleaning of a clogged sampling line, or replacement of a defective temperature control card The need for corrective maintenance becomes apparent as the operator performs the daily operations described in Section 2 6 3 of this Handbook, when the need arises, the operator should refer to the manufacturer's manual for troubleshooting procedures A detailed maintenance record should be kept on file to identify recurring system malfunctions. A sample maintenance log is presented in Figure 5 1

Site identification 001 Pollutant CO

Location MUNICIPAL INCINERATOR Instrument ACME NDIR

Address 3336 JEFFERSON AVENUE Serial number 288-7040

Date	Initials of technician	Event initiating maintenance	maintenance activity	Comments
6-2-80	C.J.	Span drift	Replace temp control card.	Daily span check Indicated span drift Oven temp control card was found to be defective and replaced.

Figure 5.1. Analyzer maintenance log.

6.0 Auditing Procedure

An audit is an independent assessment of the accuracy of data generated by an ambient air analyzer or a network of analyzers. Independence is achieved by having the audit performed by an operator other than the one conducting the routine field measurements and by using audit standards, reference materials, and equipment different from those routinely used in monitoring

The audit should be an assessment of the measurement process under normal operations--that is, without any special preparation or adjustment of the system Routine quality assurance checks (e.g., those in Section 2 6 3) conducted by the operator are necessary for obtaining and reporting good quality data, but they are not to be considered part of the auditing procedure.

Three audits are recommended: two performance audits and a system audit. The performance audits are described in detail in Subsection 6.1, and the system audit is described in Subsection 6.2 These audit activities are summarized in Table 6.1 at the end of this section (See Sections 2.0.11 and 2.0 12 for detailed procedures for a system audit and a performance audit, respectively)

Proper implementation of an auditing program will ensure the integrity of the data and assess the accuracy of the data. The technique for estimating the accuracy of the data is presented in Section 2.0 8 of this volume of the Handbook.

6.1 Performance Audits

The following subsections describe the recommended performance audits:

6.1.1 *Calibration Audit* —

A calibration audit consists of challenging the continuous analyzer with known concentrations of CO within the measurement range of the analyzer. Known concentrations of CO can be generated by using individual cylinders for each concentration or by using one cylinder of a high CO concentration and diluting it to the desired levels with zero-air. In either case, the gases used must be traceable to an NBS-SRM or a commercially available CRM (Section 2.6.2); acceptable protocol for demonstrating traceability is presented in Section 2.0.7. A dynamic dilution system must be capable of measuring and controlling flow rates to within ±2 percent of the required flow. Flow meters must be calibrated under the conditions of use against a reliable standard such as a soap bubble meter or a wet test meter; all volumetric flow rates should be corrected to STP at 25°C (77°F) and 760 mm (29.92 in.) Hg, but if both the CO and the zero air flow rates are measured with the same type device at the same temperature and pressure, the STP correction factor in the audit equations can be disregarded. *Note:* If a wet test meter or a bubble meter is used for flow measurement, the vapor pressure of water at the temperature of the meter must be subtracted from the barometric pressure.

The audit schedule depends on the purpose for which the monitoring data are being collected. For SLAMS monitoring, each analyzer must be audited at least once a year. Each agency should audit 25 percent of the Reference or Equivalent analyzers each quarter.[8] If an agency operates fewer than four analyzers, they should be randomly selected for reauditing so that one analyzer is audited each calendar quarter and each analyzer audited at least once a year. For PSD monitoring, each Reference or Equivalent analyzer must be audited at least once during a *sampling* quarter.[9]

6.1.2 *Calibration Audit Procedures* —

The analyzer should be challenged with at least one audit gas of known concentration from each of the following concentrations within the measurement range of the analyzer being audited:

Audit point	*CO concentration range, ppm*
1	*3 to 8*
2	*15 to 20*
3	*35 to 45*
4	*80 to 90*

The difference in CO concentration (ppm) between the audit value and the measured value is used to calculate the accuracy (Section 2.0.8) of the analyzer.

Information on the station, analyzer, audit device, reference materials, and audit procedures are of prime importance because the validity of the audit results depends on accurate documentation (Figures 6 1 and 6 2). The following procedure has been developed to aid in conducting the audit

1. Record the station's number, name, and address on the audit summary report (Figure 6 1)
2. Identify the person(s) performing the audit and indicate the date of the audit
3. Record the type of audit device used. If it was purchased, record the manufacturer's name, model, and serial number, if it was assembled by the user, assign an identification number so that audits can be referenced to that particular apparatus
4. Identify the CO cylinder(s) used for auditing and the NBS-SRM or commercially available CRM used to verify the concentration As required, the CO cylinder(s) should be reanalyzed every 6 months (Section 2.0.7)
5. Identify the device used to measure flow rates, if applicable
6. Connect the audit system outlet line to the inlet of the CO analyzer. Analyzers must operate in the normal sampling mode during the audit, and the test atmosphere must pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling and through as much of the ambient air inlet system as practicable. The exception to this rule that is permitted for certain CO analyzers during precision and span checks does not apply for audits.
7. Turn on the zero-air flow, and be sure that the zero air output exceeds the analyzer intake by at least 10 percent.
8. Record the analyzer zero value on the audit summary report
9. Generate the first up-scale audit point by challenging the analyzer with a CO concentration within one of the required concentration ranges; obtain a stable trace, and record the audit value and the analyzer response on the audit summary report
10. Determine the analyzer's response (ppm) from the analyzer's latest calibration relationship; if the relationship is reported as slope and

1 Station Downtown
1470 North Street

2 Analyzer mfr ACME
Model 120
S/N 14677

3 Audit performed by Tom Brown Date 1-10-80

4 Audit device mfr ACME Model 02
S/N 14561

5 CO standard used Calgas Concentration 200 ppm
Verified against NBS-SRM CO cylinder 1288
By Tom Brown Date 1-5-80

6 Flow measured with ACME mass flow meter

7 Analyzer response to zero-air CO zero = 5 % scale

8 Analyzer latest calibration relationship

Equation 6-1

$$ppm = \frac{Y-a}{b}$$

Equation 6-2

$$[CO]_A = \frac{[CO]_{STD} F_{CO}}{F_D + F_{CO}}$$

Equation 6-3

$$\% \text{ difference} = \frac{[CO]_R - [CO]_A}{[CO]_A} 100$$

Y = % scale

b = slope of calibration line
a = intercept of calibration line

F_D = flow rate of dilution air corrected to 25°C and 760 mm Hg, l/min
F_{CO} = flow rate of CO standard corrected to 25°C and 760 mm Hg, l/min

$[CO]_{STD}$ = CO standard concentration, ppm
$[CO]_A$ = CO audit concentration, ppm
$[CO]_R$ = analyzer CO response, ppm

Analyzer	Audit value, ppm	Response, % scale	Response, ppm (Eq 6-1)	% difference (Eq 6-3)
CO	7.0	19	7.0	0.0
	20.0	45	20.0	0.0
	44.0	94	44.5	1.1

Figure 6.1. Example of an audit summary

Yes	No	
✓		1 *Zero and span checks performed at least biweekly*
✓		2 *Temperature variations monitored*
✓		3 *Flow meters routinely calibrated to ±2% accuracy against a reliable standard such as a soap bubble meter or wet test meter*
✓		4 *Flow rates monitored routinely*
✓		5. *Excessive noise minimized*
✓		6 *Data processing checks performed*
✓		7 *Multipoint calibration performed routinely, and results of the calibrations recorded*
✓		8 *Quality control charts maintained for zero and span checks*
✓		9 *Maintenance performed routinely on pertinent components per manufacturer's manual*
✓		10. *Calibration gases traceable to an NBS-SRM*
✓		11 *Sample introduction system check made weekly*
✓		12 *Particulate filter (if used) changed per manufacturer's manual*
✓		13 *Recording system checked and serviced before each sampling period*
✓		14. *Recorded data checked for signs of system malfunction*
✓		15. *Data quality records maintained — completeness, accuracy, precision, and representativeness*
✓		16 *Calibration gases periodically assayed against an NBS-SRM*

Comments _____

Figure 6.2. Checklist for use by auditor (Measurement of Continuous CO in Ambient Air)

intercept, use Equation 6-1 of Figure 6.1.

11. Repeat steps 9 and 10 for two more audit points.

12. Calculate the percent difference for each audit point by using Equations 6-2 and 6-3 of Figure 6.1 and record on the audit summary report. Results of the audit are used to estimate the accuracy of ambient air quality data (as described in Section 2.0 8).

6.1.3 *Data Reduction Audit* — Data reduction involves reading a strip chart record, calculating an average, and either transcribing or recording the results on the SAROAD form. The audit is an independent check of the entire data reduction process, and should be performed by an individual other than the one who originally reduced the data. Initially, the data processing check should be performed for 1 day out of every 2 weeks of data. For two 1-hour periods within each day audited, make independent readings of the strip chart record and continue through the actual transcription of the data on the SAROAD form. The 2 hours selected during each day should be those for which the trace is either most dynamic (in terms of spikes), or for which the average concentration is the highest.

The data processing check is made by calculating the difference:

$$d = [CO]_R - [CO]_A \qquad \text{Equation 6-4}$$

where

d = the difference between the measured value and the corresponding check value, ppm

$[CO]_R$ = the recorded analyzer response, ppm

$[CO]_A$ = the audit value of the CO concentration, ppm

If d exceeds ±2 ppm, *all* of the remaining data in the 2-week period should be checked.

6.2 System Audit

A system audit is an onsite inspection and review of the quality assurance activities used for the total measurement system (sample collection, sample analysis, data processing, etc.). System audits are normally qualitative appraisals of system quality conducted at the startup of a new monitoring system and periodically, as appropriate, to audit significant changes in system operation.

An example form for a system audit is shown in Figure 6.2. The items on this form should be checked for applicability to the particular local, State, or Federal agency.

See Sections 2.0.11 and 2.0.12 for detailed procedures and forms for a system audit and a performance audit, respectively.

Table 6.1. Activity Matrix for Audit Procedure

Audit	*Acceptance limits*	*Frequency of method of measurement*	*Action if requirements are not met*
Multipoint calibration audit	*The difference in concentrations between the measured values and the audit values is used as a measure of accuracy. (Sec. 2.0.8)*	*Perform at least once per quarter; see Subsec. 6.1.1 for procedure.*	*If differences are outside the agency acceptance limits, locate the problem and correct.*
Data processing audit	*Adhere to stepwise procedure for data reduction, Sec. 2.6.4; no difference should exceed ±2 ppm.*	*Perform independent data processing check on a sample of the recorded data; e.g., check 1 day out of every 2 weeks of data, 2 hours for each day.*	*Check all remaining data if one or more data reduction checks exceed ±2 ppm.*
System audit	*Use method described in this section of the Handbook.*	*Perform at the start-up of a new monitoring system, and periodically as appropriate; observation and checklist (Fig. 6.2).*	*Initiate improved methods and/or training programs.*

7.0 Assessment of Monitoring Data for Precision and Accuracy

For continuous analyzers, perform a check every two weeks to assess the precision of the data. Use these data to estimate single instrument precision as described in Section 2.0.8 of this volume of the Handbook. The precision check procedures described in Section 2.6.3 are consistent with those given in References 8 and 9.

Estimates of single instrument accuracy for ambient air quality measurements from continuous methods are calculated according to the procedure in Section 2.0.8. The audit procedure is described in Section 2.6.6.

8.0 Recommended Standards for Establishing Traceability

Two considerations are essential for ensuring data of the desired quality.

1. The measurement process must be in statistical control at the time of the measurement
2. The systematic errors, when combined with the random variation in the measurement process, must result in an acceptable uncertainty

Evidence of good quality data includes documentation of the quality control checks and the independent audits of the measurement process by the recording of data on specific forms or on a quality control chart and by using materials, instruments and measurement procedures that can be traced to appropriate standards of reference

For traceability to be established, data must be obtained routinely by repeat measurements of standard reference samples (primary, secondary, and/or working standards). A condition of process control also must be established. Working calibration standards should be traceable to standards of higher accuracy

The CO calibration standards must be traceable to an NBS-SRM (as listed in Table 8 1) or to a commercially available CRM.

A list of gas manufacturers who produce approved CRM is available by writing to:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory (MD-77)
Research Triangle Park, North Carolina 27711
ATTN. List of CRM Manufacturers

Table 8 1 *NBS-SRM's for CO Monitors*

SRM	*Type*	*Vol/unit, liters at STP*	*Nominal CO concentration, ppm*
1680	*CO in nitrogen*	*870*	*500*
1681	*CO in nitrogen*	*870*	*1000*
2613	*CO in air*	*870*	*18.1*
2614	*CO in air*	*870*	*43.0*

9.0 Reference Methods*

Appendix C—Measurement Principle and Calibration Procedure for the Measurement of Carbon Monoxide in the Atmosphere (Non-Dispersive Infrared Photometry)

Measurement Principle

1. Measurements are based on the absorption of infrared radiation by carbon monoxide (CO) in a non-dispersive photometer Infrared energy from a source is passed through a cell containing the gas sample to be analyzed, and the quantitative absorption of energy by CO in the sample cell is measured by a suitable detector. The photometer is sensitized to CO by employing CO gas in either the detector or in a filter cell in the optical path, thereby limiting the measured absorption to one or more of the characteristic wavelengths at which CO strongly absorbs. Optical filters or other means may also be used to limit sensitivity of the photometer to a narrow band of interest. Various schemes may be used to provide a suitable zero reference for the photometer The measured absorption is converted to an electrical output signal, which is related to the concentration of CO in the measurement cell.

2. An analyzer based on this principle will be considered a reference method only if it has been designated as a reference method in accordance with Part 53 of this chapter.

3. *Sampling considerations.* The use of a particle filter on the sample inlet line of an NDIR CO analyzer is optional and left to the discretion of the user or the manufacturer. Use of filter should depend on the analyzer's susceptibility to interference, malfunction, or damage due to particles.

Calibration Procedure

1. Principle. Either of two methods may be used for dynamic multipoint calibration of CO analyzers: (1) One method uses a single certified standard cylinder of CO, diluted as necessary with zero air, to obtain the various calibration concentrations needed. (2) The other method uses individual certified standard cylinders of CO for each concentration needed. Additional information on calibration may be found in Section 2.0.9 of Reference 1.

2. Apparatus. The major components and typical configurations of the calibration systems for the two calibration methods are shown in Figures 1 and 2.

2.1 Flow controller(s). Device capable of adjusting and regulating flow rates. Flow rates for the dilution method (Figure 1) must be regulated to $\pm 1\%$.

2.2 Flow meter(s). Calibrated flow meter capable of measuring and monitoring flow rates. Flow rates for the dilution method (Figure 1) must be measured with an accuracy of $\pm$ 2% of the measured value.

2.3 Pressure regulator(s) for standard CO cylinder(s). Regulator must have nonreactive diaphragm and internal parts and a suitable delivery pressure.

2.4 Mixing chamber. A chamber designed to provide thorough mixing of CO and diluent air for the dilution method.

2.5 Output manifold. The output manifold should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold

3. Reagents.

3.1 *CO concentration standard(s).* Cylinder(s) of CO in air containing appropriate concentration(s) of CO suitable for the selected operating range of the analyzer under calibration; CO standards for the dilution method may be contained in a nitrogen matrix if the zero air dilution ratio is not less than 100:1. The assay of the cylinder(s) must be traceable either to a National Bureau of Standards (NBS) CO in air Standard Reference Material (SRM) or to an NBS/EPA-approved commercially available Certified Reference Material (CRM). CRM's are described in Reference 2, and a list of CRM sources is available from the address shown for Reference 2. A recommended protocol for certifying

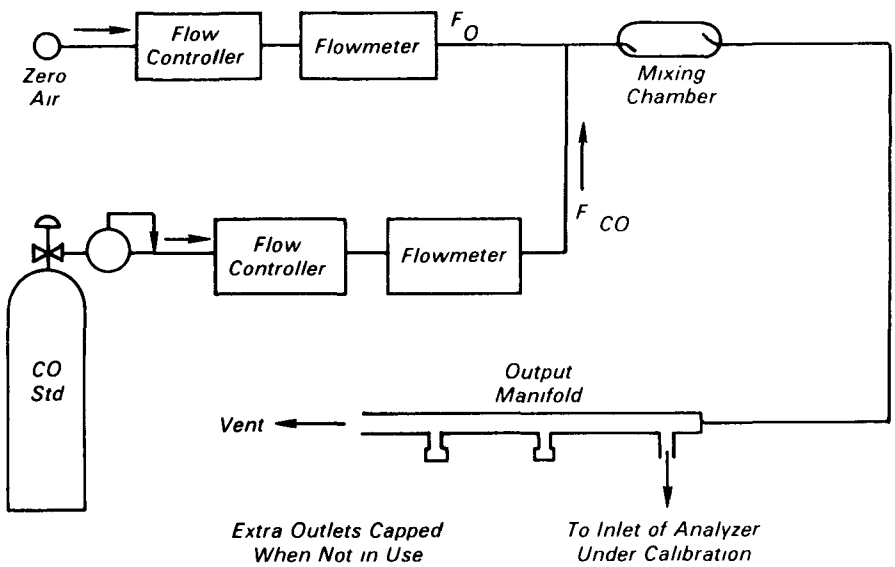


Figure 1. Dilution method for calibration of CO analyzers

*40 CFR 50 Appendix C (as amended 47 FR 54922, December 6, 1982)

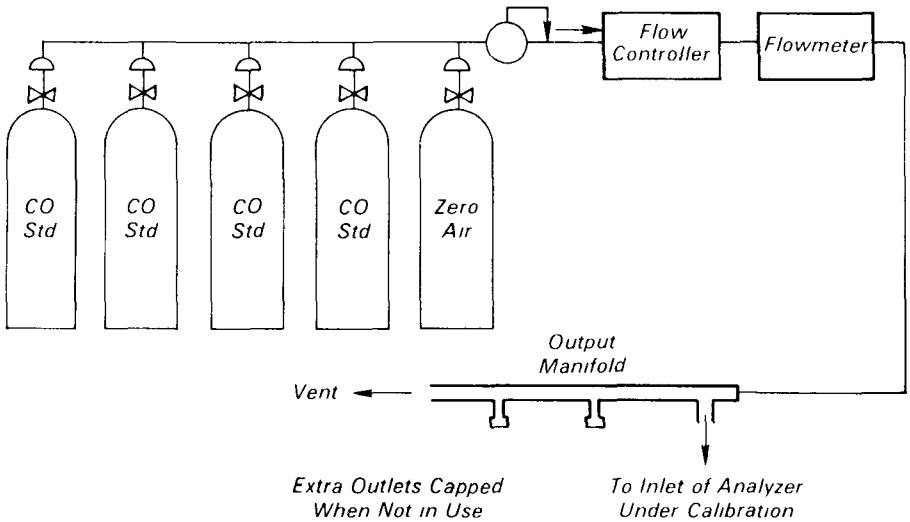


Figure 2. Multiple cylinder method for calibration of CO analyzers

CO gas cylinders against either a CO SRM or a CRM is given in Reference 1 CO gas cylinders should be recertified on a regular basis as determined by the local quality control program

3.2 *Dilution gas (zero air)* Air, free of contaminants which will cause a detectable response on the CO analyzer The zero air should contain <0.1 ppm CO A procedure for generating zero air is given in Reference 1.

4. Procedure Using Dynamic Dilution Method.

4.1 Assemble a dynamic calibration system such as the one shown in Figure 1 All calibration gases including zero air must be introduced into the sample inlet of the analyzer system. For specific operating instructions refer to the manufacturer's manual

4.2 Insure that all flowmeters are properly calibrated, under the conditions of use, if appropriate, against an authoritative standard such as a soap-bubble meter or wet-test meter All volumetric flowrates should be corrected to 25°C and 760 mm Hg (101 kPa) A discussion on calibration of flowmeters is given in Reference 1.

4.3 Select the operating range of the CO analyzer to be calibrated

4.4 Connect the signal output of the CO analyzer to the input of the strip chart recorder or other data collection device All adjustments to the analyzer should be based on the appropriate strip chart or data device readings. References to analyzer responses in the procedure given below refer to recorder or data device responses

4.5 Adjust the calibration system to deliver zero air to the output manifold The total air flow must exceed the total demand of the analyzer(s) connected to the output manifold to insure that no ambient air is pulled into the manifold vent Allow the analyzer to sample zero air until a stable response is obtained After the response has stabilized, adjust the analyzer zero control Offsetting the analyzer zero adjustments to + 5 percent of scale is recommended to facilitate observing negative zero drift Record the stable zero air response as Z_{CO}

4.6 Adjust the zero air flow and the CO flow from the standard CO cylinder to provide a diluted CO concentration of approximately 80 percent of the upper range limit (URL) of the operating range of the analyzer. The total air flow must exceed the total demand of the analyzer(s) connected to the output manifold to insure that no ambient air is pulled into the manifold vent The exact CO concentration is calculated from

$$[CO]_{OUT} = \frac{[CO]_{STD} \times F_{CO}}{F_D + F_D} \quad (1)$$

Where.

$[CO]_{OUT}$ = diluted CO concentration at the output manifold, ppm,

$[CO]_{STD}$ = concentration of the undiluted CO standard, ppm,

F_{CO} = flow rate of the CO standard corrected to 25°C and 760 mm Hg, (101 kPa), L/min, and

F_D = flow rate of the dilution air corrected to 25°C and 760 mm Hg, (101 kPa), L/min

Sample this CO concentration until a stable response is obtained. Adjust the analyzer span control to obtain a recorder response as indicated below

$$\text{Recorder response (percent scale)} = \frac{[CO]_{OUT}}{URL} \times 100 + Z_{CO} \quad (2)$$

Where

URL = nominal upper range limit of the analyzer's operating range, and

Z_{CO} = analyzer response to zero air, % scale

If substantial adjustment of the analyzer span control is required, it may be necessary to recheck the zero and span adjustments by repeating Steps 4 5 and 4.6 Record the CO concentration and the analyzer's response

4.7 Generate several additional concentrations (at least three evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing F_{CO} or increasing F_D. Be sure the total flow exceeds the analyzer's total flow demand For each concentration generated, calculate the exact CO concentration using Equation (1). Record the concentration and the analyzer's response for each concentration Plot the analyzer responses versus the corresponding CO concentrations and draw or calculate the calibration curve

5. Procedure Using Multiple Cylinder Method.

Use the procedure for the dynamic dilution method with the following changes

5.1 Use a multi-cylinder system such as the typical one shown in Figure 2.

5.2 The flow meter need not be accurately calibrated, provided the flow in the output manifold exceeds the analyzer's flow demand.

5.3 The various CO calibration concentration required in Steps 4 6 and 4 7 are obtained without dilution by selecting the appropriate certified standard cylinder.

References

1. Quality Assurance Handbook for Air Pollution Measurement Systems Volume II—Ambient Air Specific Methods, EPA-600/4-77-027a, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina 27711, 1977.

2 A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials. EPA-600/7-81-010, U S Environmental Protection Agency, Environmental Monitoring Systems Laboratory (MD-77), Research Triangle Park, North Carolina 27711, January 1981.

10.0 References

1. 40 CFR 50.8.
2. 40 CFR 53.
3. 40 CFR 50, Appendix C (As amended 47 FR 54922, December 6, 1982)
4. U.S. Department of Commerce. Catalog of NBS Standard Reference Materials. NBS Special Publication 260, 1981-1983 Edition National Bureau of Standards, Washington, D.C. November 1981.
5. U S. Environmental Protection Agency. Field Operations Guide for Automatic Air Monitoring Equipment Office of Air Programs Publication Nos. APTD-0736, PB 202-249, and PB 204-650, October 1972.
6 U S. Environmental Protection Agency. Screening Procedures for Ambient Air Quality Data. EPA-450/2-78-037, July 1978
7. U.S Environmental Protection Agency. Aeros Manual Series Volume II: Aeros User's Manual. EPA-450/2-76-029, OAQPS No. 1.2-039, December 1976.
8. 40 CFR 58, Appendix A.
9. 40 CFR 58, Appendix B.

11.0 Data Forms

Blank data forms are provided on the following pages for the convenience of the Handbook user. Each blank form has the customary descriptive title centered at the top of the page; however, the section-page documentation in the top right-hand corner of each page of other sections has been replaced with a number in the lower right-hand corner that will enable the user to identify and refer to a similar filled-in form in a text section. For example, Form CO-1.1 indicates that the form is Figure 1.1 of the CO method description. Future revisions of this form, if any, can be documented as 1.1A, 1.1B, and so forth. The data forms included are listed below.

Form	Title
1.1	Procurement Log
2 1	Calibration Summary
2.2	CO Calibration and Linearity Checks
2.3	Calculation Form for the Method of Least Squares
3.1	Operational Checklist
3.2	Level 1 Zero and Span Check Data Form
3.3	Precision Check Form
4.1	Data Form for Recording Hourly Averages
5.1	Analyzer Maintenance Log
6.1	Audit Summary
6.2	Checklist for Use by Auditor

Procurement Log

Item description	Quantity	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ordered	Received			

Calibration Summary

1 Station _____ 2 Analyzer _____

_____ Model _____

_____ S/N _____

3 Calibration by _____ Date _____

4. Calibrator mfr. _____

Model _____ S/N _____

5. CO standard _____ Concentration _____

Verified against NBS-SRM _____ Cylinder pressure _____

By _____ Date _____

6 Flow-measuring device _____ Traceability _____

7. Barometric pressure _____ Shelter temperature _____

8. Analyzer's sample flow rate _____

9 Zero knob setting _____ Span knob setting _____

Calibration Equations

Equation 2-1

F_D or F_{CO} = F (STP correction factor)

Equation 2-2

$$\text{STP Correction factor} = \frac{BP}{760} \times \frac{298}{AT+273}$$

Equation 2-3

$$[CO]_{OUT} = \frac{[CO]_{STD} \times F_{CO}}{F_D + F_{CO}}$$

Equation 2-4

$$\%\ \text{scale} = \frac{[CO]_{OUT} \times 100}{URL} + Z_{CO}$$

F = uncorrected flow rate for dilution air or CO standard gas, l/min

F_D = flow rate of dilution air corrected to 25°C and 760 mm Hg, l/min

F_{CO} = flow rate of CO standard corrected to 25°C and 760 mm Hg, l/min

BP = barometric pressure, mm Hg

AT = temperature of gas being measured, °C

$[CO]_{OUT}$ = concentration at the output manifold, ppm

$[CO]_{STD}$ = concentration of the undiluted standard, ppm

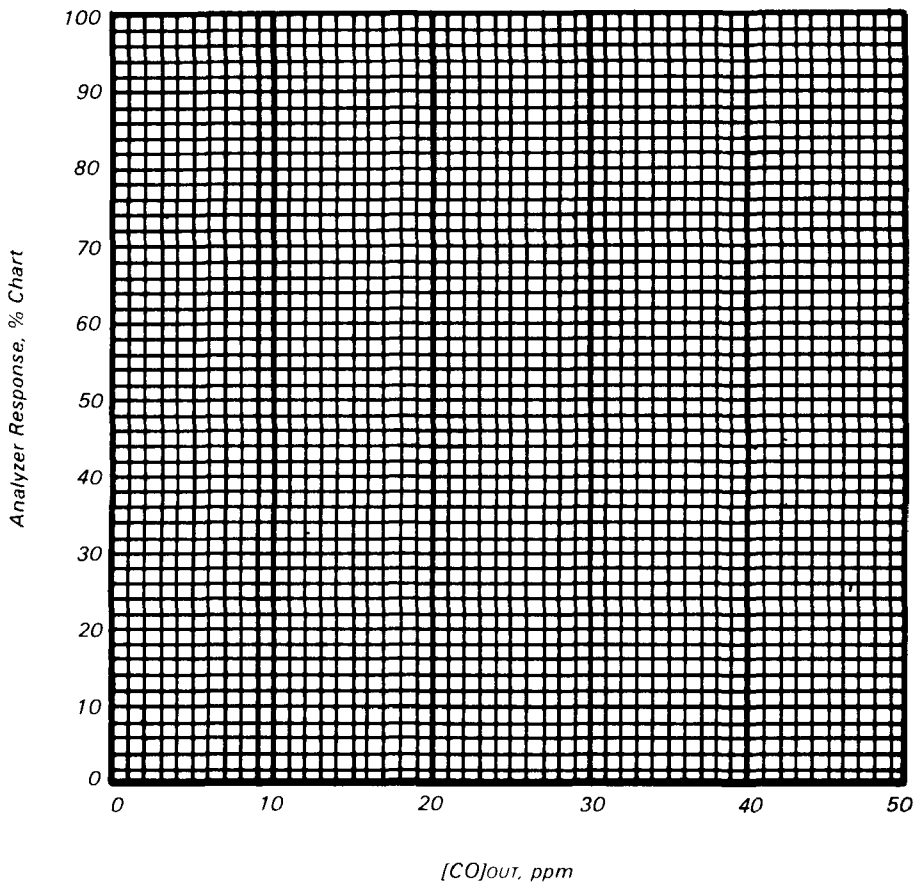
Z_{CO} = recorder response to zero air

CO Calibration and Linearity Checks

Calibration points	1 F_{CO} l/min (Eq 2-1 & 2-2)[a]	2 F_D l/min (Eq 2-1 & 2-2)	3 $[CO]_{OUT}$ ppm (Eq 2-3)	4 % scale (Eq 2-4)
Zero				
80% URL				
1				
2				
3				

[a]*Equations 2-1 through 2-4 are given in Figure 2 1 and in the text*

Calibration Relationship



Slope (b) of calibration relationship _____

Intercept (a) of calibration relationship _____

Calculation Form for the Method of Least Squares

Calibration point	*Concentration, ppm* x	x^2	*Recorder reading, % scale* y	y^2	xy
Zero					
80% URL					
1					
2					
3					

Σx = _____, Σx^2 = _____, Σy = _____, Σy^2 = _____, Σxy = _____ $x = \Sigma x/n$ = _____, $y = \Sigma y/n$ = _____, *and*

n = number of calibration points.

The equation of the line fitted to the data is written as:

$Y = \bar{y} + b(x-\bar{x}) = (\bar{y}-b\bar{x}) + bx = a + bx$

where Y = predicted mean response for corresponding x

b = slope of the fitted line

a = intercept where the line crosses the y-axis

$$b = \frac{\Sigma xy - \frac{(\Sigma x)(\Sigma y)}{n}}{\Sigma x^2 - \frac{(\Sigma x)^2}{n}} = _____ = _____ .$$

$a = \bar{y} - b\bar{x}$ = _____ .

Operational Checklist

Site identification _____ *Date* _____

Site location _____ *Technician* _____

Site address _____

_____ 1. *Inspect thermograph for temperature variations greater than ±2°C (4°F); identify time frame of any temperature level out of tolerance*

Comments: _____

_____ 2. *Inspect sample introduction system for moisture, particulate buildup, foreign material, breakage, leaks*

Comments: _____

_____

_____ 3. *Is sample line connected to manifold?*

Comments: _____

_____ 4. *Inspect data recording system*

	OK	Corrective action taken
● Legibility of trace	____	____
● Ink supply	____	____
● Paper supply	____	____
● Chart speed	____	____
● Signal range	____	____
● Time synchronization	____	____

Comments: _____

_____ 5. *Inspect analyzer operational parameters*

	OK	Corrective action taken
● Sample flow rate	____	____
● Oven temp light flashing	____	____
● Analyzer in sampling mode	____	____
● Zero and span potentiometers locked at correct settings	____	____

Comments: _____

_____ 6. *Zero the analyzer*

_____ 7. *Is unadjusted zero within tolerance?*

Comments: _____

_____ 8. *Span the analyzer*

_____ 9. *Is unadjusted span within tolerance?*

Comments: _____

_____ 10. *Enter zero and span values on data form, Figure 3.2*

_____ 11. *Return to sampling mode*

_____ 12. *Record pressures of zero and span cylinders*

Zero air _____ *Span air* _____

_____ 13. *Close valve on zero and span cylinders*

Signature of technician _____

Level 1 Zero and Span Check Data Form

Site identification _____ *Pollutant* _____

Location _____ *Analyzer* _____

Address _____ *Serial number* _____

Adjusted zero _____ *Adjusted span* _____

Date	Operator	Unadjusted zero, % chart	Span concentration, ppm	Unadjusted analyzer response,		Difference, ppm
				% chart	ppm	

Precision Check Form

Site ID _____ *Pollutant* _____

Location _____ *Analyzer* _____

Address _____ *Serial number* _____

Date	*Operator*	*Precision test gas concentration, ppm*	*Analyzer response*		*Difference, ppm*
			% chart	*ppm*	

Data Form for Recording Hourly Averages

City _____ *Site number* _____

Site location _____ *Pollutant* _____

Checker _____ *Operator* _____

Calibration curve: Slope (b) = _____ *Intercept (a) =* _____ *x = (y-a)/b*

Date	Hour	Reading		Zero baseline		Difference		y, Add + 5		x, ppm	
		Orig	Check	Orig	Check	Orig	Check	Orig	Check	Orig	Check

Analyzer Maintenance Log

Site identification _____ *Pollutant* _____

Location _____ *Instrument* _____

Address _____ *Serial number* _____

Date	*Initials of technician*	*Event initiating maintenance*	*maintenance activity*	*Comments*

Audit Summary

1. *Station* _____ 2. *Analyzer mfr.* _____

_____ *Model* _____

_____ *S/N* _____

3 *Audit performed by* _____ *Date* _____

4. *Audit device mfr.* _____ *Model* _____

S/N _____

5. *CO standard used* _____ *Concentration* _____

Verified against NBS-SRM _____

By _____ *Date* _____

6. *Flow measured with* _____

7. *Analyzer response to zero-air: CO zero =* _____ *% scale*

8. *Analyzer latest calibration relationship* _____

Equation 6-1

$$ppm = \frac{Y-a}{b}$$

Equation 6-2

$$[CO]_A = \frac{[CO]_{STD} F_{CO}}{F_D + F_{CO}}$$

Equation 6-3

$$\%\ difference = \frac{[CO]_R - [CO]_A}{[CO]_A} 100$$

Y = *% scale*

b = *slope of calibration line*
a = *intercept of calibration line*

F_D = *flow rate of dilution air corrected to 25°C and 760 mm Hg, l/min*
F_{CO} = *flow rate of CO standard corrected to 25°C and 760 mm Hg, l/min*

$[CO]_{STD}$ = *CO standard concentration, ppm*
$[CO]_A$ = *CO audit concentration, ppm*
$[CO]_R$ = *analyzer CO response, ppm*

Analyzer	*Audit value, ppm*	*Response, % scale*	*Response, ppm (Eq 6-1)*	*% difference (Eq 6-3)*
CO				

Checklist for Use by Auditor

Yes	No	
____	____	1. *Zero and span checks performed at least biweekly*
____	____	2. *Temperature variations monitored*
____	____	3 *Flow meters routinely calibrated to ±2% accuracy against a reliable standard such as a soap bubble meter or wet test meter*
____	____	4. *Flow rates monitored routinely*
____	____	5. *Excessive noise minimized*
____	____	6 *Data processing checks performed*
____	____	7. *Multipoint calibration performed routinely, and results of the calibrations recorded*
____	____	8 *Quality control charts maintained for zero and span checks*
____	____	9 *Maintenance performed routinely on pertinent components per manufacturer's manual*
____	____	10 *Calibration gases traceable to an NBS-SRM*
____	____	11 *Sample introduction system check made weekly*
____	____	12. *Particulate filter (if used) changed per manufacturer's manual*
____	____	13 *Recording system checked and serviced before each sampling period*
____	____	14. *Recorded data checked for signs of system malfunction*
____	____	15. *Data quality records maintained — completeness, accuracy, precision, and representativeness*
____	____	16. *Calibration gases periodically assayed against an NBS-SRM*

Comments: _____

_____

United States
Environmental Protection
Agency

Environmental Monitoring Systems
Laboratory
Research Triangle Park NC 27711

Research and Development

EPA-600/4-77-027a

EPA

Test Method

Section 2.9 Equivalent Method for the Determination of Sulfur Dioxide in the Atmosphere (Fluorescence)

Outline

Section	Documentation	Number of Pages
Summary	2.9.0	1
Method Highlights	2 9.0	1
Method Description		
1. Procurement of Apparatus and Supplies	2.9.1	5
2. Calibration of Equipment	2.9.2	10
3. Operation and Procedure	2.9.3	7
4. Data Reduction, Validation, and Reporting	2.9.4	1
5. Maintenance	2.9.5	2
6. Audit Procedure	2.9.6	1
7. Assessment of Monitoring Data for Precision and Accuracy	2.9.7	1
8. Recommended Standards for Establishing Traceability	2.9.8	1
9. Equivalent Method	2.9.9	1
10. References	2.9.10	1
11. Data Forms	2.9.11	4

Summary

The Reference Method for the determination of sulfur dioxide in the atmosphere (i.e., pararosaniline method) is discussed in Section 2.1 of this Handbook. Many organizations, however, will find it advantageous to conduct continuous monitoring of SO_2 in ambient air by employing automated monitoring techniques. For use in air quality surveillance systems, state and local agencies are required[1] to use analyzers that are EPA designated reference or equivalent methods.

A current list of all designated reference and equivalent methods is maintained by EPA and updated whenever a new method is designated. This list may be obtained from any EPA Regional Office or from the Environmental Monitoring Systems Laboratory, Department E, MD-77, Research Triangle Park, North Carolina 27711. Moreover, any analyzer offered for sale as a reference or equivalent method after April 16, 1976, must bear a label or sticker indicating that the analyzer has been

designated as a reference or equivalent method by EPA. Further discussion of the concepts of reference and equivalent methods appears in Section 2.0.4 of this Handbook.

Quality assurance procedures for measuring SO_2 with a fluorescence automated sampler are not instrument specific, therefore the quality assurance functions described below are applicable to all fluorescent analyzers designated as EPA equivalent methods

Method Highlights

In this quality assurance document for the fluorescent SO_2 Equivalent Methods, the procedures are designed to serve as guidelines for the development of agency quality assurance programs. Because recordkeeping is a critical part of quality assurance activities, several data forms are included to aid in the documentation of necessary data. The blank data forms (Section 2.9.11) may be used as they are, or they may be used as guidelines for preparing forms more appropriate to the individual agency; partially filled-in forms are interspersed throughout the text of the method description to illustrate their uses. Activity matrices at the end of pertinent sections can be used for quick review of the material covered in the text sections. Where appropriate, reference is made to corresponding sections in Section 2.5 of this Handbook in order to minimize the repetition of discussion in this section. This is applicable primarily to Sections 2.9.4, 2.9.6, and 2.9.11, where the corresponding sections of Section 2.5 (i.e., 2.5.4, 2.5.6, and 2.5.11) can be substituted for these sections. The only exceptions are changes in two figures of Section 2.9.11. Following is a brief summary of the material covered in this SO_2 method description.

1. *Procurement of Equipment*

Section 2.9.1 gives the specifications, criteria, and design features of the equipment and material required for the operation and quality assurance of a continuous fluorescent SO_2 analyzer. The selection of the correct equipment and supplies is a prerequisite to a quality assurance program. This section is designed to provide a guide for the procurement and initial check of equipment and supplies.

2. *Calibration of Equipment*

Section 2.9.2 provides procedures and forms to be used in selecting and checking calibration equipment, performing a multi-point calibration, and evaluating calibration data Subsections 2.1 and 2 2 deal primarily with minimum acceptable requirements for equipment and standards to be used in the generation of SO_2 concentrations. Subsection 2.4 provides a step-by-step description of the recommended calibration procedure for a fluorescent SO_2 analyzer along with example calculations. The data forms (Figures 2 1 and 2.2 of Section 2.9.2) are to be used in documentation of calibration data The primary element of quality control is dynamic instrument calibration.

3. *Operation and Procedure*

Section 2.9.3 outlines protocol to be followed by the operator during each site visit. Checks should include visual inspection of the shelter, sample introduction system, analyzer and recorder In addition, analyzer performance checks consisting of zero, span, and precision points are to be made. To provide for documentation and accountability of activities, a checklist similar to the example provided in Figure 3.1 of Section 2.9.3 should be compiled and then filled out by the field operator as each activity is completed. Analyzer Level 1 zero and span checks must be carried out at least once every two weeks. Level 2 zero and span checks should be conducted between the Level 1 checks at a frequency desired by the user. The user may desire to perform additional Level 1 zero and span checks and perform no level 2 checks. Span concentrations for either a Level 1 or Level 2 check should be between 70 and 90% of the measurement range. In addition, a one point precision check is to be done at least every two weeks at an SO_2 concentration between 0.08 and 0.10 ppm. These data are compiled and used to report precisions of a SLAMS or a NAMS network. Data forms similar to Figures 3.2 and 3.3 of Section 2.9.3 are to be used in documenting the analyzer performance checks. An essential part of the quality assurance program is a scheduled series of checks for the purpose of verifying the operational status of the monitoring system.

4. *Data Reduction*

Section 2.9.4 is identical to Section 2.5.4 and only the summary of quality assurance activities is provided.

5. *Maintenance*

Section 2.9.5 addresses recordkeeping and scheduled activities pertinent to preventive and corrective maintenance. An analyzer maintenance log is presented in Figure 5.1 of Section 2.9.5. Preventive and corrective maintenance are necessary to minimize loss of air quality data due to analyzer malfunctions and out of control conditions.

6. *Assessment of Data for Accuracy and Precision*

Section 2.9.6 is identical to Section 2.5.6. Section 2 9.7 describes the techniques for assessment of data for accuracy and precision.

7. *Reference Information*

Section 2.9.8 discusses the traceability of working standards to established standards of higher accuracy, a necessary prerequisite for obtaining accurate data.

Section 2.9.9 contains a brief description of an equivalent method and references further information in Section 2.0.4, and Section 2.9.10 contains pertinent references.

Section 2.9.11 contains blank data forms for the convenience of the user. Only two data forms are provided in this section; all other data forms are identical to the corresponding form in Section 2.5.11 The identification in the lower right hand corner should be changed from FPD-X- (Section 2.5.11) to FLR-X for field use.

1.0 Procurement of Apparatus and Supplies

Continuous sulfur dioxide monitoring activities using fluorescent analyzers require the procurement of basic sampling equipment and peripheral supplies. These include, but are not limited to the following:

1. Equivalent method fluorescent SO_2 analyzer (see Subsection 1.1 for an address for obtaining an up-to-date list of analyzers)
2. Strip chart recorder or data logging system
3. Sampling lines
4. Sampling manifold
5. Calibration equipment
6. NBS-SRM or commercial CRM calibration standard
7. Working gas traceable to NBS or CRM standard
8. Zero-air source
9. Spare parts and expendable supplies
10. Record forms
11. Independent audit system.

It is recommended that the person responsible for purchasing materials maintain a log book to record the vendor name; the part number and price; the dates ordered and received; and other pertinent information. An example of a log is Figure 1.1 The log will serve as a reference for future procurement needs and as a budgeting tool for planning future monitoring programs. Quality assurance activities for procurement of apparatus and supplies are summarized in Table 1.1 at the end of this section.

1.1 SO_2 Analyzer

As stated in the Code of Federal Regulations,[1] each method for measuring SO_2 shall be either a reference or equivalent method when such monitoring is undertaken for determining compliance with the National Ambient Air Quality Standards (NAAQS's).

Currently those analyzers designated as equivalent methods use one of the following four detection principles: flame photometric, coulometric, fluorescence, or second-derivative spectrometry. Because an analyzer uses one of these measurement principles does not make it an equivalent method. It must be so designated by EPA. Information help in a decision of which analyzer to purchase may be found in Reference 2. Only the fluorescent method is discussed in this section.

Options that are available range from automatic zero and span functions to complete telemetry systems, whereby daily zero and span checks and real-time data are transmitted from the site to a central location. Although these options have advantages, their absence from the basic monitor will not detract from performance. The necessity and desirability of options is dictated by the availability of field personnel, the accessibility of the site, and the limitations of the budget.

The buyer should purchase only analyzers designated by EPA as an equivalent method, and should request that the manufacturer supply documented evidence that the analyzer performs within specifications (Table 4.1, Section 2.0 4 of this Handbook). The best evidence is a strip chart record showing the specific analyzer's zero drift, span drift, electronic noise, rise time, fall time, and lag time. The strip chart also serves as a reference for determining whether the performance of the analyzer deteriorated over time with use. In addition, the user should reverify these performance characteristics during the initial calibration by using abbreviated forms of the test procedures provided in 40 CFR 53.[1]

Acceptance of the analyzer should be based on results of these performance tests. Once accepted, the reference and equivalent analyzers are warranted for one year by the manufacturers to operate within the performance specifications

An up-to-date list of analyzers designated as reference or equivalent methods for SO_2 is available by writing to:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Department E, MD-77
Research Triangle Park, North Carolina 27711

1.1.1 *Principle of Fluorescent Detection* - This principle is based on detection of the characteristic fluorescence released by the sulfur dioxide molecule when it is irradiated by ultraviolet light This fluorescent light is also in the ultraviolet region of the spectrum, but at a different wavelength than the incident radiation. The fluorescent wavelengths usually monitored are between 190 and 230 nm. In this region of the spectrum, there is relatively little quenching of the fluorescence by other molecules occurring in ambient air. As in flame photometry, the light is detected by a photo multiplier tube (PMT) that, through the use of electronics, produces a voltage proportional to the light intensity and SO_2 concentration

The fluorescent light reaching the PMT is usually modulated to facilitate the high degree of amplification necessary. Some analyzers mechanically "chop" the incident irradiation before it enters the reaction chamber This process is accomplished by a fan-blade-like chopper rotating at a constant speed, which alternately blocks and passes the light to the chamber. Other instruments electronically pulse the incident light source at a constant rate.

Potential interferences to the fluorescent technique include any species that either quenches or exhibits fluorescence. Both water vapor and oxygen strongly quench the fluorescence of SO_2 at some wavelengths. Where water vapor presents a problem, it can be removed by a dryer within the instrument. In most analyzers, the water interference is minimized by careful selection of the incident radiation wavelength. Difference in oxygen concentrations between the two matrices can become significant if a low-level SO_2-in-nitrogen cylinder gas is diluted to prepare a calibration standard. In such a case, the nitrogen in the pollutant flow stream may "dilute" the oxygen in the dilution air stream, significantly decreasing oxygen concentration. This situation can be avoided by keeping the concentration of SO_2 in the cylinder gas high enough that the nitrogen contributed by the pollutant flow stream is insignificant with respect to the total flow volume.

Aromatic hydrocarbons such as naphthalene exhibit strong fluorescence in the same spectral regions as SO_2 and are major interferents These aromatics must be

removed from the sample gas stream by an appropriate scrubber upstream of the reaction chamber. The scrubbers may operate at ambient or elevated temperature. Certain elevated-temperature scrubbers, however, have the potential for converting ambient hydrogen sulfide (which normally does not interfere with the fluorescent technique) into SO_2. In these cases, the hydrocarbon scrubber must be preceded by a scrubber for H_2S

1.1.2 *Specific Fluorescent Analyzers* - Currently, four (4) instrument manufacturers have EPA designated equivalent fluorescent SO_2 analyzers The manufacturers and their respective designated equivalent methods are: Thermo Electron Corporation (TECO), EQSA-0276-009,[3] Beckman, EQSA-0678-029;[4] Monitor Labs, Inc., EQSA-0779-039;[5] and Meloy (Columbia Scientific Industries Corp.) EQSA-0580-046 [6]

The TECO Series 43 fluorescent SO_2 monitor utilizes a pulsed UV light to excite the SO_2 molecules. TECO states six (6) major reasons for using a pulsed UV lamp:[3]

1. Long bulb life
2. High intensity—improved signal to noise ratio
3. Small bulb size
4. Low power requirements—less than 1 watt
5. Long-term stability
6. Chopped signal processing—no dark current drift

Before passing into the reaction chamber the sample air passes through a permeation dryer, to remove water vapor, and an aromatic hydrocarbon cutter (replace every 18 months of operation). The instrument operates with a sample flow rate between 472 and 1888 cm^3/min.

The Beckman Model 953 fluorescent SO_2 monitor uses a continuous UV light source (deuterium lamp) but mechanically chops the light signal before it enters the reaction chamber.

The sample air passes through a selective scrubber, for the removal of H_2S and mercaptans (change every 12 months), and a heated temperature controlled reactor which removes polynuclear aromatic compounds (replace every 6 months). The sample then passes into a heated, temperature-controlled fluorescence reaction chamber. The chamber is heated to reduce condensation of water vapor. The instrument operates with a sample flow rate of 400 to 700 cm^3/min.

The Monitor Labs Model 8850 uses UV light from an arc tube to excite the SO_2 molecules. The UV light passes through a mechanical chopper before entering the reaction chamber Sample air passes through a five (5)-micron teflon particulate filter and a catalyst (replaced every 12 months) for removal of aromatic hydrocarbons before entering the heated (40°C) reaction cell The instrument operates with a sample flow rate of 500 ± 50 cm^3/min.

The Meloy Model SA700 fluorescent SO_2 analyzer operates with a continuous wave of UV light from a deuterium lamp The instrument uses a UV detector to monitor lamp intensity in the reactor cell and compensates and adjusts the UV source as the source ages and as contamination accumulates on optical surfaces. The instrument uses no optical or mechanical chopper.

The sample air passes through a membrane dryer to remove water vapor and a hydrocarbon scrubber must be replaced as part of scheduled annual maintenance The instrument operates with a sample flow rate of 200 to 500 cm^3/min.

1.2 Strip Chart Recorder

Strip chart recorders are commercially available with a wide variety of prices and specifications. Factors to be considered when purchasing a recorder are:

1. Compatibility with the output signal of the analyzer
2. Chart width (minimum of 15 cm is recommended for desired accuracy of data reduction)
3. Chart speed (≥2.5 cm/h)
4. Response time
5. Precision and reliability
6. Flexibility of operating variables (speed and range)
7. Maintenance requirements.

1.3 Sampling Lines and Manifolds

Sampling lines and manifolds should be Teflon or glass to minimize reaction with and degradation of the SO_2. The residence time within the sampling lines should be minimized to reduce the possibility of interaction of the SO_2 sample with interim surfaces. If particulate filters are employed, they should be of Teflon construction

1.4 Calibration Equipment

The recommended calibration procedure requires both a permeation tube that is traceable to NBS standards in a temperature-controlled environment and a diluent airstream free of SO_2 (<0.001 ppm). A detailed discussion of this calibration procedure appears in Section 2 9 2. Calibration may also be conducted by diluting an SO_2 standard gas with zero air

The calibration system (purchased or built) must meet the guidelines outlined in the *Federal Register.*[1] Calibration systems of the types described are commercially available. Several manufacturers of continuous SO_2 analyzers either offer compatible calibration systems or can inform the user on where to purchase such systems When purchasing a calibration system, the following factors should be considered.

1. The permeation tube must be traceable to NBS standard reference materials (NBS-SRM).
2. The method for measuring air flow through the calibrator must be accurate within ±2% of the actual flow
3. The temperature control module must be capable of maintaining the permeation tube at a predetermined temperature within ±0 1°C (0.2°F). The ability to make an independent check of the temperature within the permeation tube chamber is desirable.
4. The calibrator must be portable if it is to be used at more than one site.
5. Maintenance requirements should be minimal.

Permeation tubes are commercially available or may be prepared in the laboratory.[2,7] The working permeation tube must be traceable to an NBS-SRM. If the permeation tube supplied with the calibrator is not certified, or if the user prepares his own tubes, the user must conduct certification tests and thus purchase an NBS-SRM. The following permeation tubes are available as NBS-SRM's:[8]

SRM	Type	Tube length, cm	Nominal permeation rate, μg/min at 25°C
1625	SO_2 permeation tube	10	2.8
1626	SO_2 permeation tube	5	1.4
1627	SO_2 permeation tube	2	0.56

An acceptable protocol for demonstrating the traceability of commercial permeation tubes to NBS-SRM's is described in Section 2.0.7 of this volume of the Handbook.

The user will need a source of zero air that is free of contaminants that would cause any detectable response with the SO_2 analyzer. Zero-air is commercially available in cylinders or can be generated by the user. Because fluorescent SO_2 analyzers may be sensitive to the composition of synthetically prepared zero-air, a clean air system utilizing ambient air may be more desirable to use for zero and dilution purposes. If ambient air is not used, the zero-air cylinder must contain the major constituent gases normally found in ambient air, especially oxygen which is known to quench the fluorescence response.

1.5 Spare Parts and Expendable Supplies

In addition to the basic equipment discussed above, it is necessary to maintain an inventory of spare parts and expendable supplies. The manufacturer's manual specifies which parts require periodic replacement and the frequency of replacement. Based on these specifications, the management of the monitoring network can determine which parts and how many of each should be available at all times. A generalized list of spare parts and expendable supplies is provided below (for specific requirements, refer to the manufacturer's manual):

1. Particulate filters
2. Selective scrubbers for the removal of aromatic hydrocarbons
3. Sampling lines
4. Pump diaphragms
5. Drier columns
6. Activated charcoal
7. Recorder chart paper and ink or pens
8. Calibration gas
9. Record forms
10. Spare fittings.

1.6 Reanalysis of Calibration Working Standards

All working standards for calibrations should be reanalyzed at least once every 6 mo. (Subsection 7.2.6 of Section 2.0.7 describes the procedures for analysis and for reanalysis of permeation devices). Flow-measuring devices should be recalibrated using the procedures and schedules in Section 2.1.2 of this Handbook

1.7 Record Forms

Recordkeeping is critical for all quality assurance programs. Standard forms similar to those in this Handbook should be developed for individual programs. Three questions to consider in the development and storage of record forms are:

1. Does the form serve a necessary function?
2. Is the documentation complete?
3. Will the forms be filed so that they can be retrieved easily when needed?

1.8 Audit System

An independent audit system is a necessary part of the quality assurance program Two types of audit systems may be used:

1. A system using an NBS traceable permeation tube (Subsection 1.4), or
2. A dynamic dilution system with a tank of SO_2 certified traceable to an NBS-SRM or a commercially available Certified Reference Material (CRM) and a zero-air supply (Section 2.5.6).

In either case, the system used for auditing must not be the same as that used to calibrate the analyzer.

Procurement Log

Item Description	Quantity	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ord	Rec.			
Fluorescence Analyzer Model PF R92	1	06483	ACME	4-8-82	6-24-82	$5,000		
ACME II Strip Chart Recorder	1	06484	ACME	4-8-82	5-15-82	$700		

Figure 1.1. Example of a procurement log.

Table 1.1. Activity Matrix for Procurement of Equipment and Supplies

Equipment and supplies	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Fluorescence SO_2 analyzer	Performance according to specifications in Table 4.1, Sec 2.0.4	Have the manufacturer provide a strip chart recording of specific analyzer's performance; verify performance specifications at installation	Have the manufacturer make proper adjustments; recheck the performance
Strip chart recorder	Compatible with output signal of analyzer; chart width of 15 cm (6 in.) is recommended; accurate chart speed	Check upon receipt	Return to supplier
Sampling lines and manifolds	Constructed of Teflon or glass	As above	As above
Calibration devices	Must meet guidelines of Reference 1	See Reference 1	As above
SO_2 permeation tube	Traceable to NBS-SRM; meets limits in traceability protocol for accuracy and stability (Sec 2.0.7)	Analyze against an NBS-SRM; protocol in Sec 2.0.7	Obtain new working standard, check for traceability
Zero-air	Clean dry ambient air, free of contaminants that cause detectable responses with the SO_2 analyzer	See Sec 2.9.2	Obtain air from another source or regenerate
Record forms	Standard form developed	N/A	Revise forms as appropriate
Audit system	Must not be the same system as used for calibration, either an NBS traceable permeation tube or a dynamic dilution system (Subsec 1.8)	Check the system against a known standard	Locate problem; correct, or return to supplier

2.0 Calibration of Equipment

The accuracy and precision of data derived from the air monitoring equipment are dependent on the quality assurance procedures used, primarily the dynamic instrument calibration. Calibration determines the relationship between the observed and the true values of the variable being measured. Table 2.2 at the end of this section summarizes the quality assurance activities for calibration.

Dynamic calibration involves introducing gas samples of known concentrations into an instrument in order to adjust the instrument to a predetermined sensitivity and to derive a calibration relationship. This relationship is derived from the instrument's responses to successive samples of different known concentrations. Introducing these standard gas mixtures in decreasing order of concentration will minimize the response times. As a minimum, three reference points and one zero point are recommended to define this relationship. Linearity of fluorescent analyzers is also checked at this time. The true value of the calibration gas must be traceable to NBS-SRM's (Section 2.0.7).

Most currently available monitoring instrument systems (e.g., the fluorescent SO_2 analyzer) are subject to drift and variation in internal parameters, and thus cannot be expected to maintain accurate calibration over long periods of time. Therefore, it is necessary to dynamically check the calibration relationship on a predetermined schedule. Precision is determined by a one-point check at least once every 2 weeks. Accuracy is determined by a three-point audit once each quarter. Zero and span checks (Subsection 3.4.2) must be used to document within-control conditions; these checks are also used in data reduction and validation.

2.1 Calibration Gases

The recommended method of dynamically calibrating a fluorescent SO_2 analyzer requires both a certified permeation tube traceable to an NBS-SRM in a temperature-controlled environment (±0.1°C) and diluent air void of SO_2 (<0.001 ppm). To conduct biweekly precision checks and Level 1 zero and span checks, the user will need a supply of zero air, a cylinder of SO_2 (50 to 100 ppm) in nitrogen, and a dynamic dilution system or a calibration system with a permeation tube capable of generating the precision check point at 0.08 to 0.1 ppm and a span check point at 70 to 90 percent of the analyzer's measurement range. To implement a quality assurance program for calibration, the user will therefore need the following:

1. An SO_2 permeation tube or device that is traceable to an NBS-SRM
2. Zero air
3. An SO_2 span gas that is traceable to an NBS-SRM or commercially available CRM
4. A calibration system.

2.1.1 *SO_2 Permeation Tubes* - The NBS-SRM's provide a reference against which all calibration gas mixtures must be compared. See Section 2.9.1 (Subsection 1.4) for an address for obtaining a list of NBS-SRM's which are available for SO_2 analyzers.

One function of NBS is to supply standards, but they do not supply working calibration gases. Therefore the user is advised either to purchase commercially available certified permeation tubes that are traceable to NBS standards or to make the tubes.[2] In either case, the user is responsible for the verification and reanalysis of working standards versus NBS-SRM's or CRM's. Procedures the user must follow to verify working calibration gases are outlined in Section 2.0.7.

2.1.2 *Dilution Air* - Zero-air, free of contaminants which could cause a detectable response in the fluorescent SO_2 analyzer, must be used for the calibration, the precision check, and the Level 1 zero and span checks. This air is used to establish the analyzer zero base line and to dilute the SO_2 to the required concentrations. Zero-air may be supplied from cylinders or from a clean air system.

Because the fluorescent reaction has some degree of sensitivity to aromatic hydrocarbons, CO_2 levels, and to the oxygen/nitrogen ratio,[3] it is recommended that a clean air system be used. The air for this system must be drawn from outside the station to prevent excess CO_2 levels. Water vapor and aromatic hydrocarbons should be removed from the zero air.

If compressed air cylinders are used, the air should have the following properties for use with fluorescent analyzers:

1. The same O_2 and N_2 percentage composition as ambient air (20.94% O_2, 78 08% N_2).
2. A CO_2 content similar to that of ambient air (between 300 and 400 ppm).
3. Less than 0.1 ppm aromatic hydrocarbons.

2.1.3. *SO_2 Precision and Span Gases* - Aluminum or steel cylinders containing 50 to 100 ppm SO_2 in N_2 are available from most specialty gas suppliers. Aluminum cylinders have been demonstrated by NBS to have superior stability for storing SO_2 mixtures, and they are preferred whenever possible. These gases can be diluted to the desired concentration by using zero-air and a dynamic dilution system The cylinder gas concentration should be certified to NBS-SRM or commercially available CRM (Certified Reference Materials) using EPA Traceability Protocol No. 2 (Section 2.0.7). NBS-SRM or commercially available CRM at 50 and 100 ppm SO_2 in N_2 should be used for the traceability analysis. A CRM may be used directly for precision or span checks. However, due to the limited supply of NBS-SRM, an SRM should not be used directly for routine precision or span checks. A list of gas manufacturers who have approved CRM's is available by writing to:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory (MD-77)
Research Triangle Park, North Carolina 27711

ATTN: List of CRM Manufacturers

(*Note:* CRM's are cylinder gases prepared by gas manufacturers according to an NBS-EPA procedure to within ±1% of existing SRM concentrations. Each CRM lot of 10 to 50 cylinders is audited by EPA. Each lot receives written approval from NBS and this approval must accompany any CRM sold.)

Precision and span gases may also be generated by a calibrator using an SO_2 permeation tube traceable to an NBS-SRM.

2.2 Calibration System

The calibration system consists of two primary parts.

1 The temperature controlled permeation device
2. A dynamic dilution system.

2.2.1 *Temperature Controlled Permeation System* - The purpose of a permeation system is to generate a low SO_2 concentration at a constant rate. This is done by holding a permeation tube at a constant temperature (±0.1°C) for which the permeation rate is known. The SO_2 permeating from this tube is carried away by a low flow of gas (usually clean dry air or N_2) to a mixing chamber where it is accurately diluted with zero air to the concentration desired.

2.2.2 *Dynamic Dilution System* - A dynamic dilution system is required to dilute the SO_2 output from either the temperature-controlled permeation system or an SO_2 gas cylinder to the desired concentration. All parts in contact with the SO_2 output must be glass or Teflon. The system must be capable of controlling and measuring flow rates to within ±2% of stated flow.

2.3 Dynamic Multipoint Calibration Principles

Dynamic calibration involves introducing gas samples of known concentrations to an instrument in order to adjust the instrument to a predetermined sensitivity and to derive a calibration relationship. A minimum of three reference points and one zero point uniformly spaced covering 0 to 80 percent of the operating range are recommended to define this relationship.

The recommended method of dynamically calibrating an SO_2 analyzer requires a certified permeation tube traceable to an NBS-SRM in a temperature controlled environment (±0.1°C) and diluent air that is free of SO_2 (<0.001 ppm). Temperature must be verified with an NBS traceable thermometer prior to calibration.

The permeation tube is held at a constant temperature for a minimum of 24 hours to allow the SO_2 to diffuse from the tube at a known rate. The low flow of zero air that is passed over the permeation tube serves as a carrier for the SO_2. This purged air is then diluted with different quantities of zero air to generate the desired concentrations.

The analyzer's recorded response is compared with the known concentration to derive the calibration relationship. This relationship is used to convert the analyzer's responses during sampling into ppm's of SO_2. The recorded response may be either voltage output or percent chart (% chart) as long as it is consistent with that used to determine the calibration relationship.

Biweekly precision checks are used to calculate the variability of the calibration relationship over a period of time. Three-point audits conducted quarterly are used to check the analyzer's accuracy. These precision checks and the 3 (or 4) point audits are used to generate precision/accuracy data for the reporting organization. They are not intended for use in reducing or validating data since they are performed infrequently. Level 1 zero and span checks must be used to document within-control conditions and to validate the collected data.

2.4 Calibration Procedures

The procedures for multipoint calibration of an SO_2 analyzer by an SO_2 permeation system are specified in the *Federal Register.*[1] To facilitate these procedures, operational and calculation data forms have been developed as aids in conducting calibrations and quality assurance checks. Detailed descriptions of the calibration theory and procedures for SO_2 permeation systems are in the *Federal Register.*[1]

Documentations of all data on the station, instrument, calibrator, reference standard, and calibration procedures are of prime importance since the validity of the data collected by the instrument is dependent on the quality of the calibration. Calibration must be performed with a calibrator that meets all conditions specified in Subsection 2.2.

2.4.1 *General Calibration Recommendations* - It is important that the fluorescent analyzer be operated during calibration under conditions identical to those during normal ambient air sampling. No modifications or alterations shall be made to the analyzer's components, flow system, prescribed flow rate, or other parameters. Concentrations of SO_2 intended for calibration must be generated continuously by means entirely independent of the analyzer. The flow rate of the calibration gas must exceed the sample flow rate of the analyzer. The calibration gas should flow through a manifold, and the analyzer should draw its sample through the regular ambient air sampling line, which is attached to a port of the vented calibration manifold.

2.4.2 *Calibration Procedure for SO_2* - The procedure for multipoint calibration of a fluorescent analyzer is necessarily general. That given here is for fluorescent analyzers equipped with a linearized output. Where analyzer-specific explanations are necessary, the reader is referred to the manufacturer's instruction manual.

The following procedure using the forms shown in Figures 2 1 and 2.2, is given to aid in the collection and documentation of calibration data.

1. Record the official name and address of the station on the form, where appropriate, the name and address should be the same as that appearing on the SAROAD site identification form to eliminate any confusion by persons not familiar with the station.
2. Identify the analyzer being calibrated by the manufacturer's name, model, and serial number.
3. Identify the person performing the calibration and the date of calibration
4. Identify the calibrator used. If the calibrator was purchased, record the manufacturer's name, model and serial number. Calibrators assembled by the user should be assigned an identification number so that calibrations can be referenced to that particular apparatus.
5. Identify, by supplier and tube number, the reference standard to be used. Provide a record of NBS traceability for any tube used in a calibration and include the data of verification and the name of the person who verified the reference standard.
6. Identify the device used to measure the flow of the dilution air.
7. Record the barometric pressure and the shelter temperature.
8. Record the analyzer sample air flow.
9. Record the zero and span knob settings after the calibration is completed. (These settings can be used as a basis of comparison when changes are later determined in the instrument performance.)
10. Record the temperature at which the permeation tube is maintained during calibration and use the recorded

temperature to determine the SO_2 permeation rate ($\mu g/min$) from the permeation tube data form supplied by the manufacturer. Record this value.

11. Measure and record the temperature (AT) of the calibrators air flow at the same point that the flow rate measurement is made.
12. If flow rates are measured using a bubble meter or wet test meter determine the vapor pressure of water at temperature (AT) from Table 2.1 and record.

Use calibration equations (Figure 2.1), the SO_2 calibration and linearity check table, and the plot of the calibration data (Figure 2.2) for systematically recording the data determined during the calibration of the fluorescent SO_2 analyzer. Because zero and calibration adjustments differ among analyzers, the manufacturer's manual should be consulted before performing the following calibration using Figure 2.2. References to analyzer responses in the procedure below refer to recorder responses.

1. Select the operating range of the analyzer to be calibrated. See the manufacturer's manual for ranges for which the analyzer is considered an equivalent method.
2. Connect the recorder output cable(s) of the analyzer to the input terminals of the strip chart recorder(s). All adjustments to the analyzer should be performed based on the appropriate strip chart readings. (*Note:* The recorder must be operating properly prior to the system calibration.)
3. Attach the analyzer sample line to the output manifold of the calibrator. Adjust the zero air flow from the calibrator into the analyzer. The zero air flow must exceed the total demand of the analyzer connected to the output manifold to ensure that no ambient air is pulled into the manifold vent.
4. Allow the analyzer to sample zero air until a stable response is obtained (a response that does not vary by more than ±2% over a 5 min time period); then adjust the analyzer zero control. Offsetting the analyzer zero adjustment to +5% of the strip chart scale is recommended to facilitate observing negative zero drift. Record the stable zero air response under column 4 of the calibration table (Figure 2.2).
5. Determine the 80% URL of the analyzer (e.g., for an operating range of 0 to 0.5 ppm the 80% URL would be 0.80 x 0.5 = 0.4 ppm).
6. Calculate the total air flow (F_T) required to generate 0.4 ppm by rearranging Equation 2-3 of Figure 2.1 and by substituting the known values,

$$F_T = \frac{PR}{ppm\ SO_2} \times \frac{MV}{M}$$

Equation 2-5

This flow rate will be in L/min at STP.

7. Adjust the air dilution until the total air flow (dilution air + purge air) from the calibrator is that determined in step 6; then remeasure the total air flow, and record its value on the 80% URL line under column 1.
8. Calculate the STP correction factor using Equation 2-1 and record it

$$\text{STP correction factor} = \frac{BP - VP}{760} \times \frac{298}{AT+273}$$

Equation 2-1

A correction for vapor pressure (VP) of water is made only if air flow is measured with a bubble tube or wet test meter.

9. Correct the measured total air flow (F) to STP of 760 mm Hg and 298K using Equation 2-2.

$$F_T = F \times \text{STP correction factor}$$

Equation 2-2

Record this value under column 2 of Figure 2.2.

10. Calculate the exact concentration of SO_2 (ppm) being generated using Equation 2-3.

$$ppm\ [SO_2]^{OUT} = \frac{PR}{F_T} \times \frac{MV}{M}$$

Equation 2-3

Record this value on the 80% URL line under column 3.

11. Calculate the required recorder response for span adjust (80% URL), using Equation 2-4.

$$\%\ scale = \frac{[SO_2]_{OUT}}{URL} \times 100 + Z_{SO_2}$$

Equation 2-4

Allow the analyzer to sample until the response is stable, and then adjust the analyzer span until the required recorder response is obtained. (If adjustment of the span control is necessary, recheck the zero and span adjustments by repeating steps 4 through 10.) Record the SO_2 recorder response on the 80 percent URL line under column 4.

12. After the zero and 80% URL points have been set, determine at least two approximately evenly spaced points between zero and 80 percent URL without further adjustment to the instrument. Generate these additional points by increasing the dilution flow. For each concentration generated, calculate the exact SO_2 concentration by measuring the total flow and by using Equations 2-2 and 2-3. Check the permeation tube temperature before each calibration point to determine if changes larger than ±0.1°C have occurred. Record the required information for each point under the appropriate column in the table of Figure 2.2.
13. Plot the analyzer responses (% chart) on the y-axis versus the corresponding calculated concentrations $[SO_2]_{OUT}$ on the x-axis to obtain the calibration relationship as shown in Figure 2.2. Determine the straight line of best fit (to all points including the zero point) by using the method of least squares (e.g., see Appendix J of Volume I of this Handbook[9]). This determination can be made with a programmed calculator, or with the calculation data form, Figure 2.3. Because the time required to manually perform the calculation using the data form is considerably longer than that using a programmed calculator, it is suggested that the latter be used whenever possible.
14. After determining the slope (b) and the intercept (a) where the line crosses the y-axis, draw the fitted line for each set of points. On the y-axis of the graph, locate and plot the y intercept (a). Using the equation Y = a + bx, calculate the predicted value (Y) using the 80% URL concentration for the x value. Plot this second point on the graph. Draw a straight line

through these two points to give a best-fit line. Figure 2.4 shows a calibration line plotted using this procedure.

15. After the best fit line has been drawn for the SO_2 calibration, determine whether the analyzer response is linear, that is, no calibration point should differ from the best-fit line by more than 2% of full scale. Perform a simple test for linearity by plotting a point 2% of scale above and 2% of scale below the points where the fitted line crosses the 0.1 and 0.4 ppm lines. Draw two straight lines, one through the +2% points and one through the -2% points (Figure 2.4), to define the limits between which the calibration points can fall for the calibration curve to be considered linear Repeat any points falling outside these limits to eliminate calibration errors; if the repeated points are still outside the limits, consult the manufacturer's manual on how to correct the nonlinearity

2.4.3 *Example of a Calibration* -

1. Complete items 1 through 8 of Figure 2 1 to document information concerning the station, analyzer, calibrator reference standard, and person performing the calibration, and consult the manufacturer's operation manual before starting the calibration.
2. Select the operating range of the analyzer. For this example, we will assume a 0 to 0.5 ppm range.
3. Make sure that the recorder is calibrated and operating properly and is connected to the correct output terminal of the analyzer.
4. Connect the analyzer's sample line to the manifold of the calibrator, and adjust the zero air flow from the calibrator to exceed the total flow demand of the analyzer.
5. Allow the analyzer to sample the zero air until a stable response is obtained; adjust the analyzer zero control; offset the analyzer zero adjustments to +5% of recorder scale to facilitate observing negative zero drift and record the stable zero air responses of 5% under column 4 (Figure 2.2).
6. Calculate the STP correction factor (Equation 2-1) by substituting the known values in item 13 of the calibration form. The correction factor for this example is 0.94.
7. Determine the 80% URL of the analyzer For this example, it is 0.80 x 0.5 = 0.4 ppm. Now calculate the flow rate needed to generate 0.4 ppm by Equation 2-5, substituting the known values.

$$F_T = \frac{1.54\ \mu g/min}{0.4\ ppm} \times \frac{24.45\ L/mol}{64\ g/mol} =$$

1 47 l/min at STP

$$F = \frac{F_T}{0.94} = 1.56\ L/min \text{ at actual conditions.}$$

Adjust the dilution air until the total air flow (dilution air + purge air) from the calibrator is approximately 1.56 l/min. Remeasure the total air flow and record this value on the 80% URL line under column 1.

Note: Make certain the flow of calibration gas from the calibrator exceeds the sample flow rate of the monitor

Now correct the measured flow (F) from step 7 to STP conditions, using Equation 2-2,

$$F_T = 1.56\ L/min \times 0.94 = 1.47\ L/min$$

Record this value under column 2 of the calibration table.

8. Calculate the exact concentration of SO_2(ppm) being generated, using Equation 2-3,

$$ppm\ [SO_2]_{OUT} = \frac{1.54\ \mu g/min}{1\ 47\ L/min} \times \frac{24.45\ L/mol}{64\ g/mol} = 0.400\ ppm$$

Record this value under column 3 of the calibration table.

9. Calculate the required recorder response for span adjust (80% URL) using Equation 2-4,

$$\%\ scale = \frac{0.400\ ppm}{0.5\ ppm} \times 100 + 5\% = 85.0\%$$

Allow the analyzer to sample until the response is stable, and then adjust the analyzer span until the recorder response is 85.0% of scale. (If adjustment of the span control is necessary, recheck the zero and span adjustments by repeating steps 5 through 9.) Record the SO_2 recorder response on the 80% URL line under column 4. Record the analyzers zero and span knob settings under item 9 of the calibration form

10. Generate two evenly spaced concentration points between zero and the 80% URL by increasing the total flow (F_T). Allow each trace to stabilize before moving to the next calibration point, and then record the required information in the appropriate column of the SO_2 calibration table. Do not readjust the analyzer zero or span setting
11. Plot on Figure 2 2 the analyzer response (% chart) from column 4 on the y-axis versus the corresponding calculated concentration $[SO_2]_{OUT}$ from column 3 on the x-axis A straight line of best fit is now calculated by the method of least squares For this example, the slope (b) is determined to be 200 with a y-intercept of 5%. The calibration relationship is now plotted as in Figure 2 3. To determine linearity, draw +2% and -2% lines parallel to the calibration line For this example, the analyzer response is linear.

2.5 Calibration Frequency

To ensure accurate measurements of the SO_2 concentrations, calibrate the analyzer at the time of installation, and recalibrate it.

1. No later than 3 mo after the most recent calibration or performance audit which indicated the analyzer response to be acceptable or;
2. Following any one of the activities listed below:
   a. an interruption of more than a few days in analyzer operation,
   b. any repairs,
   c. physical relocation of the analyzer, or
   d. any other indication (including excessive zero or span drift) of possible significant inaccuracy of the analyzer

Following any of the activities listed in item 2 above, perform Level 1 zero and span checks to determine if a calibration is necessary. If the zero and span drifts do not exceed the calibration limits in Table 9.1 of Section 2.0.9 (Subsection 9.1.3) (or stricter limits set by the local monitoring agency) a calibration need not be performed. If either the zero or the

span drift exceeds its respective limit, investigate the cause of the drift, take corrective action, and calibrate the analyzer. Individual agencies may wish to use limits which are tighter than those in Table 9.1.

Calibration Data Forms

1 Station Downtown 1468 ACTERMAN ST. BUTLERTOWN, KY

2. Analyzer AJAX FLUORESCENCE SO_2 MODEL 201 SN 14280

3. Calibration performed by TOM BROWN Date 4-9-82

4 Calibrator used HOME BUILT SO_2 NO. 3

5. SO_2 standard AJAX SO_2 PERM TUBE NO. 144

verified against NBS-SRM 1626 TUBE 128

By TOM BROWN Date 3-8-82

6. Flow measured with PRECISION BUBBLE METER

7 Barometric pressure 731 mm Hg Shelter temperature 20 °C

8 Analyzer sample flow readings AIR 500/cc/min

9 Zero knob setting 458 Span knob setting 527

10 Permeation equilibrium temperature 25.0 °C

Permeation rate (PR) 1.54 μg/min

11 Temperature at which air flow rate was measured (AT) 23.0 °C

12 Vapor pressure of water at temperature (AT) 21.1 mm Hg

Calibration Equations

Equation 2-1

$$\text{STP correction factor} = \frac{BP\text{-}VP}{760} \times \frac{298}{AT + 273}$$

Equation 2-2

$$F_T = F \times \text{STP correction factor}$$

Equation 2-3

$$\text{ppm } [SO_2]_{OUT} = \frac{PR}{F_T} \times \frac{MV}{M}$$

Equation 2-4

$$\text{Response (\% scale)} = \frac{[SO_2]_{OUT}}{URL} \times 100 + Z_{SO_2}$$

BP = barometric pressure, mm Hg

VP = vapor pressure of water, mm Hg at AT (Table 2 1)

AT = temperature at which air flow rate was measured, °C

F = uncorrected flow rate

F_T = total air flow rate, corrected to 25°C and 760 mm Hg, L/min

PR = permeation rate at equilibrium temperature, μg/min

MV = molecular volume of SO_2 at 25°C and 760 mm Hg 24.45 L/mol)

M = molecular weight of SO_2 (64 g/mol)

$$\frac{MV}{M} = \frac{24.45 \text{ L/mol}}{64 \text{ g/mol}} = 0.382 \text{ L/g}$$

URL = upper range limit of analyzer

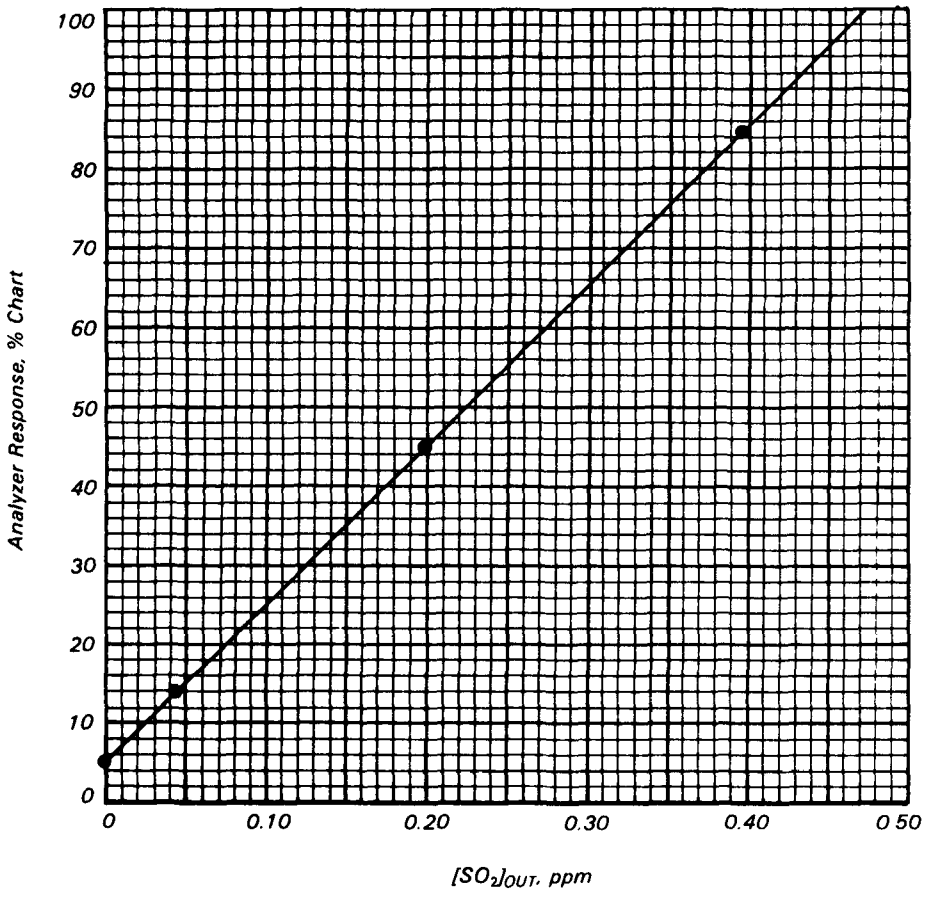
Z_{SO_2} = recorder response to zero air

Figure 2.1. Example of a calibration data form

SO_2 Calibration and linearity check.

Calibration points	1 F, L/min	2[a] F_T at STP L/min Equation 2-2	3 $[SO_2]_{OUT}$, ppm Equation 2-3	4 % Scale Equation 2-4
Zero			0.0	5.0
80% URL	1.56	1.47	0.400	85.0
1	3.09	2.90	0.202	45.4
2	13.09	12.30	0.0418	14.6

13. $F_T = F \times STP$, $STP = \left(\frac{(731) - (21)}{760}\right)\left(\frac{298}{(23) + 273}\right) =$ 0.94



Calibration Relationship

Slope (b) of calibration relationship (Y = a + bx) = 200

Intercept (a) of calibration relationship = 5%

Figure 2.2. Example of a calibration data form (linearity check and calibration relationship).

Calibration point	x	x^2	y	y^2	xy
Zero	0.000	0.000	5.0	25	0.0
80% URL	0.400	0.160	85.0	7225	34.0
1	0.202	0.041	45.4	2061	9.2
2	0.045	0.002	14.0	196	0.6
3					
4					

x = concentration, ppm y = recorder reading, % scale

Σx = 0.647 Σx^2 = 0.203 Σy = 149.4 Σy^2 = 9507 Σxy = 43.8 $\bar{x} = \Sigma x/n$ = 0.162

$\bar{y} = \Sigma y/n$ = 37.35

The equation of the line fitted to the data is written as

$$Y = \bar{y} + b(x - \bar{x}) = (\bar{y} - b\bar{x}) = bx = a + bx$$

where

Y = the predicted mean response for the corresponding x,

b = the slope of the fitted line,

a = the y-intercept,

n = the number of calibration points,

$$b = \frac{\Sigma xy - \frac{(\Sigma x)(\Sigma y)}{n}}{\Sigma x^2 - \frac{(\Sigma x)^2}{n}} = \frac{1.165}{0.063} = 18.6$$

$a = \bar{y} - b\bar{x}$ = 5.015

Figure 2.3. Calculation form for the method of least squares

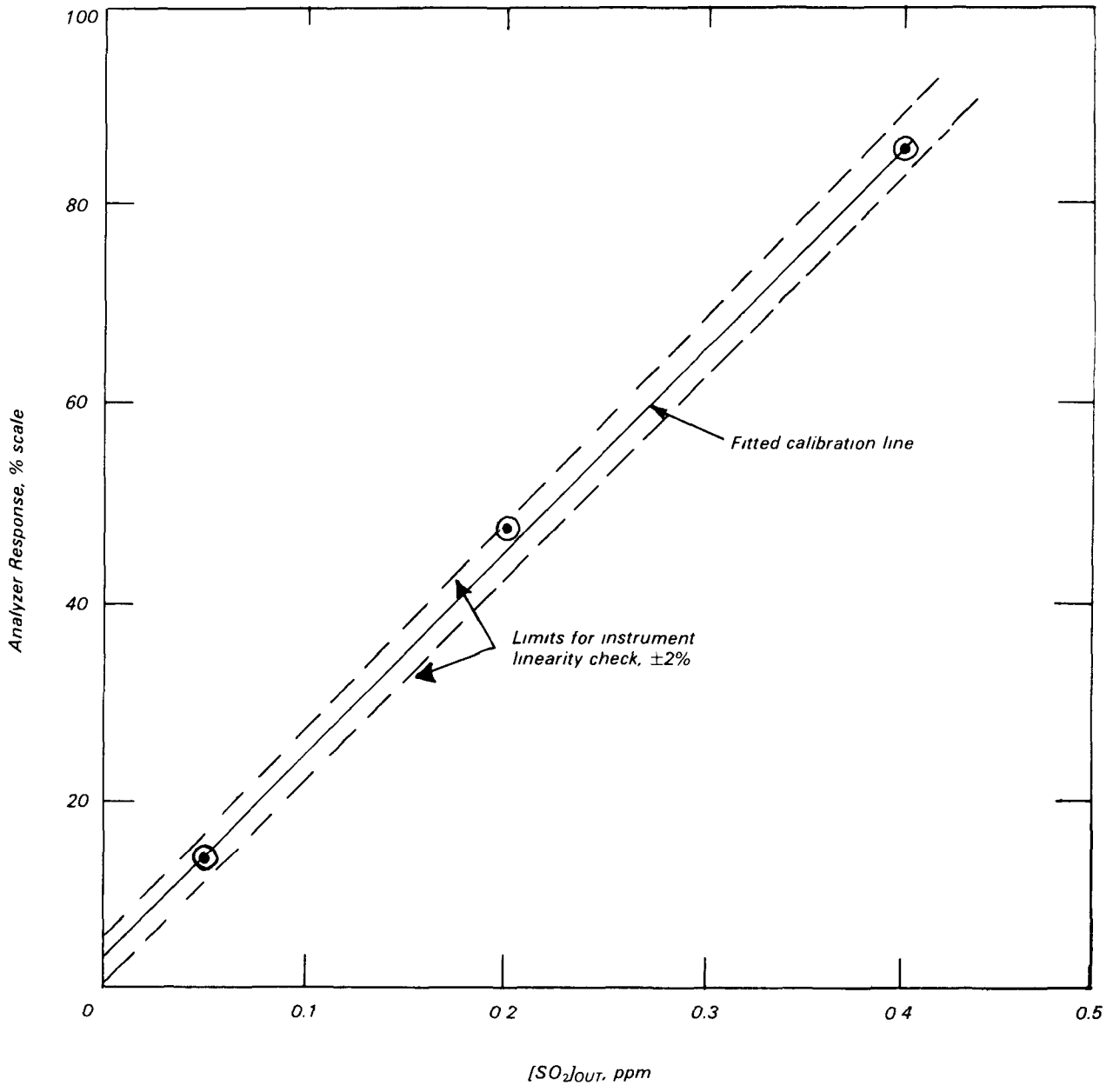


Figure 2.4. *Example of an SO_2 calibration relationship*

Table 2.1. *Saturation Vapor Pressure Over Water (°C, mm. Hg)*

Temp. °C	0.0	0.2	0.4	0.6	0.8
15	12.788	12.953	13.121	13.290	13.461
16	13.634	13.809	13 987	14.166	14.347
17	14.530	14 715	14.903	15.092	15.284
18	15.477	15 673	15.871	16.071	16.272
19	16.477	16.685	16.894	17 105	17.319
20	17.535	17 753	17.974	18.197	18.422
21	18.650	18.880	19.113	19.349	19.587
22	19.827	20.070	20 316	20.565	20.815
23	21.068	21.324	21.583	21.845	22.110
24	22.377	22.648	22.922	23.198	23.476
25	23.756	24.039	24.326	24.617	24.912
26	25.209	25.509	25.812	26.117	26.426
27	26.739	27.055	27.374	27.696	28.021
28	28.349	28.680	29 015	29.354	29.697
29	30.043	30.392	30.745	31.102	31.461
30	31.824	32.191	32.561	32.934	33.312
31	33.695	34.082	34.471	34.864	35.261
32	35.663	36.068	36.477	36.891	37.308
33	37.729	38.155	38.584	39.018	39.457
34	39.898	40.344	40.796	41.251	41.710
35	42.175	42.644	43.117	43.595	44.078

Table 2.2. *Activity Matrix for Calibration Procedures*

Calibration activities	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Permeation tube	*Traceable to NBS standards*	*Subsec 2.0.7 for frequency and method*	*Return to supplier, or make another permeation tube*
Dilution gas	*Zero-air free of contaminants; Sec 2.0.7, Subsec 7.1, and TAD*[10]	*TAD*[10]	*Return to supplier, or take corrective action with generation system*
Span gases	*Cylinder gases certified to NBS-SRM or commercial CRM cylinder gas or to an NBS-SRM permeation tube* *Gases generated by calibrator using an SO_2 permeation tube*	*Assay against an NBS-SRM semi-annually; Sec 2.0.7*	*Working as standard is unstable and/or measurement method is out of control; take corrective action (e.g., obtain new span gases)*
Multipoint calibration	*Calibration procedure in Subsec 2.2, and the* Federal Register,[1] *completed Figs 2.1 and 2.2*	*Perform at least once every quarter, or anytime a level span check indicates a discrepancy, or after maintenance which may affect the calibration; Subsec 2.5*	*Repeat the calibration*

3.0 Operation and Procedure

Essential to quality assurance are scheduled checks for verifying the operational status of the monitoring system. At least once each week the operator should visit the site. Every two weeks, Level 1 zero and span checks must be made on the analyzer. Level 2 zero and span checks should be conducted at a frequency desired by the user. Level 1 and 2 checks are described in-depth in Section 2.0.9 of this Handbook.

At least once every two weeks, an independent precision check at a concentration between 0.08 and 0.10 ppm SO_2 must be conducted. Table 3.1 at the end of this section summarizes the quality assurance activities for the routine operations discussed in the following sections.

For documentation and accountability of activities, a checklist should be compiled and then filled out by the field operator as each activity is completed. A simplified example checklist is given in Figure 3.1. A more comprehensive check list should be developed for specific sampling stations.

In Subsections 3.1 and 3.2, reference is made to the sampling shelter and the sample inlet system, but the design and construction of these components are not within the scope of this Handbook. For more information refer to an in-depth study of these in Reference 11.

3.1 Shelter

The shelter's role in quality assurance is to provide a temperature-controlled environment in which the sampling equipment can operate at its optimum. The mean shelter temperature should be between 22° and 28°C (72° and 82°F). A thermograph should be installed at the shelter to continuously record daily fluctuations in temperature. Fluctuations greater than ±2°C (±4°F) may cause the electronic components of the analyzer to drift and may introduce error into the data. Fluctuations outside of these limits should be identified, and the data for the affected time period should be flagged to indicate possible discrepancies.

3.2 Sample Introduction System

The sample introduction system consists of an intake port, the particulate and moisture traps, the sampling manifold and blower, and the sampling line to the analyzer. The field operator, as part of the quality assurance program, should inspect each of these components for breakage, leaks, and buildup of particulate matter or other foreign objects; check for moisture deposition in the sample line or manifold; see that the sample line is connected to the manifold; see that any component of the sample introduction system that is not within tolerance is either cleaned or replaced immediately. See Section 2.0.2 for more details.

3.3 Recorder

During each weekly visit to the monitoring site, the field operator should use the following list to check the recorder for proper operation:

1. Ink trace for legibility
2. Ink level in reservoir
3. Chart paper for supply
4. Chart speed control setting
5. Signal input range switch
6. Time synchronization.

Any operational parameter that is not within tolerance must be corrected immediately.

3.4 Analyzer

Specific instructions in the manufacturer's manual should be read thoroughly before attempting to operate the analyzer As part of the quality assurance program, each site visit should include a visual inspection of the external parameters of the analyzer, the zero and span checks; and a biweekly precision check when applicable.

3.4.1 *Visual Inspection* - The field operator should inspect the external operating parameters of the analyzer; these will vary from instrument to instrument, but in general they will include the following:

1. Correct settings of flow meters and regulators.
2. Cycling of temperature control indicators.
3. Temperature level, if equipped with a pyrometer.
4. Verification that the analyzer is in the sampling mode rather than the zero or the calibration mode.
5. Zero and span potentiometers locked and set at proper values.

3.4.2 *Zero and Span Checks* - Zero and span checks must be used to document within-control conditions and to provide interim checks on the response of the instrument to known concentrations. A quality control chart can be used to provide a visual check to determine if the analyzer is within control conditions. If a response is outside of the prescribed limits, the analyzer is out of control and the cause must be determined and corrected. A zero check should be conducted at the same time that the span check is performed.

Level 1 and Level 2 zero and span checks are recommended and must be conducted in accordance with Subsection 9.1 of Section 2.0.9. Level 1 zero and span checks must be conducted every two weeks. Level 2 checks should be conducted between the Level 1 checks at a frequency desired by the user. Span concentrations for either Level 1 or 2 checks should be between 70% and 90% of the measurement range. The data should be recorded on the zero and span check form, Figure 3.2.

Zero and span checks are used to provide:

1. Data to allow analyzer adjustment for zero and span drift
2. A decision point for calibrating the analyzer
3. A decision point for invalidating the monitoring data.

Items 1 and 2 are described in detail in Subsection 9.1.3 of Section 2.0.9 and item 3 is described in Subsection 9.1.4 of the same section.

When the response from a span check is outside of the control limits, the cause for the extreme drift should be determined, and corrective action should be taken. Some of the causes for drift are:

1. Lack of preventive maintenance
2. Fluctuations in electrical power supply
3. Major fluctuations in sample flow
4. Change in zero air source
5. Change in span gas concentration
6. Degradation of photomultiplier tube

7. Degradation of UV light source
8. Electronic and physical components not within manufacturer's specifications.

Corrective actions for the above can be found in the manufacturer's instruction/operations manual

3.4.3 *Precision Check* - For continuous analyzers, periodic checks are used to assess the data for precision. A one-point precision check must be carried out at least once every 2 weeks on each analyzer at an SO_2 concentration between 0.08 and 0.10 ppm. The analyzer must be operated in its normal sampling mode, and the precision test gas must pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling. The standards from which precision check test concentrations are obtained must be traceable to NBS-SRM's or NBS/EPA-approved commercially available Certified Reference Material (CRM). Direct use of a CRM as a working standard is acceptable, but direct use of an NBS-SRM as a working standard is discouraged because of the limited supply and expense of SRM's. Standards used for calibration may also be used. The precision check procedure is as follows:

1. Connect the analyzer to a precision gas that has a concentration between 0.08 and 0.10 ppm. An SO_2 precision gas may be generated by an SO_2 permeation tube or by dilution of a high concentration (50 to 100 ppm) SO_2 standard gas. If a precision check is made with a zero and span check, it must be made prior to any zero or span adjustments.
2. Allow the analyzer to sample the precision gas until a stable trace is obtained at the recorder.
3. Record this value on the precision check data form (Figure 3.3), and mark the chart as "unadjusted precision check." Information from the check procedure is used to assess the precision of the monitoring data; see Section 2.0.8 for procedures for calculating and reporting precision.

Site ID 001 Date 3-1-79

Site name MUNICIPAL INCINERATOR Technician G. JONES

Site address 3336 JEFFERSON AVENUE, CHICAGO, IL

✓ 1. Inspect thermograph for temperature variations greater than ±2°C (4°F). Identify time frame of any temperature level out of tolerance.
Comments: TEMP W/IN TOLERANCE LEVELS

✓ 2. Inspect sample introduction system for moisture, particulate buildup, foreign objects, breakage, and leaks.
Comments: ACCUMULATION OF PARTICULATE IN TRAP. TRAP REMOVED AND CLEANED

✓ 3. Check to see if sample line connected to manifold.
Comments: OKAY

___ 4 Inspect data recording system

	OK	Corrective action taken
• Legibility of trace	✓	
• Ink supply		✓
• Paper supply	✓	
• Chart speed selector	✓	
• Signal input range switch	✓	
• Time synchronization		✓

Comments

✓ 5. Inspect analyzer's operational parameters

	OK	Corrective action taken
• Sample flow rate	✓	
• Oven temperature light flashing	✓	
• Analyzer in sample mode	✓	
• Zero and span potentiometers locked at correct setting	✓	

Comments: NONE

✓ 6. Zero the analyzer

✓ 7. Check to see if unadjusted zero is within tolerance
Comments. ZERO OKAY AT 4.5%

✓ 8. Span the analyzer

✓ 9. Check to see if unadjusted span is within tolerance.
Comments: SPAN OKAY AT 80%

✓ 10 Enter zero and span values on span check data form

✓ 11. Return to sample mode.

Figure 3.1. Example of an operational checklist (frontside).

✓ 12. *Record cylinder pressure of zero and span tanks.*

Zero air 1300 PSI

Span air 1600 PSI

_____ 13. *Close valves on zero and span tanks.*

Signature of technician Greg Jones

Figure 3.1. *Example of an operational checklist (backside).*

Site ID 001 Pollutant SO_2

Location MUNICIPAL INCINERATOR Analyzer FLUORESCENCE

Address 3336 JEFFERSON AVE. Serial number 4710.0

Adjusted zero 5% Adjusted span 85% OF CHART

Date	Time	Operator	Unadjusted zero, % chart	Span concentration, ppm	Unadjusted span, % chart
2-1-80	0930	RBC	4	0.40	84

Figure 3.2. Example of a Level 1 zero and span check data form.

Site ID 001 Pollutant SO_2

Location MUNICIPAL INCINERATOR Analyzer FLUORESCENCE

Address 3336 JEFFERSON AVE. Serial number 4710.0

Date	Time	Operator	Precision test gas concentration, ppm	Analyzer response,		Difference*, ppm
				% chart	ppm	
2-1-80	1030	ABC	0.10	24	0.095	-0.005

*Difference = analyzer response - test gas concentration.

Figure 3.3. *Example of precision check form.*

Table 3.1. *Daily Activity Matrix*

Characteristic	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Shelter temperature	*Mean temperature between 22° and 28°C (72° and 82°F), daily fluctuations not greater than ±2°C (4°F)*	*Edit thermograph chart daily for variations greater than ±2°C (4°F)*	*Mark strip chart for the affected time period; repair or adjust temperature control system*
Sample introduction system	*No moisture, foreign material, leaks, or obstructions; sample line connected to manifold*	*Visually inspect weekly*	*Clean, repair, or replace as needed*
Recorder	*Adequate ink and chart paper; legible ink traces; correct settings of chart speed and range switches; correct time*	*Visually inspect weekly*	*Replenish ink and chart paper; adjust recorder time to agree with clock; note on chart*
Analyzer operational settings	*Flow and regulator indicators at proper settings; temperature indicators cycling or at proper levels; analyzer set in sample mode; zero and span controls locked*	*Visually inspect weekly*	*Adjust or repair as needed*
Analyzer operational check	*Zero and span within tolerance limits; Subsec 9.1.3 of Sec 2.0.9*	*Check level 1 zero and span every 2 weeks; check Level 2 between Level 1 checks at frequency desired by user*	*Isolate source of error, and repair; then recalibrate the analyzer*
Precision check	*Precision assessed as described in Sec 2.0.8 and Subsec 3.4.3*	*Check every 2 weeks, Subsec 3.4.3*	*Calculate; report precision; Sec 2.0.8*

4.0 Data Reduction, Validation, and Reporting

This section is the same as that of Section 2.5.4. Table 4.1 summarizes the quality assurance activities for the data reduction, validation, and reporting.

Table 4.1. *Activity Matrix for Data Reduction, Validation, and Reporting*

Activity	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Data reduction	*Stepwise procedure, Subsec 4.1*	*Follow the method in Subsec 4.1*	*Review the reduction procedure*
Data validation			
Span drift check	*Level 1 span drift check <25%, Sec 2.0.9*	*Check at least every 2 weeks; Sec 2.5.3; Ref 12 recommends screening procedures to identify gross anomalies*	*Invalidate data; take corrective action; increase frequency of Level 1 checks until data are acceptable*
Strip chart edit	*No sign of malfunction*	*Visually edit each strip chart; Subsec 4.2*	*Void data for time interval for which malfunction detected*
Data reporting	*Data transcribed to SAROAD hourly data form; Ref 13*	*Visually check*	*Review the data transcribing procedure*

5.0 Maintenance

5.1 Preventive Maintenance

Because maintenance requirements vary from instrument to instrument, the supervisor should refer to the manufacturer's manual for a specific analyzer. After becoming familiar with these requirements, the supervisor should develop a suitable preventive maintenance schedule.

5.2 Corrective Maintenance

Corrective maintenance is defined as nonscheduled activities that become necessary due to system malfunctions. A few examples of corrective maintenance are: replacing a damaged pump diaphragm; cleaning a clogged sampling line; and replacing the selective scrubber for aromatic hydrocarbons. The need for corrective maintenance becomes apparent as the operator performs the operations described in Section 2.9.3. When the need for corrective maintenance arises, the operator should refer to the owner's manual for troubleshooting procedures. A detailed record of corrective maintenance activities should be kept on file for each analyzer at the site to identify recurring malfunctions; maintenance log appears in Figure 5.1.

Caution: When replacing, aligning, and otherwise servicing the deuterium source lamp, always wear UV-absorbing glasses to protect the eyes from the ultraviolet radiation produced. Ordinary prescription spectacles with *glass* lenses are suitable. *Plastic* lenses may not provide adequate protection.

Site number 001 Pollutant SO_2

Site location Municipal Incinerator Instrument ACME Fluorescence

Site address 3336 JEFFERSON AVE. Serial number 288-7045-B

Date	Technician	Event initiating maintenance	Maintenance activity	Comments
2-1-80	ABC	Loss of upscale chart deflection	Replace UV light source	Recorder trace fell below baseline. UV light source replaced. Analyzer recalibrated.

Figure 5.1. Analyzer maintenance log

6.0 Auditing Procedure

Table 6.1 summarizes the quality assurance activities for audits. This section is the same as Section 2.5.6. See References 14 and 15 for the frequency and brief descriptions of audit procedures.

Table 6.1. *Activity Matrix for Audit Procedure*

Audit	*Acceptance limits*	*Frequency of method of measurement*	*Action if requirements are not met*
Multipoint calibration audit	*Difference between measured and audit values is used as measure of accuracy; Sec 2.0.8*	*Perform at least once a quarter; Subsec 6.1.3 for procedure*	*Recalibrate the analyzer*
Data reduction audit	*Stepwise procedures for data reduction, Subsec 6.2; no audit difference exceeding ±0.02 ppm*	*Perform independent data processing check on a sample of the recorded data; check 1 day of every 2 weeks of data, 2 hours each day*	*Check all remaining data if one or more data reduction checks exceed ±0.02 ppm*
Systems audit	*Method in this section of the Handbook*	*At startup of new monitoring system, and periodically observe as appropriate; checklist, Fig 6.4*	*Initiate improved methods and/or training programs*

7.0 Assessment of Monitoring Data for Precision and Accuracy

For continuous analyzers, in SLAMS, NAMS, or PSD networks a biweekly check is performed to determine if the measurement process is within control and to assess the data for precision. These data can be used to calculate estimates of single instrument precision, and reporting organization precision as prescribed in Section 2.0.8 of this volume of the Handbook. The precision check procedures described in Section 2.9.3, Subsection 3.4.3 are consistent with those in References 14 and 15.

Estimates of single instrument accuracy as well as reporting organization accuracy for ambient air quality measurements from continuous methods are based on the results of the in-depth accuracy audit and are calculated according to the procedure in Section 2.0.8. The audit is described in Section 2.9.6.

8.0 Recommended Standards for Establishing Traceability

To achieve data of desired quality, two considerations are essential:

1. The measurement process must be in statistical control at the time of the measurement, and
2. The systematic errors, when combined with the random variation in the measurement process, must result in an acceptable uncertainty.

As evidence in support of good quality data, it is necessary to perform quality control checks and independent audits of the measurement process; to document these data (e.g., by means of specific data forms or a quality control chart); and to use materials, instruments, and measurement procedures that can be traced to appropriate standards of reference.

Data must be routinely obtained by repeat measurements of standard reference samples (primary, secondary, and/or working standards), and a condition of process control must be established. The working standards must be traceable to either NBS-SRM's or commercially available CRM's, such as those listed below:

NBS-SRM's Available for Use in Establishing Traceability of Permeation Tubes[8]

SRM	Type	Tube length, cm	Nominal permeation rate, μg/min at 25°C
1625	SO_2 permeation tube	10	2.8
1626	SO_2 permeation tube	5	1.4
1627	SO_2 permeation tube	2	0.56

NBS-SRM's Available for Use in Establishing Traceability of Compressed Cylinder Gases

SRM	Type	Nominal concentration
1693	SO_2 in N_2	50 ppm
1694	SO_2 in N_2	100 ppm

A list of gas manufacturers who have approved CRM is available by writing to:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory (MD-77)
Research Triangle Park, North Carolina 27711
ATTN: List of CRM Manufacturers

9.0 Equivalent Method

A method description is not given herein. The concepts of equivalent analyzers are discussed in Section 2.0.4 of this volume of the Handbook. The analyzer must also comply with the performance specifications in Table 4.1 of Section 2.0.4. An instruction manual including the calibration procedure must accompany the analyzer when it is delivered to the purchaser. This instruction manual has been reviewed and approved by EPA as part of the equivalency test program. The user of the analyzer should use the method description in this section of the Handbook and the instruction manual.

A list of equivalent methods may be obtained from any EPA regional office or from the Environmental Monitoring Systems Laboratory, Department E, MD-77, Research Triangle Park, N.C. 27711. Any analyzer offered for sale as an equivalent method after April 16, 1976, must bear a label indicating this designation by EPA.

10.0 References

1. Code of Federal Regulations 40. Protection of the Environment. Parts 50 to 69. Revised July 1, 1977
2. Summary of Performance Test Results and Comparative Data for Designated Equivalent Methods for SO_2, EPA Document No. QAD/M-79.12.
3. Thermo Electron Corporation, Environmental Instruments Division Instruction Manual Model 43 Pulsed Fluorescent SO_2 Analyses Equipped with an Aromatic Hydrocarbon Cutter. TE5405-112-77, Revision C. Hopkinton, Massachusetts.
4. Beckman Instruments, Inc. Beckman Model 953 Fluorescent Ambient Sulfur Dioxide Analyzer. Fullerton, CA. May 1979.
5. Monitor Labs, Inc. Monitor Labs, Inc. Model 8850 Fluorescent SO_2 Analyzer Instruction Manual. Document 8850 Rev. D. San Diego, CA. September 1979.
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8. Catalog of NBS Standard Reference Materials. NBS Special Publication 260, 1981 - 83 Edition. U.S. Department of Commerce, NBS, Washington, D.C. November 1981.
9. Quality Assurance Handbook for Air Pollution Measurement Systems. Vol. I. EPA-600/9-76-005. March 1976
10. Use of the Flame Photometric Detector Method for Measurement of Sulfur Dioxide in Ambient Air, A Technical Assistance Document, EPA-600/4-78-024, May 1978.
11. Field Operations Guide for Automatic Air Monitoring Equipment. U.S. Environmental Protection Agency, Office of Air Programs; October 1972. Publication No. APTD-0736, PB 202-249, and PB 204-650.
12. U.S. Environmental Protection Agency, Sreening Procedures for Ambient Air Quality Data. EPA-450/2-78-037, July 1978.
13. AEROS Manual Series, Volume II: AEROS Users Manual, U.S. Environmental Protection Agency, Research Triangle Park, N.C., EPA-450/2-76-029, OAQPS No. 1.2 - 039, December 1976.
14. Appendix A - Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS), *Federal Register*, Vol. 44, No. 92, pp. 27574-27582, May 1979.
15. Appendix B - Quality Assurance Requirements for Prevention of Significant Deterioration (PSD) Air Monitoring, *Federal Register*, Vol. 44, No. 92, pp. 27582 27584, May 1979.

11.0 Data Forms

Blank data forms are provided on the following pages for the convenience of the Handbook user. Each blank form has the customary descriptive title centered at the top of the page. However, the section-page documentation in the top right-hand corner of each page of other sections has been replaced with a number in the lower right-hand corner that will enable the user to identify and refer to a similar filled-in form in a text section. For example, Form SO_2 (FLR)-2.1 indicates that the form is Figure 2.1 of the SO_2 (FLR) method description. Future revisions of this form, if any, can be documented by 2.1A, 2.1B, etc. Only the data forms that are distinct from those of Section 2.5.11 are included here; however, all of the data forms are listed below.

Form	Title
1.1 (see 2.5.11)	Procurement Log
2.1	Calibration Data Form
2.2 (see 2.5.11)	Example of a Calibration Data Form
2.3 (see 2.5.11)	Calculation Form for the Method of Least Squares
3.1	Operational Checklist
3.2 (see 2.5.11)	Span Check Data Form
3.3 (see 2.5.11)	Precision Check Form
4.1 (see 2.5.11)	Data Form for Recording Hourly Averages
5.1 (see 2.5.11)	Maintenance Log
6.1 (see 2.5.11)	Audit Summary Form
6.2 and 6.3 (see 2.5.11)	Audit Calculation Form
6.4 (see 2.5.11)	Checklist for Use by Auditor

Calibration Data Form

1. Station _____ 2. Analyzer _____

_____ _____

_____ _____

3. Calibration performed by _____ Date _____

4. Calibrator used _____

5. SO_2 standard _____

verified against NBS-SRM _____

By _____ Date _____

6. Flow measured with _____

7. Barometric pressure _____ mm Hg Shelter temperature _____ °C

8. Analyzer sample flow readings _____

9 Zero knob setting _____ Span knob setting _____

10. Permeation equilibrium temperature _____ °C

Permeation rate (PR) _____ µg/min

11. Temperature at which air flow rate was measured (AT) _____ °C

12. Vapor pressure of water at temperature (AT) _____ mm Hg

Calibration Equations

Equation 2-1

$$\text{STP correction factor} = \frac{BP\text{-}VP}{760} \times \frac{298}{AT + 273}$$

Equation 2-2

$$F_T = F \times \text{STP correction factor}$$

Equation 2-3

$$\text{ppm } [SO_2]_{OUT} = \frac{PR}{F_T} \times \frac{MV}{M}$$

Equation 2-4

$$\text{Response (\% scale)} = \frac{[SO_2]_{OUT}}{URL} \times 100 + Z_{SO_2}$$

BP = barometric pressure, mm Hg

VP = vapor pressure of water, mm Hg at AT (Table 2.1)

AT = temperature at which air flow rate was measured, °C

F = uncorrected flow rate

F_T = total air flow rate, corrected to 25°C and 760 mm Hg, L/min

PR = permeation rate at equilibrium temperature, µg/min

MV = molecular volume of SO_2 at 25°C and 760 mm Hg 24.45 L/mol)

M = molecular weight of SO_2 (64 g/mol)

$$\frac{MV}{M} = \frac{24.45 \text{ L/mol}}{64 \text{ g/mol}} = 0.382 \text{ L/g}$$

URL = upper range limit of analyzer

Z_{SO_2} = recorder response to zero air

Operational Checklist (Frontside)

Site ID _____ *Date* _____

Site name _____ *Technician* _____

Site address _____

_____ 1 *Inspect thermograph for temperature variations greater than ±2°C (4°F). Identify time frame of any temperature level out of tolerance*
Comments: _____

_____ 2. *Inspect sample introduction system for moisture, particulate buildup, foreign objects, breakage, and leaks.*

Comments: _____

_____ 3. *Check to see if sample line is connected to manifold.*

Comments: _____

_____ 4. *Inspect data recording system.*

	OK	Corrective action taken
● *Legibility of trace*	___	_____
● *Ink supply*	___	_____
● *Paper supply*	___	_____
● *Chart speed selector*	___	_____
● *Signal input range switch*	___	_____
● *Time synchronization*	___	_____

Comments: _____

_____ 5 *Inspect analyzer's operational parameters*

	OK	Corrective action taken
● *Sample flow rate*	___	_____
● *Oven temperature light flashing*	___	_____
● *Analyzer in sample mode*	___	_____
● *Zero and span potentiometers locked at correct setting*	___	_____

Comments: _____

_____ 6. *Zero the analyzer*

_____ 7 *Check to see if unadjusted zero is within tolerance*

Comments _____

_____ 8 *Span the analyzer*

_____ 9. *Check to see if unadjusted span is within tolerance*

Comments: _____

_____ 10. *Enter zero and span values on span check data form*

_____ 11 *Return to sample mode*

_____ *12. Record cylinder pressure of zero and span tanks.*

Zero air _____

Span air _____

_____ *13 Close valves on zero and span tanks.*

Signature of technician _____

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Environmental Protection
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Environmental Monitoring Systems
Laboratory
Research Triangle Park NC 27711

Research and Development

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Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III. Stationary Source Specific Methods

Addition Section 3.12

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Section 3.12
Method 9—Visible Determination of the Opacity of Emissions from Stationary Sources

Outline

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Summary

Many stationary sources discharge plume-shaped visible emissions into the atmosphere Method 9 (EPA Reference Method) is used to determine the opacity of this plume by qualified observers. The method includes procedures for the training and certification of observers and procedures to be used by these observers in the field to determine plume opacity. This section of the Quality Assurance (QA) Handbook primarily concerns procedures used by the observers Only Section 3.12.1 reviews the training and certification procedures, which are described in Reference 1.

The appearance of a plume as viewed by an observer depends upon a number of variables, some of which may be controllable and some of which may not be controllable in the field. Variables which can be controlled to an extent to which they no longer exert a significant influence upon plume appearance include: angle of the observer with respect to the plume; angle of the observer with respect to the sun; point of observation of attached and detached steam plumes and angle of the observer with respect to a plume emitted from a rectangular stack with a large length to width ratio. The

method includes specific criteria applicable to these variables.

Other variables which may not be controllable in the field are luminescence and color contrast between the plume and the background against which the plume is viewed. These variables exert an influence upon the appearance of a plume as viewed by an observer, and can affect the ability of the observer to accurately assign opacity values to the observed plume. Research studies of plume opacity have demonstrated that a plume is most visible and presents the greatest apparent opacity when viewed against a contrasting background. It follows from this, and is confirmed by field trials, that the opacity of a plume, viewed under conditions where a contrasting background is present can be assigned with the greatest degree of accuracy. However, the potential for a positive error is also the greatest when a plume is viewed under such contrasting conditions. Under conditions presenting a less contrasting background, the apparent opacity of a plume is less and approaches zero as the color and luminescence contrast decrease toward zero. As a result, significant negative bias and negative errors can be made when a plume is viewed under less contrasting conditions. A negative bias decreases rather than increases the possibility that a plant operator will be cited for a violation of opacity standards due to observer error.

Method 9 is applicable for the determination of the opacity of emissions from stationary sources pursuant to 60.11(b). Studies have been undertaken to determine the magnitude of positive errors that qualified observers can make while reading plumes under contrasting conditions and using the procedures specified in Method 9. The results of these studies, which involve a total of 769 sets of 25 readings each, are as follows:

1. In the case of black plumes, 100 percent of the sets were read with positive error of less than 7.5 percent opacity; 99 percent were read with a positive error of less than 5 percent opacity.
2. In the case of white plumes, 99 percent of the sets were read with a positive error (higher values) of less than 7.5 percent opacity; 95 percent were read with a positive error of less than 5 percent opacity.

The positive observational error associated with an average of twenty-five readings is therefore established. The accuracy of the method must be taken into account when determining possible violations of applicable opacity standards.

Note: Proper application of Method 9 by control agency personnel in determining the compliance status of sources subject to opacity standards often involves a number of administrative and technical procedural steps not specifically addressed in the *Federal Register* method. Experience has shown these steps are necessary to lay a proper foundation for any subsequent enforcement action. To clearly delineate items that are EPA procedural policy and requirements of the Method 9 from additional quality assurance procedures, a wording scheme was developed. All of Sections 3.12.1, 3.12.2, 3.12 3, 3.12 6, and 3 12.7 are suggested quality assurance procedures except where noted as EPA policy or *Federal Register* citings. Section 3.12.4 notes EPA requirements with directive statements using words such as shall, should, and must. QA procedures are noted either with suggestive statements using words such as recommended, suggested, and beneficial or by stating that the entire subsection is recommended. The use of these QA procedures should provide a more consistent program, improved observer effectiveness and efficiency, and improved data documentation.

Method Highlights

Section 3.12 primarily describes Method 9 procedures for the determination of plume opacity. Section 3.12.1 briefly reviews the quality assurance procedures to be used in the observer training and certification procedures described in detail in Reference 1. The remaining sections describe the field procedures.

Section 3.12.10 provides blank data forms recommended for use by the observer and other personnel, as required. Partially completed forms are included in Sections 3.12.1 through 3.12.7 of the Method Description. Each form in Section 3.12.10 has a subtitle (e.g., Method 9, Figure 2.1) to allow easy reference to the corresponding completed form.

The following paragraphs present a brief discussion of the contents of this section of the QA Handbook.

1. *Certification and Training of Observers* The primary purpose of this section is to provide a brief summary of the certification and training procedures described in Reference 1. It includes a definition and a brief history of opacity, and it discusses observer training procedures and certification and recertification of observers.

2. *Procurement of Apparatus and Supplies* Section 3.12.2 presents specifications criteria and design features to aid the procurement of useful equipment that would provide good quality visible emissions data. The following are some recommended equipment items not specifically required by Method 9: watch, compass, range finder, Abney level or clinometer, sling psychrometer, binoculars, camera, safety equipment, clipboard, and accessories. Table 2.1 summarizes the quality assurance aspects of equipment procurement.

3. *Preobservation Operations* Section 3.12.3 summarizes the preobservation activities: gathering facility information, providing prior notification, establishing protocol, and performing equipment checks. Table 3.1 summarizes these procedures.

4. *On-Site Field Observations* Section 3.12.4 contains detailed procedures for determining the visible emissions (VE). This section not only includes the recommended procedures for performing the perimeter survey, plant entry, and VE determination; it also contains a subsection on special observation problems. This subsection explains how to take VE readings under less than ideal conditions (e.g., when the observer position is restricted). The main feature of this section is the presentation of detailed instructions on how to complete the recommended VE data form, and examples of completed forms.

5. *Postobservation Operations* Section 3.12.5 presents a brief discussion concerning the data reporting procedures, data summary, data validation, and equipment check. Section 3.12.6 contains a discussion of the calculations required for completing the data forms and reports. It also includes procedures for calculating the path length through the plume and for predicting steam plume formation by use of a psychrometric chart and pertinent measurements.

6. *Auditing Procedures* Section 3.12.7 recommends performance and system audits for use with field VE determinations. The two performance

audits are an audit by senior observer/supervisor and a data calculation audit. A system audit is suggested, along with a Method 9 checklist, as shown in Figure 7 1. Table 7.1 summarizes the quality assurance activities for audits.

7. *References and Bibliography* Sections 3.12.8 and 3 12.9 contain the Method 9 and suggested references and bibliography.

8. *Data Forms* Section 3.12.10 provides blank data forms which can be taken from the QA Handbook for field use or serve as the basis of a revised form to be used by the Agency. Partially completed forms are included in the corresponding section of the QA Handbook

1.0 Certification and Training of Observers

The purpose of this section is to summarize the content of the QA manual for VE training programs.[1] Since the observer must be properly certified or a qualified VE reader in order to have his/her opacity reading accepted, it is important that he/she fully understand this phase of his/her training

1.1 Definition and Brief History of Opacity

The VE evaluation system evolved from the concept developed by Maximillian Ringelmann in the late 1800's, in which a chart with calibrated black grids on a white background was used to measure black smoke emissions from coal-fired boilers. The Ringelmann Chart was adopted by the U S. Bureau of Mines in the early 1900's and was used extensively in efforts to assess and control emissions In the early 1950's, the Ringelmann concept was expanded to other colors of smoke by the introduction of the concept of "equivalent opacity."

The Federal government has discontinued the use of Ringelmann numbers in EPA Method 9 procedures for New Source Performance Standards (NSPS). Current procedures are based solely on opacity Although some State regulations still specify the use of the Ringelmann Chart to evaluate black and gray plumes, the general trend is toward reading all emissions in percent opacity

In practice, the evaluation of opacity by the human eye is a complex phenomenon and is not completely understood However, it is well documented that visible emissions can be assessed accurately and with good reproducibility by properly trained/certified observers

The relationships between light transmittance, plume opacity, Ringlemann number, and optical density are presented in Table 1 1 A literal definition of plume opacity is the degree to which the transmission of light is reduced or the degree to which visibility of a background as viewed through the diameter of a plume is reduced. In terms of physical optics, opacity is dependent upon transmittance (I/I_o) through the plume, where I_o is the incident light flux and I is the light flux leaving the plume along the same light path. Percent opacity is defined as follows:

$$\text{Percent opacity} = (1-I/I_o) \times 100.$$

Many factors influence plume opacity readings: particle density, particle refractive index, particle size distribution, particle color, plume background, path length, distance and relative elevation to stack exit, sun angle, and lighting conditions. Particle size is particularly significant; particles decrease light transmission by both scattering and direct absorption. Thus, particles with diameters approximately equal to the wavelength of visible light (0.4 to 0.7 μm) have the greatest scattering effect and cause the highest opacity.

1.2 Training of Observer

Field inspectors and observers are required to maintain their opacity evaluation skills by periodically participating in a rigorous VE certification program. Accordingly, EPA's Stationary Source Compliance Division (SSCD) and Environmental Monitoring Systems Laboratory (EMSL) have provided the QA training document[1] to individuals who conduct VE training and certification programs. This section summarizes the training program

1.2.1 Frequency of Training Sessions — Certification schools should be scheduled at least twice per year since Method 9 requires a semiannual recertification. It is highly recommended that training be an integral part of the certification program. A spring/fall schedule is preferable because of weather considerations. Certifying previous graduates while the smoke school is in session is more efficient and less costly than scheduling a separate session.

1.2.2 Classroom Training — The training is accomplished most effectively by holding an intensive 1- or 2-day classroom lecture/discussion session Although this training is not required, it is highly recommended for the following reasons:

1 Increases the VE observer's knowledge and confidence for the day-to-day field practice and application
2. Reduces training time required to achieve certification.
3. Trains the smoke reader in the proper recording and presentation of data that will withstand the rigors of litigation and strengthens an agency's compliance and enforcement program.
4. Provides a forum for the periodic exchange of technical ideas and information

Some states require classroom training for initial certification only. It is recommended, however, that observers attend the classroom training at 3-year intervals to review proper field observation techniques and method changes and to participate in the exchange of ideas and new information.

1.2.3 Lecture Material — Example lecture material for a thorough training program is presented in Section 3 1 and Appendix A of Reference 1 A typical six-lecture classroom training program consists of the following:

Lecture 1—Background, principles, and theory of opacity.
Lecture 2—Sources of VE's, presented by someone thoroughly familiar with source conditions, related particle characteristics, and opacity reading procedures and problems
Lecture 3—Proper procedures for conducting field observations under a variety of conditions

Table 1.1. Comparison of Light, Extinction Terms

Light transmission, %	Optical density units	Plume opacity, %	Ringelmann number
0	N/A[a]	100	5
20	0.70	80	4
40	0 40	60	3
60	0.22	40	2
80	0.10	20	1
100	0 00	0	0

[a]N/A = not applicable.

Lecture 4—Influence and impact of meteorology on plume behavior
Lecture 5—Legal aspects of VE and opacity measurements
Lecture 6—Actual observation/testing procedures

1.2.4 Training Equipment — An integral part of the training program is the design and operation of the smoke generator and its associated transmissometer, as specified in Method 9 (reproduced in Section 3 12 8) Such a program is essential because proper observer certification cannot take place without the proper equipment Section 4 of Reference 1 presents performance specifications and operating procedures for smoke generators which, if followed under a good QA program, will ensure nationwide uniformity and consistency with Method 9 criteria

The design and operation of the smoke generator has evolved significantly since the mid-1960's The basic components of the smoke generator now include:

1. Black and white smoke generating units,
2. Fan and stack,
3. Transmissometer system, and
4. Control panel and strip chart recorder

Table 1 2 lists the design and performance specifications for the smoke generator It must generate smoke with an opacity range of 0 to 100 percent and be sufficiently accurate to allow the operator to control and stabilize the opacity of the smoke It is recommended that the generator also achieve and hold opacities in 5 percent increments at ±2 percent for a minimum of 5 s

White smoke is produced by dispensing, at regulated rates, No 2 fuel oil into the propane-heated vaporization chamber The opacity varies in proportion to the volume of fuel oil vaporized and is regulated by adjusting the flow of fuel oil

Black smoke is produced by the incomplete combustion of toluene in the double-wall combustion chamber The toluene flowrate is also controlled by valves and flowmeters

1.2.5 Equipment Calibration Procedures — Detailed calibration procedures are included in a QA procedures manual for VE training programs [1] The generator transmissometers must be calibrated every six months or after each repair The National Bureau of Standards (NBS) traceable standards (optical filters) for linearity response are available from Quality Assurance Division, Environmental Monitoring Systems Laboratory, U S EPA, Research Triangle Park, North Carolina 27711 It is strongly recommended that the calibration be performed before and after each certification course to ascertain whether any significant drift or deviation has occurred during the training period The "zero and span" check must be repeated before and after each test run. If the drift exceeds 1 percent opacity after a typical 30-min test run, the instrument must be corrected to 0 and 100 percent of scale before resuming the testing

All of the smoke generator performance verification procedures (e g., repair and maintenance work, spectral response checks, calibration check, and response time checks) should be documented in writing and dated, a bound logbook is highly recommended These records become part of the permanent files on the VE training program

1.2.6 Setup, Operating, and Shutdown Procedures — Detailed procedures and a parts list are given in Section 4 4 of Reference 1.

1.2.7 Storage and Maintenance of the Smoke Generator — Proper storage and maintenance procedures are essential for smoke generators to increase their useful operating life and to provide reliability

1.2.8 Common Problems, Hazards, and Corrective Actions — The generator has hot surfaces that can cause serious burns It is recommended that attendees be advised to stay away from the generator during training and test runs It is also recommended that gas and fuel lines be correctly checked for leaks prior to each use of the generator to prevent fire and explosive hazards to the operator and nearby attendees

Occasional breakdowns or malfunctions of the generator usually occur at the most inopportune times The problem must be diagnosed and repairs made expeditiously to provide the proper training and maintain the interest of the course attendees Some common malfunctions are listed in Section 4 of the QA training manual.[1]

1.3 Certification of Observer

This section summarizes the certification part of the training program. The first part of the certification program is to acclimate the smoke readers The following procedure is recommended. Both black and white plumes are produced at certain levels, and during this production, the opacity values are announced. After some standards exposure, four plumes are presented to the trainee for evaluation. The correct values of the four plumes are announced to provide the trainee with immediate feedback The majority of the trainees should be ready to take the test after a few sets. Certification runs are made in blocks of 50 readings (25 black smoke and 25 white smoke) The trainees who successfully meet the criteria receive a letter of certification and a copy of their qualification form. The school retains the original of the qualification form for a minimum of three years, to be available for any legal proceedings that might occur According to Method 9, certification is valid for a period of *only six months* Neither certification or recertification procedures require the observer to attend the lecture program; however, it is recommended that the observer attend the series during initial certification and thereafter every three years It is also recommended that all persons unable to pass after 10 qualification runs, be provided additional training before allowing qualification runs to be made

Test forms vary greatly because of the specific needs and experiences of each agency. Figure 1.1 illustrates one suggested form The form should be printed on two-copy paper, the original for the official file and the carbon copy for the trainee to grade after each certification run. The test

Table 1.2. *Smoke Generator Design and Performance Specifications*

Parameter	*Performance*
Light source	*Incandescent lamp operated at ±5% of nominal rated voltage*
Photocell spectral response	*Photopic (daylight spectral response of the human eye)*
Angle of view	*15° maximum total angle*
Angle of projection	*15° maximum total angle*
Calibration error	*±3% opacity, maximum*
Zero and span drift	*±1% opacity, 30 min*
Response time	*5 s, maximum*

Affiliation STATE OF VIRGINIA Name TOM ROSE Run Number 1-B

Course location RICHMOND Sunglasses NO

Date 4-15-82 Sky CLEAR Wind 3-5 MPH

Distance and direction to stack 150 FT. NNE

Reading number	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	Error
1	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
2	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
3	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
4	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
5	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
6	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
7	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
8	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
9	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
10	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
11	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
12	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
13	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
14	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
15	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
16	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
17	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
18	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
19	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
20	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
21	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
22	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
23	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
24	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
25	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____

Deviation _____

Reading number	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	Error
1	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
2	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
3	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
4	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
5	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
6	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
7	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
8	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
9	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
10	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
11	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
12	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
13	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
14	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
15	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
16	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
17	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
18	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
19	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
20	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
21	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
22	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
23	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
24	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
25	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____

Deviation _____

Figure 1.1. Sample certification test form

form must be filled in completely. Certification requires that *both* of the following criteria be satisfied:

1 No reading may be in error by more than 15 percent opacity.
2. The average [absolute] error must not exceed 7.5 percent for either set of 25 white or 25 black smoke readings. The certification runs may be repeated as often as necessary. However, it is recommended that all persons who have not passed after ten certification runs be given additional training prior to conducting additional certification runs.

The detailed testing and grading procedures required to ensure a valid test are outlined in Section 5 of the QA training manual.[1] The Agency should maintain a bound logbook, arranged by training session, for at least three years, as evidence that the observer has been certified as a qualified VE evaluator by a recognized smoke training and certification group. Each trainee who successfully meets the Method 9 criteria receives a letter of certification and a copy of his/her qualification form This letter includes the date of expiration

1.4 Recertification

Method 9 requires an individual to be recertified every six months.

1.5 In-the-Field Training

After the observer's initial certification, it is recommended that a senior observer accompany the new observer on a field observation trip and that both individuals simultaneously record (using the same time piece) their opacity readings as a QA check (see Section 3 12.7). A comparison of these readings will indicate any problems the new observer might have in conducting observations under field conditions A significant discrepancy between the readings of the two observers, in individual or average values, indicates the need for further in-field training and continuance of the senior observer (not necessarily the same one) QA check After satisfactory checks have been made on two consecutive field observations, the new observer can confidently conduct inspections without a senior observer. The suggested standard for a satisfactory check for 6-min (minimum) of consecutive readings is:

1. No difference in individual readings should exceed 20 percent
2. The difference of the average value between observers should not exceed 10 percent.

1.6 Smoke School Certification Quality Assurance Program

It is recommended that any government agency planning to develop a smoke school certification program obtain a copy of the "Recommended Quality Assurance Techniques and Procedures for Visible Emission Training Programs "[1] Table 1 3 contains an activity matrix for certification and training of observers.

Table 1.3. *Activity Matrix for Certification and Training of Observers*

Activity	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Classroom training of observer	*Classroom training per Ref. 1 (suggested)*	*Initially and every 3 years*	*Review training procedures per Ref. 1*
Smoke generator	*Should be able to generate smoke with an opacity range of 0 to 100%; hold opacities ±2% for at least 5 s*	*Before each certification test run; use method in Ref 1*	*Adjust and make repeat check of operation*
Setup, operating, and shutdown procedures	*Adherence to procedures in Ref. 1*	*Each test run*	*Review procedures*
Storage and maintenance	*As above*	*As above*	*As above*
Transmissometer			
Design and performance specifications	*Specifications in Table 1.2*	*Upon receipt, repair, and at 6-mo intervals use method in Ref 1*	*Adjust and repeat specification check until specifications are met*
Calibration	*±3% opacity maximum*	*Every 6 mo or after repair, before and after each certification course is recommended; use method in Ref 1*	*Adjust and recalibrate until acceptance limits are met*
Zero and span	*Opacity drift <1% after a typical 30-min test run*	*As above*	*Instruments must be corrected to 0 and 100% before testing is resumed*
Certification of observer	*No reading must be in error by more than 15% **and** average absolute error must not exceed 7 5% for either white or black smoke readings*	*Take smoke reading test until a successful test has been completed*	*Retake test until successful completion*
Recertification	*As above*	*Every 6 mo take a smoke reading test until a successful test has been completed*	*As above*
In-the-field training	*No reading in error by more than 20% difference **and** average absolute error should not exceed 10% difference during the field observation*	*Checks are made on the first two field observations subsequent to the initial certification; comparison is made between new certified observer and an experienced observer*	*Continue comparisons until acceptance limits are met during two field observations*

2.0 Procurement of Apparatus and Supplies

Method 9 does not specifically require any equipment or supplies Therefore, this entire section includes quality assurance procedures that are recommended to assist the observer in documenting data Nevertheless, this section provides specifications criteria or design features, as applicable, to aid in the selection of equipment that may be useful in collecting VE data Procedures and limits for acceptance checks are also provided During the procurement of equipment and supplies, it is suggested that a procurement log (Figure 2 1) be used to record the descriptive title of the equipment, the identification number (if applicable), and results of any acceptance checks Table 2 1 at the end of this section contains a summary of the quality assurance activities for procurement and acceptance of apparatus and supplies

2.1 Stopwatch

A watch is used to time the 15-second intervals between opacity readings The watch should provide a continuous display of time to the nearest second

2.2 Compass

A compass is useful for determining the direction of the emission point from the spot where the VE observer stands and for determining the wind direction at the source For accurate readings, the compass should be magnetic with resolution better than 10° It is suggested that the compass be jewel-mounted and liquid-filled to dampen the needle swing; map reading compasses are excellent for this purpose

2.3 Range Finder

A range finder is used to measure the observer's distance from the emission point and should be capable of determining distances to 1000 meters with an accuracy of ±10 percent The accuracy of the range finder should be checked upon receipt and periodically thereafter with targets at known distances of approximately 500 meters and 1000 meters

Item description	*Quantity*	*Purchase order number*	*Vendor*	*Date*		*Cost*	*Disposition*	*Comments*
				Ordered	*Received*			
Stopwatch	2	Z 5096	Fisher Scientific	5/1/82	5/14/82	$52.94	checked-ready to use.	

Figure 2.1. *Example of a procurement log*

2.4 Abney Level or Clineometer

An Abney level is a device for determining the vertical viewing angle For visible emission observation purposes, it should measure within 5 degrees. The accuracy should be tested by placing the level flat on a table that has been previously leveled with a referring level and checking it at a 45° angle by placing it on a 45° inclined plane constructed with the plane as the hypotenuse of a right triangle with equal base and height

2.5 Sling Psychrometer

The sling psychrometer is used in cases where it is suspected that the atmospheric conditions will promote the formation of a steam plume (see Subsection 6 3) The psychrometer should consist of two thermometers, accurate to 1/2°C, mounted on a sturdy assembly whereby the thermometers may be swung rapidly in the air. One thermometer should be fitted with a wettable cotton wick tube on the bulb Thermometer accuracy should be checked by placing the bulbs in a fresh ice water bath at 0°C

2.6 Binoculars

It is recommended that the observer obtain binoculars preferably with a magnification of at least 8 x 50 or 10 x 50 The binoculars should have color-corrected coated lenses and a rectilinear field of view. Color correction can be checked by viewing a black and white pattern such as a Ringelmann card at a distance greater than 50 ft, no color rings or bands should be evident, only black and white The rectilinear field of view can be tested by viewing a brick wall at a distance greater than 50 ft There should be no distortion of the brick pattern as the field of view is changed. The binoculars are helpful for identifying stacks, searching the area for emissions and aid in characterizing behavior and composition of plume

2.7 Camera and Accessories

A camera is often used in VE observations to document the emissions before and after the actual opacity determination A 35-mm camera with through-the-lens light metering is recommended for this purpose Useful accessories include a "macro" lens or a 250-mm to 350-mm telephoto lens, and a 6-diopter closeup lens (for photographing logbook and evidence of particulate deposition) A photo logbook is necessary for proper documentation, and the observer should always be sure to purchase enough fresh color negative film (ASA 100 recommended) for his/her purposes

2.8 Clipboard and Accessories

For documenting the visible emission observation, the observer should have a 10 in x 12 in masonite or metal clipboard, several black ball-point pens (medium point), a large rubber band, and a sufficient number of visible emission observation forms

2.9 Safety Equipment

The following safety equipment, which should be approved by the Occupational Safety and Health Association (OSHA), is recommended for the VE observer:

- Hard hat in high-visibility yellow or orange
- Safety glasses, goggles, or eye shields
- Ear protectors
- Safety shoes (steel-toed for general industrial use)

Specially insulated safety shoes are necessary in certain areas, such as the top of coke ovens

Table 2.1. *Activity Matrix for Procurement of Recommended Equipment and Supplies*

Equipment	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Watch	*Continuous display*	*Check upon receipt*	*Return to supplier*
Compass	*Magnetic with 10° resolution*	*Check upon receipt*	*Return to supplier*
Range finder	*Accuracy of ±10% over distances to 1000 m*	*Check upon receipt and quarterly with targets at known distances of about 500 m and 1000 m*	*Adjust or return to supplier*
Abney level	*Accurate within ±5°*	*Check at 0° and 45°*	*Same as above*
Sling psychrometer	*Each thermometer accurate to 1/2°C (1°F)*	*Check thermometer accuracy with ice water bath at 0°C*	*Repair or return to supplier*
Binoculars	*Magnification of 8 x 50 or 10 x 50, color-corrected coated lenses and a rectilinear field of view*	*Check upon receipt by viewing selected objects*	*Return to supplier*
Camera	*35-mm camera with through-the-lens light metering*	*Check quality of photos on receipt and after processing film*	*Return to supplier for repair*
Clipboard/ accessories/forms	*10 in. by 12 in clipboard; black ball-point pens, VE observation forms*	*Check supplies periodically*	*Replenish supplies*
Safety equipment	*Hardhat—yellow or orange, safety glasses and shoes, ear protectors*	*Check supply of safety equipment periodically*	*Maintain equipment availability*

3.0 Preobservation Operations

The following procedures are not required by Method 9 but are recommended in order to provide more consistent data collection and better data documentation and verification of representative plume viewing conditions Not all procedures are needed for every observation

Before making on-site VE determinations, the observer should gather the necessary facility data, provide prior notifications when applicable, establish an observation protocol, and check for availability of supplies and properly maintained equipment. Table 3.1 at the end of this section summarizes the quality assurance activities for preobservation operations

3.1 Gather Facility Information

The observer should be thoroughly familiar with the source facility, operation, emissions, and applicable regulations In preparation for the on-site visit, the observer should review the Agency's information (in the official source file) on the source in question. The observer should:

1. Determine the pertinent people to be contacted
2. Become familiar with the processes and operations at the facility and identify those facilities to be observed.
3. Review the permit conditions, requirements, and recent applications
4. Determine applicable emission regulations
5. Identify all operating air pollution control equipment, emission points, and types and quantities of emissions
6. Review history of previous inspections, source test results, and complaints
7. Check the file to become familiar with (or review) plant layout and possible observation sites
8. Determine normal production and operation rates.
9. Identify unique problems and conditions that may be encountered (e.g., steam plume)
10. Discuss with attorney if case development is expected
11. Obtain a copy of the facility map with labeled emission points, profile drawings, and photographs, if available. A facility map is very helpful during inspection and should be a required item for every Agency source file The map makes it easier for the observer to identify point sources and activities, and it may be used to mark any emission points that have been added or modified.
12. If an operating permit exists, obtain a copy because it may contain the VE limits for each point source and any special operating requirements.
13. Determine the status of the source with respect to any variance or exemption from the Agency's rules and regulations Observation may not be required if the source has a variance or is exempt from the regulations.
14. Review plant terminology
15. Use references such as facility maps and previous inspection reports to determine if the viewing position is restricted because of buildings or natural barriers If the viewing position requires observations to be taken at a particular time of day (morning or evening) because of sun angle, consider this when planning the inspection.
16. Determine the possibility of water vapor in the plume condensing (see Section 3.12.6). This determination may prevent a wasted trip to the facility on days when a persistent water droplet plume is anticipated because of adverse ambient conditions.

Note. If the observer is not familiar with the type of facility or operation, he/she should consult available reference material and inspection manuals on the source category

3.2 Prior Notification

The usual procedure is to make the VE determination without prior notification unless the plant must be entered first to obtain a good view of the emission point of interest However, this procedure is not always possible, especially in remote locations, when operations are intermittent, or when specific personnel must be present or contacted Determining VE for compliance with State Implementation Plan (SIP) or NSPS opacity regulations requires on-site observations during conditions of typical or normal maximum operations If the facility is notified of the time of this evaluation, some operating conditions may be altered. If this situation appears likely, it is EPA's policy not to give prior notification EPA is obligated to notify State/local agencies of inspections and generally prefers to invite the applicable agency to participate. The observer should notify the affected facility and control agencies as soon as practical following any official opacity readings.

3.3 Establish Observation Protocol

Based on information collected under Section 3.1 and any prior experience with the source, an observation protocol should be established. First, the observer should determine whether one, two, or more observers will be required. For example, two observers may be required to simultaneously make the VE determination and gather other on-site data (e.g , take photographs, draw a new modified facility map if one is not available from the plant or gather other needed plant information). In certain situations where the VE observations must be correlated to process operation, the second person will closely monitor the process activity and record the exact time of the operating modes of interest Only one observer will make the VE determination unless an observer audit is being conducted. In this case, the designated observer is the one being audited.

The applicability of Method 9 (and hence the method of observation) should be determined. If Method 9 is not applicable, see Section 3 12 4, Special Problems.

A written checklist regarding an expected walk-through of the plant including questions to ask plant officials may be helpful

3.4 Perform Equipment Checks for On-Site Use

Be sure that the necessary equipment and supplies are available for making the VE determination and documenting the results All equipment should be visually checked for damage and satisfactory operation before each VE determination field trip.

Table 3.1. Activity Matrix for Preobservation Operations

Activity	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Gather facility information	*Obtain necessary facility data, Subsec 3 1*	*Check for completeness of data*	*Obtain missing data before on-site visit, if possible*
Make prior notification	*Make VE determination without prior notification except as stated in Subsec 3 2; EPA should notify State/local agencies and invite participation*	*Check the protocol for notification before each on-site visit and revise the protocol as necessary*	*Make required notifications*
Establish protocol	*Prepare observation protocol, Subsec 3.3*	*Check before on-site visit*	*Complete or prepare protocol as required*
Perform equipment check	*All equipment/supplies available and in satisfactory working order*	*Same as above*	*Replace or adjust equipment*

4.0 On-Site Field Observations

This section describes field observation procedures, including perimeter survey, plant entry, VE determination, and special observation problems. The latter subsection supplements the subsection on VE determination by providing some information on how to take VE readings when unfavorable field conditions prevent the use of the procedure described in Subsection 4 3 (e.g., when the emissions are intermittent or the observer position is restricted) The QA activities are summarized in Table 4.2 at the end of this section.

4.1 Perimeter Survey

Before and after the VE determination, it is strongly recommended that the observer make a perimeter survey of the area surrounding (1) the point of observation and (2) the emission point on which the determination is being made Such a survey also may be made during the VE determination, if warranted

A perimeter survey can be useful in determining the presence of other factors that could affect the opacity readings. For example, the representativeness of the VE readings for a given emission point could be questioned unless data is available to show that the observer excluded emissions related to material stockpiling, open burning, and ambient condensed water vapor in adjoining areas of the plant It is vital that the observer be as aware as much as possible of extenuating conditions. The perimeter survey is made to document these conditions. Common sense should be used in determining the need and extent of the survey; in some cases (e.g , a single 350-foot stack) a perimeter survey is not vital.

Perimeter surveys can be made from either outside or inside the plant property, or both This decision would depend on whether the VE observations are made from inside or outside of the plant, whether the observer actually gains entry to the plant premises, and whether the plant is sufficiently visible from outside the premises to make a reasonable survey. It is suggested that during the survey the observer should note such factors as:

1 Other stacks and emission points whose visible emissions might interfere with opacity readings
2 Fugitive emissions that result from product or waste storage piles and material handling and may interfere with observations
3. Fugitive emissions that result from unpaved road travel and may interfere with observations
4. Water vapor emissions from sludge or cooling ponds
5. Open burning
6. Any unusual activities on or around plant premises that could result in nonrepresentative emissions or interfere with opacity readings.

If deemed useful by the observer, photographs may be taken to document extenuating conditions (see discussion of confidentiality and the use of cameras in Subsection 4 2.7)

4.2 Plant Entry

The following discussion presents the recommended plant entry procedures. The VE readings themselves should not be affected by a change in these procedures. However, the usefulness of the readings in showing a possible violation of the applicable standards may be compromised by not following agency procedures for entering plants Depending on the location of emission points at the plant and the availability of observation points in the area surrounding a facility, the VE observer may not have to gain entry to the plant premises *prior* to making VE observations. It may be preferable to gain access after taking readings to check on plant process control equipment operating conditions or to complete a perimeter survey. Figure 4 1 is an example entry checklist that can be used to assist the observer in organizing the information that could be used at the time of plant entry

To maintain a good working relationship with plant officials and, most importantly, to comply with the Clean Air Act and avoid any legal conflict with trespass laws or the company's right to privacy and due process of law under the U.S Constitution, the observer must follow certain procedures in gaining entry to the plant's private premises. In most cases, consent to enter (or the absence of express denial to enter) is granted by the owner or company official Figure 4 1 lists the pertinent section of the Clean Air Act on facility entry as well as information on confidentiality of process information It is recommended that the inspector have a copy of this information available in case questions are raised by source representatives

4.2.1 Entry Point — It is recommended that the plant premises be entered through the main gate or through the entrance designated by the company officials in response to prior notification. The observer's arrival will usually occur during normal working hours unless conditions contributing to excess opacity levels are noted at certain times other than normal working hours. If only a guard is present at the entrance, it is desirable for the observer to present the appropriate credentials and to suggest that the guard's supervisor be contacted for the name of a responsible company official The observer would then ask to speak with this official, who may be the owner, operator, or agent in charge (including the environmental engineer)

4.2.2 Credentials — After courteously introducing himself/herself to the company official, the observer should briefly describe the purpose of the visit and present the appropriate credentials confirming that he/she is a lawful representative of the agency Such credentials will naturally differ depending upon the agency represented, but it is recommended that they include at least the observer's photograph, signature, physical description (age, height, weight, color of hair and eyes), and the authority for plant entry Agencies issue credentials in several forms, including letters, badges, ID cards, or folding wallets

4.2.3 Purpose of Visit — When first meeting with a company official, the observer needs to be prepared to state succinctly the purpose of the visit, including the reason for the VE determination Space is provided in the recommended form (Figure 4 1) to specify the exact purpose of the visit, and the observer can refer to this when talking with the company official

Source name and address DRI-HARD PORTLAND CEMENT 2 MILES E. OF RT. 1 ON STATE RD. 1836 ROCKY HILLS, NJ 08916	*Observer* JUDY A. SMITH *Agency* U.S. EPA REGION II *Date of VE observation* 5/5/82

Previous company contact (if applicable) GEORGE C. MEARS

Title OWNER

Purpose of visit EPA AUDIT INSPECTION AND VE OBSERVATION; REGIONAL OFFICE INSPECTS 10% OF MAJOR SOURCES IN NJ EVERY YEAR.

Emission points at which VE observations to be conducted
01 GRINDER 3-05-007-02 03 COAL-FIRED KILN 3-05-007-05
02 DRYERS #1 AND #2 3-05-007-02

Authority for entry (see reverse side)

Plant safety requirements

- ☒ Hardhat
- ☒ Safety glasses
- ☒ Side shields (on glasses)
- ☐ Goggles
- ☐ Hearing protection EARMUFFS IN MARKED AREAS; PROVIDED BY PLANT
  Specify _____
- ☒ Safety shoes (steel-toed)
- ☐ Insulated shoes
- ☐ Gloves
- ☐ Coveralls
- ☒ Dust mask suggested
- ☐ Respirator(s)
  Specify _____
- ☐ Other
  Specify _____

Company official contacted (on this visit) STANLEY O. GRAY

Title ENVIRONMENTAL ENGINEER

Figure 4.1. *Visible emission observer's plant entry checklist.*

Authority for Plant Entry: Clean Air Act, Section 114

(a)(2) the Administrator or his authorized representative upon presentation of his credentials -

(A) shall have a right of entry to, upon or through any premises of such person or in which any records required to be maintained under paragraph (1) of this section are located, and

(B) may at reasonable times have access to, and copy of any records, inspect any monitoring equipment or methods required under paragraph (1), and sample any emissions which such person is required to sample under paragraph (1)

(b) (1) Each State may develop and submit to the Administrator a procedure for carrying out this section in such State If the Administrator finds the State procedure is adequate, he may delegate to such State any authority he has to carry out this section.

(2) Nothing in this subsection shall prohibit the Administrator from carrying out this section in a State

(c) Any records, reports or information obtained under subsection (a) shall be available to the public except that upon a showing satisfactory to the Administrator by any person that records, reports, or information, or particular part thereof, (other than emission data) to which the Administrator has access under this section if made public would divulge methods or processes entitled to protection as trade secrets of such person, the Administrator shall consider such record, report, or information or particular portion thereof confidential in accordance with the purposes of Section 1905 of Title 18 of the United States concerned with carrying out this Act or when relevant in any proceeding under this Act."

Confidential Information: Clean Air Act, Section 114 (see above) 41 ***Federal Register*** *36902, September 1, 1976*

If you believe that any of the information required to be submitted pursuant to this request is entitled to be treated as confidential, you may assert a claim of business confidentiality, covering all or any part of the information, by placing on (or attaching to) the information a cover sheet, stamped or typed legend, or other suitable notice, employing language such as "trade secret," "proprietary," or "company confidential." Allegedly confidential portions of otherwise nonconfidential information should be clearly identified. If you desire confidential treatment only until the occurrence of a certain event, the notice should so state Information so covered by a claim will be disclosed by EPA only to the extent, and through the procedures, set forth at 40 CFR, Part 2, Subpart B (41 ***Federal Register*** *36902, September 1, 1976)*

If no confidentiality claim accompanies this information when it is received by EPA, it may be made available to the public by EPA without further notice to you

Figure 4.1. *Reverse side of form. (Continued)*

The principal purpose for an observer's visit to a plant will probably fall into one of three categories (1) a VE determination is being made pursuant to a neutral administrative scheme* to verify compliance with an applicable SIP or NSPS, (2) a VE determination is being made because some evidence of an opacity violation already exists, or (3) an unscheduled VE determination has just been made from an area off the plant property The statement of purpose should state clearly what has prompted the visit

At this time, the observer also should provide the company official with a copy of the opacity readings and ask that person to sign an acknowledgment of receipt of any VE readings made previous to entry In lieu of the above, the agency should provide a copy within a reasonable time

4.2.4 *Visitor's Agreements, Release of Liability (Waivers)* — The observer should not sign a visitor's agreement, release of liability (waiver), hold-harmless agreement, or any other agreement that purports to release the company from tort liability. Signing this type of release form may waive the rights of the observer and his/her employer compensation in event of personal injury or damages; the precise effect of signing an advance release of liability for negligence depends upon the laws of the state in which it is signed. If the plant official denies entry for refusal to sign a release form, the observer should proceed as described in the section on entry refusal

4.2.5 *Section 114* — Section 114 of the Clean Air Act addresses both the authority for plant entry and the protection of trade secrets and confidential information For the observer's reference, the applicable paragraphs are included on the reverse side of the entry checklist in Figure 4 1

4.2.6 *Entry Refusal* — In the event that an observer is refused entry by a plant official or that consent is withdrawn before the agreed-upon activities have been completed, the following procedural steps should be followed

1 *Tactfully* discuss the reason(s) for denial with the plant official; this is to insure that the denial has not been based on some sort of misunderstanding. Discussion might lead to resolution of the problem and the observer may be given consent to enter the premises. If resolution is beyond his/her authority, the observer should withdraw from the premises and contact his/her supervisor to decide on a subsequent course of action
2 Note the facility name and exact address, the name and title of the plant officials approached, the authority of the person issuing the denial, the date and time of denial, the reason for denial, the appearance of the facility, and any reasonable suspicions as to why entry was refused
3 The observer should be very careful to avoid any situations that might be construed as threatening or inflammatory Under no circumstances should the potential penalties of entry denial be cited.

All evidence obtained prior to the withdrawal of consent is considered admissible in court.

*Any routine of selecting sites for observation that is not directed toward any company

When denied access only to certain parts of the plant, the observer should make note of the area(s) and the official's reason for denial After completing normal activities to the extent possible and leaving the facility, the observer should contact his/her supervisor for further instructions

4.2.7 Confidentiality of Data — In conducting the VE investigation, the observer may occasionally obtain proprietary or confidential business data It is essential that this information be handled properly

The subject of confidential business information known as "a trade secret" is addressed in Section 114 of the Clean Air Act (see Subsection 4 2 5) and in the Code of Federal Regulations (40 CFR 2, 41 *Federal Register* 36902, September 1, 1976, as amended). The Code of Federal Regulations (40 CFR 2, Subpart B, 2.203) embodies a notice to be included in EPA information requests This notice is paraphrased on the reverse side of the entry checklist (Figure 4.1) for the observer's and plant official's reference The Code of Federal Regulations (40 CFR 2, Subpart B, 2 211) also includes the penalties for wrongful disclosure of confidential information by Federal employees, in addition to the penalties set forth in the United States Code, Title 18, Section 1905 Employees of other agencies should check with agency attorneys to determine their exact personal liability

From the observer's standpoint, confidential information may be defined as information received under a request of confidentiality which may concern or relate to trade secrets A trade secret is interpreted as an unpatented secret, commercially valuable plan, appliance, formula, or process used in production This information can be in written form, in photographs, or in the observer's memory *Emissions data* are not considered confidential information Also the Agency reserves the right to determine if information submitted to it under an official request should be treated as confidential

A good rule of thumb for the observer to follow is to collect only that process and operational information and to take only those photographs that are pertinent to the purpose of the plant visit. The plant official should be advised that he must *request* confidential treatment of specific information provided (see paragraph on claims of confidentiality on reverse side of entry checklist) before it will be treated as confidential pending legal determination The plant official should inform the observer of any sensitive areas of the facility or processes where proprietary or trade secret information is indicated

Photographs are often used to document visible emissions observations (see Subsection 4 3 4) Before taking photographs from inside the plant premises, the observer must have the consent of the plant official Most of an observer's photographs will be of emission points only; presumably, these should not include confidential areas of the plant If any opposition is encountered regarding the use of a camera on the plant premises, the observer should explain that the plant official should request confidential treatment of any photographs taken The observer must properly document each photograph and handle those for which confidential treatment has been requested in the same manner as other confidential data Photographic documentation of VE observations from an area of public access outside of the plant premises does not require approval from a plant official, provided the documentation is accomplished without the use of highly sophisticated equipment or techniques For example, use of a high-power telephoto lens (over 100 mm on a 35 mm camera) that yields extensive details (e g , construction layout) might be construed as surreptitiously taking confidential business information Thus, a good rule of thumb is to be sure that any pictures taken show only the details that could be seen with the naked eye from an area accessible to the public

When preparing to leave the plant, the observer should allow the plant official to examine the data collected and make claims of confidentiality All potentially confidential information should be so marked, and while on the road, the observer should keep it in a locked briefcase or file container It should be noted that emission data are not considered confidential

When the observer returns to the agency office, the potentially confidential information should be placed in a secure, lockable file cabinet designated especially for that purpose The observer's agency should have an established secure filing system and procedures for safeguarding confidential documents In all cases, the observer should make no disclosure of potentially confidential information until a company has had full opportunity to declare its intentions regarding the information and the Agency has ruled that the information is not legally confidential

4.2.8 Determination of Safety Requirements — The violation of a safety rule does not invalidate VE readings, however, the observer should always anticipate safety requirements by arriving at the plant with a hardhat, steel-toed safety shoes, safety glasses with side shields, and ear protectors Safety equipment also should include any other equipment that is specified in the agency files and noted on the entry checklist form.

Some companies require unusual safety equipment, such as specific respirators for a particular kind of toxic gas In many cases, these companies will provide the observer with the necessary equipment. In any event, the observer must be aware of and adhere to *all* safety requirements before entering the plant. Information on plant alarms and availability of first aid and medical help may be needed.

4.2.9 Observer Behavior — Observers must perform their duties in a professional, businesslike, and responsible manner They should always consider the public relations liaison part of their role by seeking to develop or improve a good working relationship with plant officials through use of diplomacy, tact, and if necessary, gentle persuasion in all dealings with plant personnel.

Specifically, observers should *be objective and impartial* in conducting observations and interviews with plant officials All information acquired during a plant visit is intended for official use only and should never be used for private gain. Observers must be careful never to speak of any person, agency, or facility in any manner that could be construed as derogatory Lastly, observers should use discretion when asked to give a professional opinion on specific products or projects and should *never* make judgments or draw conclusions concerning a company's compliance with applicable regulations Upon giving the data to the plant the observer can tell the source these are the data that were obtained and no judgment as to compliance can be made until all the data and the regulations are closely reviewed

4.3 Visible Emission Determination

This subsection describes the preferred approach to VE determination Because practical considerations do not always permit the observer to follow this procedure, however, special observation problems are discussed in Subsection 4.4.

4.3.1 Opacity Readings — The observer must be certified in accordance with Section 3 12 1, Subsection 1.3, and should use the following procedure for visually determining the opacity of emissions

Observer Position

1. The observer must stand at a distance that provides a clear view of the emissions with the sun oriented in the 140° sector to his/her back If the observer faces the emission/viewing point and places the point of a pencil on the sun location line such that the shadow crosses the observers position, the sun location (pencil) must be within the 140° sector of the line During overcast weather conditions, the position of the sun is less important
2. Consistent with number 1 above, when possible, the observer should, make observations from a position in which the line of vision is approximately perpendicular to the plume direction, when observing opacity of emissions from rectangular outlets (e g , roof monitors, open baghouses, and noncircular stacks), the observer's position should be approximately perpendicular to the longer axis of the outlet
3. When multiple stacks are involved, the observer's line of sight should not include more than one plume at a time, and in any case, during observations, the observer's line of sight should be perpendicular to the longer axis of a set of multiple stacks (e g , stub stacks on baghouses)
4. The observer must stand at a distance that provides total perspective and a good view
5. In order to comply with the sun angle requirements (see item 1) it is recommended that the observer should try to avoid the noon hours (11 00 a.m to 1 00 p.m.) in the summertime (when the sun is almost overhead) This is more critical in the southern continental United States The preferred reading distance is between 3 stack heights and 1/4 mile from the base of the stack.
6. The reading location should be safe for the observer

Opacity Observations

1. Opacity observations must be made at the point of greatest opacity in that portion of the plume where condensed water vapor is not present
2. The observer must not look continuously at the plume (this causes eye fatigue), but should observe the plume momentarily at 15-s intervals A 15-s beeper is recommended to aid in performing the VE readings
3. When steam plumes are attached, i e , when condensed water vapor is present within the plume as it emerges from the emission outlet, the opacity must be evaluated beyond the point in the plume at which condensed water vapor is no longer visible The observer must record the approximate distance from the emission outlet to the point in the plume at which the observations are made
4. When steam plumes are detached, i e . when water vapor in the plume condenses and becomes visible at a distinct distance from the emission outlet, the opacity of emissions should be evaluated near the outlet, prior to the condensation of water vapor and the formation of the steam plume, unless the opacity is higher after dissipation
5. Readings must be made to the nearest 5 percent opacity A minimum of 24 observations must be recorded. It is advisable to read the plume for a reasonable period in excess of the time stipulated in the regulations (i e , at least 10 readings more than the minimum required)
6. A clearly visible background of contrasting color is best for greatest reading accuracy However, the probability of positive error (higher values) is greater under these conditions Generally, the apparent plume opacity diminishes and tends to assume a negative bias as the background becomes less contrasting
7. It is recommended the observer wear the same corrective lenses that were worn for certification If sunglasses were not worn during certification, the observer should remove them and allow time for the eyes to adjust to the daylight before making VE determinations It is recommended that the observer not wear photo compensating sunglasses
8. The best viewing spot is usually within one stack diameter above the stack exit, where the plume is densest and the plume width is approximately equal to the stack's diameter

4.3 2 Field Data The "Visible Emission Observation Form" -- The 1977 revision of EPA Method 9 specifies the recording of certain information in the field documentation of a visible emission observation The required information includes the name of the plant, the emission location, the type of facility, the observer's name and affiliation, the date, the time, the estimated distance to the emission location, the approximate wind direction, the estimated windspeed, a description of the sky conditions (presence and color of clouds), and the plume background

Experience gained from past enforcement litigation involving opacity readings as primary evidence of emission standards violations has demonstrated a need for additional documentation when making visual determinations of plume opacity The Visible Emission Observation Form presented in Figure 4 2 is recommended This form was developed after reviewing the opacity forms used in EPA Regional Offices and State and local air quality control agencies The form includes not only the data required by Method 9, but also the information necessary for maximum legal acceptability Valid data can be collected on any form, however, the recommended form may enhance observer efficiency and data documentation A detailed description of the use of the recommended form is given in the following paragraphs

The Visible Emission Observation Form can be functionally divided into 11 major sections, as shown in Figure 4 3 Each section documents one or two aspects of the opacity determination The form endeavors to cover all the required and recommended areas of documentation in a typical opacity observation A "comments" section is included for notation of any relevant information that is not listed on the form

VISIBLE EMISSION OBSERVATION FORM

SOURCE NAME: ADMIRAL POWER PLANT	OBSERVATION DATE: 15 JULY 1982
ADDRESS: 112 OCEAN ROAD	START TIME: 1330
CITY: ADMIRAL CITY / STATE: VA / ZIP: 23451	STOP TIME: 1342
PHONE: 804-425-5101	SOURCE ID NUMBER: NEDS 45721
PROCESS EQUIPMENT: OIL FIRED BOILER	OPERATING MODE: BASE LOAD
CONTROL EQUIPMENT: ELECTROSTATIC PRECIPITATOR	OPERATING MODE: RAPPING
DESCRIBE EMISSION POINT: START BRICK STACK 25' DIA. STOP ✓	
HEIGHT ABOVE GROUND LEVEL: START 100' STOP ✓	HEIGHT RELATIVE TO OBSERVER: START 100' STOP ✓
DISTANCE FROM OBSERVER: START 400' STOP ✓	DIRECTION FROM OBSERVER: START NNE STOP ✓
DESCRIBE EMISSIONS: START LOFTING PLUME STOP ✓	
EMISSION COLOR: START GREY/WHITE STOP ✓	PLUME TYPE: CONTINUOUS ☑ FUGITIVE ☐ INTERMITTENT ☐
WATER DROPLETS PRESENT: NO ☑ YES ☐	IF WATER DROPLET PLUME: ATTACHED ☐ DETACHED ☐
POINT IN THE PLUME AT WHICH OPACITY WAS DETERMINED: START 10' ABOVE STACK EXIT STOP ✓	
DESCRIBE BACKGROUND: START SKY STOP w/BROKEN CLOUDS	
BACKGROUND COLOR: START BLUE STOP BLUE/WHITE	SKY CONDITIONS: START CLEAR STOP PARTLY CLOUDY
WIND SPEED: START 15 MPH STOP 20 MPH	WIND DIRECTION: START SW STOP ✓
AMBIENT TEMP: START 85°F STOP ✓	WET BULB TEMP: 54°F / RH, percent: 8.5%

MIN \ SEC	0	15	30	45	MIN \ SEC	0	15	30	45
1	30	35	55	55	31				
2	55	50	40	30	32				
3	35	35	35	35	33				
4	30	35	35	35	34				
5	30	30	30	30	35				
6	35	35	35	35	36				
7	30	30	35	35	37				
8	35	40	60	55	38				
9	60	40	55	60	39				
10	50	45	35	30	40				
11	30	30	30	30	41				
12	30	30	30	30	42				
13					43				
14					44				
15					45				
16					46				
17					47				
18					48				
19					49				
20					50				
21					51				
22					52				
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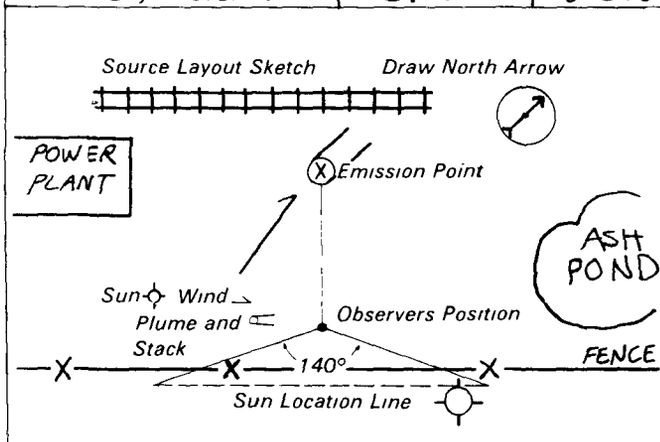
24					54				
25					55				
26					56				
27					57				
28					58				
29					59				
30					60				



AVERAGE OPACITY FOR HIGHEST PERIOD: 40%	NUMBER OF READINGS ABOVE 40 % WERE 11
RANGE OF OPACITY READINGS: MINIMUM 30%	MAXIMUM 60%
OBSERVER'S NAME (PRINT): V.E. PROFFIT	
COMMENTS: USES #6 OIL	OBSERVER'S SIGNATURE: V.E. Proffit / DATE: 15 JULY 1982
	ORGANIZATION: STATE AIR POLLUTION CONTROL BOARD
I HAVE RECEIVED A COPY OF THESE OPACITY OBSERVATIONS SIGNATURE: William P. Jance	CERTIFIED BY: EASTERN TECHNICAL ASSOC. / DATE: 18 MAY 1982
TITLE: SHIFT MANAGER / DATE: 7-15-82	VERIFIED BY: RDA / DATE: 15 AUG 1982

Figure 4.2. Visible emission observation form

VISIBLE EMISSION OBSERVATION FORM

This form is designed to be used in conjunction with EPA Method 9, "Visual Determination of the Opacity of Emissions from Stationary Sources." Any deviations, unusual conditions, circumstances, difficulties, etc., not dealt with elsewhere on the form should be fully noted in the section provided for comments. Following are brief descriptions of the type of information that needs to be entered on the form, for a more detailed discussion of each part of the form, refer to the "User's Guide to the Visible Emission Observation Form"

***Source Name** - full company name, parent company or division information, if necessary.*

***Address** - street (not mailing) address or physical location of facility where VE observation is being made*

***Phone** - self-explanatory*

***Source ID Number** - number from NEDS, CDS, agency file, etc*

***Process Equipment, Operating Mode** - brief description of process equipment (include ID no.) and operating rate, % capacity utilization, and/or mode (e.g., charging, tapping)*

***Control Equipment, Operating Mode** - specify control device type(s) and % utilization, control efficiency*

***Describe Emission Point** - stack or emission point location, geometry, diameter, color, for identification purposes*

***Height Above Ground Level** - stack or emission point height, from files or engineering drawings*

***Height Relative to Observer** - indicate vertical position of observation point relative to stack top*

***Distance From Observer** - distance to stack ±10%, to determine, use rangefinder or map*

***Direction From Observer** - direction to stack, use compass or map, be accurate to eight points of compass*

***Describe Emissions** - include plume behavior and other physical characteristics (e.g., looping, lacy, condensing, fumigating, secondary particle formation, distance plume visible, etc.)*

***Emission Color** - gray, brown, white, red, black, etc*

Plume Type:
Continuous - opacity cycle >6 minutes
Fugitive - no specifically designed outlet
Intermittent - opacity cycle <6 minutes

****Water Droplets Present** - determine by observation or use wet sling psychrometer, water droplet plumes are very white, opaque, and billowy in appearance, and usually dissipate rapidly.*

****If Water Droplet Plume:***
Attached - forms prior to exiting stack
Detached - forms after exiting stack

****Point in the Plume at Which Opacity was Determined** - describe physical location in plume where readings were made (e.g., 4 in above stack exit or 10 ft after dissipation of water plume)*

***Describe Background** - object plume is read against, include atmospheric conditions (e.g., hazy).*

***Background Color** - blue, white, new leaf green, etc*

***Sky Conditions** - indicate cloud cover by percentage or by description (clear, scattered, broken, overcast, and color of clouds)*

***Windspeed** - use Beaufort wind scale or hand-held anomometer, be accurate to ±5 mph*

***Wind Direction** - direction wind is **from**, use compass, be accurate to eight points*

***Ambient Temperature** - in °F or °C*

****Wet Bulb Temperature** - the wet bulb temperature from the sling psychrometer*

****Relative Humidity** - use sling psychrometer; use local U S Weather Bureau only if nearby*

***Source Layout Sketch** - include wind direction, associated stacks, roads, and other landmarks to fully identify location of emission point and observer position*

***Draw North Arrow** - point line of sight in direction of emission point, place compass beside circle, and draw in arrow parallel to compass needle*

***Sun Location Line** - point line of sight in direction of emission point, place pen upright on sun location line, and mark location of sun when pen's shadow crosses the observers position*

****Comments** - factual implications, deviations, altercations, and/or problems not addressed elsewhere*

***Acknowledgment** - signature, title, and date of company official acknowledging receipt of a copy of VE observation form*

***Observation Date** - date observations conducted*

***Start Time, Stop Time** - beginning and end times of observation period (e.g., 1635 or 4 35 p m).*

***Data Set** - percent opacity to nearest 5%, enter from left to right starting in left column*

***Average Opacity for Highest Period** - average of highest 24 consecutive opacity readings.*

***Number of Readings Above (Frequency Count)** - count of total number of readings above a designated opacity*

Range of Opacity Readings:
Minimum - lowest reading
Maximum - highest reading

***Observer's Name** - print in full*

***Observer's Signature, Date** - sign and date after performing final calculations*

***Organization** - observer's employer*

***Certifier, Date** - name of "smoke school" certifying observer and date of most recent certification*

***Verifier, Date** - signature of person responsible for verifying observer's calculations and date of verification*

*Required by Reference Method 9, other items suggested
**Required by Method 9 only when particular factor could affect the reading

Figure 4.2. *Reverse side of form (Continued)*

VISIBLE EMISSION OBSERVATION FORM

A

SOURCE NAME

ADDRESS

CITY | STATE | ZIP

PHONE | SOURCE ID NUMBER

B

PROCESS EQUIPMENT | OPERATING MODE

CONTROL EQUIPMENT | OPERATING MODE

C

DESCRIBE EMISSION POINT
START STOP

HEIGHT ABOVE GROUND LEVEL | HEIGHT RELATIVE TO OBSERVER
START STOP | START STOP

DISTANCE FROM OBSERVER | DIRECTION FROM OBSERVER
START STOP | START STOP

D

DESCRIBE EMISSIONS
START STOP

EMISSION COLOR | PLUME TYPE CONTINUOUS ☐
START STOP | FUGITIVE ☐ INTERMITTENT ☐

WATER DROPLETS PRESENT | IF WATER DROPLET PLUME
NO ☐ YES ☐ | ATTACHED ☐ DETACHED ☐

POINT IN THE PLUME AT WHICH OPACITY WAS DETERMINED
START STOP

E

DESCRIBE BACKGROUND
START STOP

BACKGROUND COLOR | SKY CONDITIONS
START STOP | START STOP

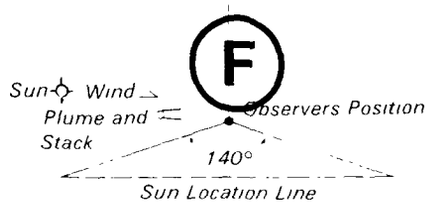
WIND SPEED | WIND DIRECTION
START STOP | START STOP

AMBIENT TEMP | WET BULB TEMP | RH,percent
START STOP

F

Source Layout Sketch Draw North Arrow

X Emission Point



G

COMMENTS

H

I HAVE RECEIVED A COPY OF THESE OPACITY OBSERVATIONS
SIGNATURE
TITLE | DATE

I

OBSERVATION DATE					START TIME					STOP TIME				
MIN \ SEC	0	15	30	45	MIN \ SEC	0	15	30	45					
1					31									
2					32									
3					33									
4					34									
5					35									
6					36									
7					37									
8					38									
9					39									
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26					56									
27					57									
28					58									
29					59									
30					60									

J

AVERAGE OPACITY FOR HIGHEST PERIOD | NUMBER OF READINGS ABOVE % WERE

RANGE OF OPACITY READINGS
MINIMUM MAXIMUM

OBSERVER'S NAME (PRINT)

OBSERVER'S SIGNATURE | DATE

K

ORGANIZATION

CERTIFIED BY | DATE

VERIFIED BY | DATE

Figure 4 3 Functional sections of visible emission observation form

Each major section of the form is discussed in the following text. A short explanation of each section's purpose, a background explanation of each data element, a description of the type of information being sought, and in some cases, appropriate entries are included. These discussions are keyed to Figure 4 3 by corresponding capital letters, and it is clearly indicated whether information is required or recommended

A SOURCE IDENTIFICATION Provides information that uniquely identifies the source and permits the observer to locate or make contact with the source

Source name		
Address		
City	*State*	*Zip*
Phone	*Source ID number*	

Source Name (Required) - include the source's complete name If necessary for complete identification of the facility, the parent company name, division, or subsidiary name should be included.
Address (Required) - Indicate the street address of the source (not the mailing address or the home office address) so that the exact physical location of the source is known If necessary, the mailing address or home office address may be listed elsewhere
City, State, Zip, Phone (Recommended) - Self-explanatory
Source ID Number (Recommended) - This space is provided for the use of agency personnel and should be used to enter the number the agency uses to identify that particular source, such as the State file number, Compliance Data System number, or National Emission Data System number

B PROCESS AND CONTROL DEVICE TYPE Includes a several word descriptor of the process and control device, indication of current process operating capacity or mode, and operational status of control equipment

Process equipment	*Operating mode*
Control equipment	*Operating mode*

Process Equipment (Required) - Enter a description of the process equipment that emits the plume or emissions to be read The description should be brief but should include as much information as possible, as indicated in the following examples:
Coal-Fired Boiler
#2 Oil-Fired Boiler
Wood Waste Conical Incinerator
Paint Spray Booth
Primary Crusher
Fiberglass Curing Oven
Reverberatory Smelting Furnace
Basic Oxygen Furnace
Operating Mode (Recommended) - Depending on the type of process equipment, this information may vary from a quantification of the current operating rate to a description of the portion of a batch-type process for which the emission opacity is being read. For example, entries could include "90 percent capacity" for a boiler or "85 percent production rate" for the shakeout area of a grey iron foundry For a steel making furnace, entries would include the exact part of the process for which readings are being made, such as "charging" or "tapping." In some cases, the observer may have to obtain this information from a plant official

Control Equipment (Required) - Specify the type(s) of control equipment being used in the system after the process equipment in question (e g , "hot-side electrostatic precipitator")
Operating Mode (Recommended) - Indicate the degree to which the control equipment is being utilized at the time of the opacity observations (e.g., 75% capacity, full capacity, shut down, off line) and the operating mode (e g , automatic) The observer will probably have to obtain this information from a plant official

C EMISSION POINT IDENTIFICATION Contains information uniquely identifying the emission point and its spatial relationship with the observer's position

Describe emission point *Start*		*Stop*	
Height above ground level		*Height relative to observer*	
Start	*Stop*	*Start*	*Stop*
Distance from observer		*Direction from observer*	
Start	*Stop*	*Start*	*Stop*

Describe Emission Point (Required) - Include the identifying physical characteristics of the point of release of emissions from the source. The description must be specific enough so that the emission outlet can be distinguished from all others at the source In subsequent enforcement proceedings, the observer must be certain of the origin of the emissions that were being read

Typical descriptions of the emission outlet include the color, geometry of the stack or other outlet, and the location in relation to other recognizable facility landmarks Any special identification codes the agency or source uses to identify a particular stack or outlet should be noted along with the source code used by the observer The source of this information should be recorded (e g , plant layout map or engineering drawing)

Height Above Ground Level (Required) - Indicate the height of the stack or other emission outlet from its foundation base This information is usually available from agency files, engineering drawings, or computer printouts (such as NEDS printouts) The information also may be obtained by using a combination of a rangefinder and an Abney level or clineometer The height may also be estimated
Height Relative to Observer (Required) - Indicate an estimate of the height of the stack outlet (or of any other type of emission outlet) above the position of the observer This measurement indicates the observer's position in relation to the stack base (i e , higher or lower than the base) and may later be used in slant angle calculations (see Section 3 12 6 and Subsection 4 4 6) if such calculations become necessary
Distance From Observer (Required) - Record the distance from the point of observation to the emission outlet This measurement may be made by using a rangefinder If necessary, a map also may be used to estimate the distance

It is important that this measurement be reasonably accurate if the observer is close to the stack (within 3 stack heights) because it is coupled with the outlet height relative to the observer to determine the slant angle at which the observations were made (see Figure 4 4). A precise determination of the slant angle may become important in calculating any positive bias inherent in the opacity readings
Direction From Observer (Required) - Specify the direction of the emission point from the observer to the closest

of the eight points of the compass (e.g., S, SE, NW, NE) or 45°. Use of a compass to make this determination in the following manner is suggested: hold the compass while facing the emission *point*, rotate the compass until the North compass *point* lies directly beneath the needle (which will be pointing towards magnetic North); then the point of the compass closest to the emission outlet will indicate the direction (Figure 4 5). A map (plant layout) also may be used to make this determination

Describe Emissions (Required) - Include both the physical characteristics of the emissions not recorded elsewhere on the form and the behavior of the resultant plume The description of the physical characteristics might include terms such as lacy, fluffy, and detached nonwater vapor condensibles

The terminology illustrated in Figure 4 6 can be used to describe plume behavior. The behavior can be used to determine the atmospheric stability on the day of the opacity observations.

Emission Color (Required) - Note the color of the emissions. The plume color can sometimes be useful in determining the composition of the emissions and will also serve to document the total contrast between the plume and its background as seen by the opacity observer during the observation period

Plume Type (Recommended) - Check "continuous" if the duration of the emissions being observed is greater than 6 minutes Check "intermittent" if the opacity cycle is less than 6 minutes Check "fugitive" if the emissions have no specifically designated outlet.

Water Droplets Present (May be required) - Check "yes" or "no" as appropriate. In some cases, the presence of condensed water vapor in the plume can be easily observed

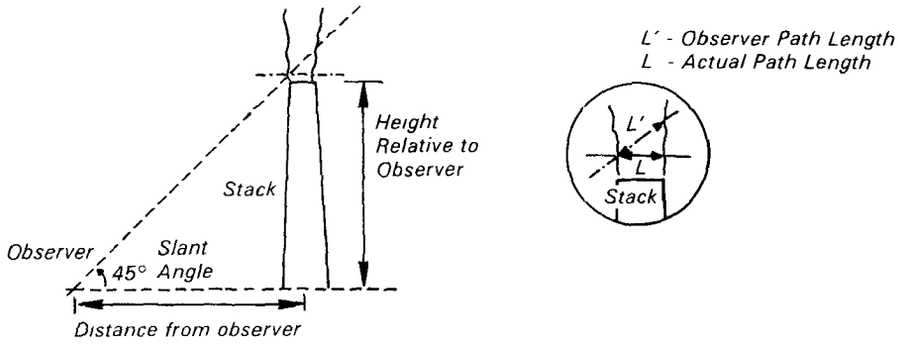


Figure 4.4. *Slant angle relationships.*

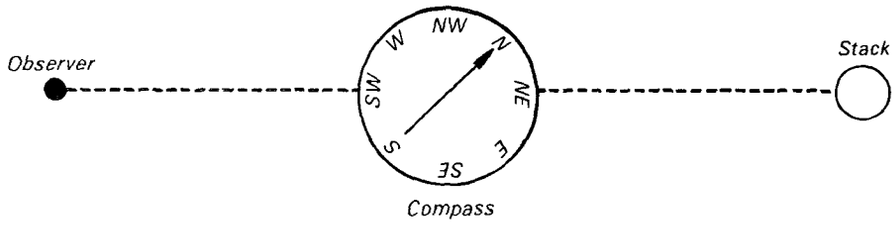


Figure 4.5. *Direction from observer is NE*

D EMISSIONS DESCRIPTION Includes information that definitely establishes what was observed while making the visible emissions determination

Describe emissions *Start* *Stop*	
Emission color *Start* *Stop*	*Plume type* *Continuous* ☐ *Fugitive* ☐ *Intermittent* ☐
Water droplets present *No* ☐ *Yes* ☐	*If water droplet plume* *Attached* ☐ *Detached* ☐
Point in the plume at which opacity was determined *Start* *Stop*	

Plumes containing condensed water vapor (or "steam plumes") are usually very white, billowy, and wispy at the point of dissipation, where the opacity decreases rapidly from a high value (usually 100%) to 0 percent if there is no residual opacity plume contributed by contaminate in the effluent.

To document the presence or absence of condensed water vapor in the plume, the observer must address two points. First, is sufficient moisture present (condensed or uncondensed) in the plume initially? Second, if enough moisture is present, are the in-stack and ambient conditions such that it will condense either before exiting the stack or after exiting (when it meets with the ambient air)? The first question can be answered by examining the process type and/or the treatment of the effluent gas after the process. Some common sources of moisture in the plume are:

- Water produced by combustion of fuels,
- Water from dryers,
- Water introduced by wet scrubbers,
- Water introduced for gas cooling prior to an electrostatic precipitator, or other control device, and
- Water used to control the temperature of chemical reactions

If water is present in the plume, data from a sling psychrometer, which measures relative humidity, in combination with the moisture content and temperature of the effluent gas can be used to predict whether the formation of a steam plume is a possibility (see Section 3.12 6).

If Water Droplet Plume: (May be required) - Check "attached" if condensation of the moisture contained in the plume occurs within the stack and the steam plume is visible at the stack exit Check "detached" if condensation occurs some distance downwind from the stack exit and the steam plume and the stack appear to be unconnected.

Point in the Plume at Which Opacity was Determined (May be required) - Describe as succinctly as possible the physical location in the plume where the observations were made. This description is especially important in the case where condensed water vapor and/or secondary plume is present. For example, were the readings made prior to formation of the steam plume? If the readings were made subsequent to dissipation (e.g., in the case of an attached steam

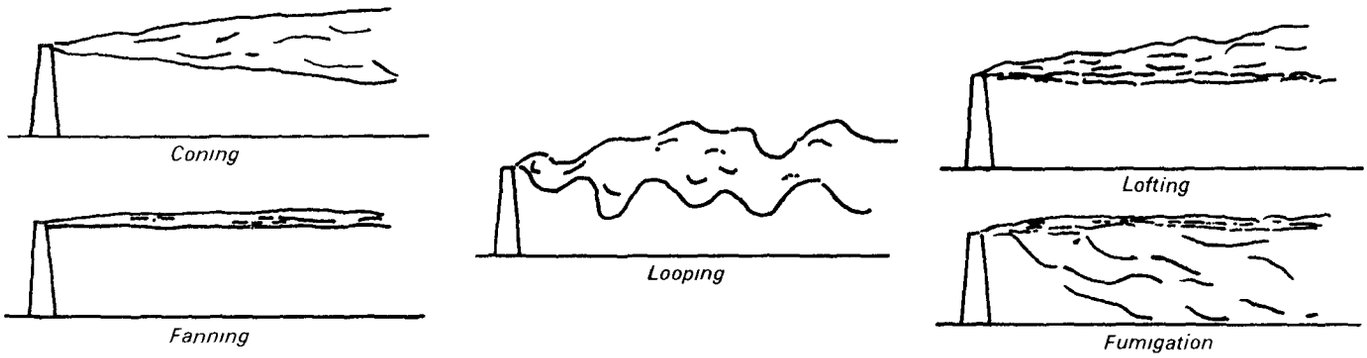


Figure 4.6. *Plume behavior descriptors.*

plume), then specify how far downwind of the dissipation point and how far downwind of the stack exit the reading was made. This information can be used to estimate the amount of dilution that occurred prior to the point of opacity readings. Descriptions such as 4 feet above outlet and 80 feet downstream from outlet, 10 feet after steam dissipation are appropriate.

Figure 4.7 shows some examples of the correct location for making opacity readings in various steam plume and secondary plume situations

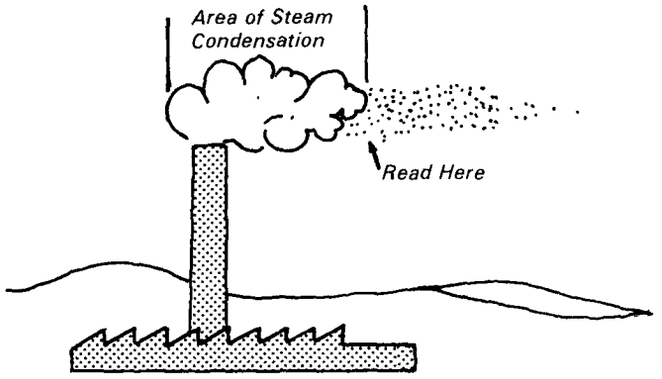
Describe Background (Required) - Describe the background that the plume is obscuring and against which the opacity is being read. While describing the background, note any imperfections or conditions, such as texture, that might affect the ease of making readings Examples of background descriptions are roof of roof monitor, stand of pine trees, edge of jagged stony hillside, clear blue sky, stack scaffolding, and building obscured by haze

Background Color (Required) - Accurately note the background color (e g., new leaf green, conifer green, brick red, sky blue, and gray stone).

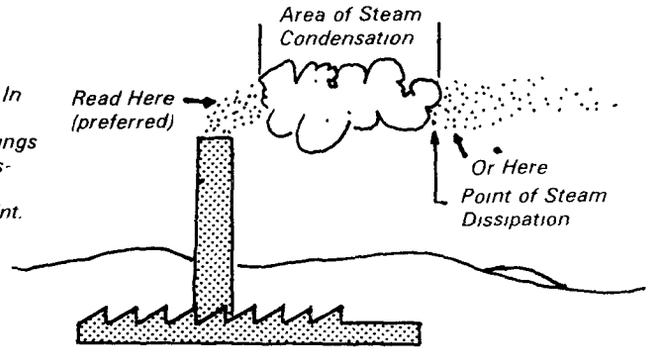
E OBSERVATION CONDITIONS
Covers the background and ambient weather conditions that occur during the observation period and could affect observed opacity

Describe background Start Stop		
Background color Start Stop	*Sky conditions* Start Stop	
Windspeed Start Stop	*Wind direction* Start Stop	
Ambient temp Start Stop	*Wet bulb temp*	*Relative humidity*

Attached steam plume



Detached steam plume. In rare cases, it may be necessary to make readings at the point of steam dissipation if the plume is more opaque at that point.



Plume from a sulfuric acid plant with detached steam plume. Plume is clear at stack exit. Secondary acid mist is formed in area of steam condensation.

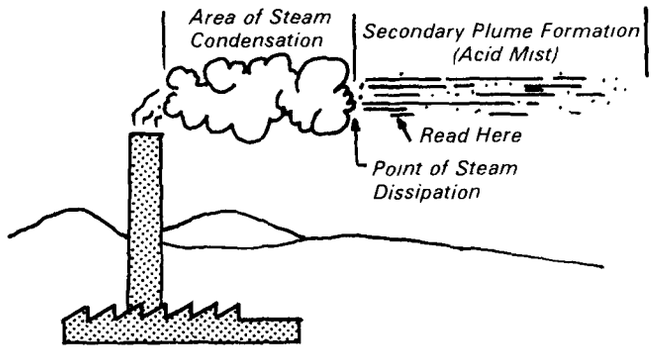


Figure 4.7. *Location for reading opacity under various conditions*

Sky Conditions (Required) - Indicate the percent cloud cover of the sky This information can be indicated by using straight percentages (e.g , 10% overcast, 100% overcast) or by description, as shown below.

Term	*Amount of cloud cover*
Clear	*<10%*
Scattered	*10% to 50%*
Broken	*50% to 90%*
Overcast	*>90%*

Windspeed (Required) - Give the windspeed accurately to ±5 miles per hour The windspeed can be determined using a hand-held anemometer (if available), or it can be estimated by using the Beaufort Scale of Windspeed Equivalents in Table 4 1

Wind Direction (Required) - Indicate the direction *from which* the wind is blowing. The direction should be estimated to eight points of the compass by observing which way the plume is blowing If this type of estimation is not possible, the direction may be determined by observing a blowing flag or by noting the direction a few blades of grass or handfull of dust are blown when tossed into the air Keep in mind that the wind direction at the observation point may be different from that at the emission point; the wind direction at the emission point is the one of interest.

Ambient Temperature (Required) - The outdoor temperature at the plant site is measured by a thermometer (in degrees Fahrenheit or centigrade) obtained from a local weather bureau or estimated Be certain to note which temperature scale is used. This is done in conjunction with the wet bulb temperature and is only needed when there are indications of a condensing water droplet plume

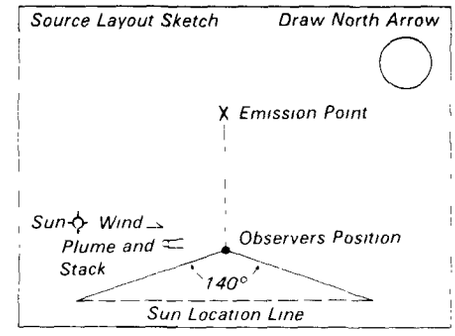
Wet Bulb Temperature (May be required) - Record the wet bulb temperature from the sling psychrometer This is to be done only when there are indications of a condensing water droplet plume

Relative Humidity (May be required) - Enter the relative humidity measured by using a sling psychrometer in conjunction with a psychrometric chart. This information can be used to determine if water vapor in the plume will condense to form a steam plume (see Section 3 12 6) If a sling psychrometer is not available, data from a *nearby* U S Weather Bureau can be substituted

Table 4.1. *The Beaufort Scale of Windspeed Equivalents*

General description	*Specifications*	*Limits of velocity 33 ft (10 m) above level ground, mph*
Calm	*Smoke rises vertically*	*Under 1*
	Direction of wind shown by smoke drift but not by wind vanes	*1 to 3*
Light	*Wind felt on face; leaves rustle; ordinary vane moved by wind*	*4 to 7*
Gentle	*Leaves and small twigs in constant motion, wind extends light flag*	*8 to 12*
Moderate	*Raises dust and loose paper, small branches are moved*	*13 to 18*
Fresh	*Small trees in leaf begin to sway, crested wavelets form on inland waters*	*19 to 24*
	Large branches in motion; whistling heard in telegraph wires, umbrellas used with difficulty	*25 to 31*
Strong	*Whole trees in motion; inconvenience felt in walking against the wind*	*32 to 38*
	Twigs broken off trees; progress generally impeded	*39 to 46*
Gale	*Slight structural damage occurs (chimney pots and slate removed)*	*47 to 54*
	Trees uprooted, considerable structural damage occurs	*55 to 63*
Whole gale	*Rarely experienced, accompanied by widespread damage*	*64 to 75*
Hurricane		*Above 75*

F OBSERVER POSITION AND SOURCE LAYOUT Clearly identifies the observer's position in relation to the emission point, plant landmarks, topographic features, sun position, and wind direction



Source Layout Sketch (Required) - This sketch should include as many landmarks as possible. At the very least, the sketch should locate the relative position of the observed outlet in such a way that it will not be confused with others at a later date, and clearly locate the position of the observer while making the VE readings. The exact landmarks will depend on the specific source, but they might include

- Other stacks
- Hills
- Roads
- Fences
- Buildings
- Stockpiles
- Rail heads
- Tree lines
- Background for readings

To assist in subsequent analysis of the reading conditions, sketch in the plume (indicate the direction of wind travel). The wind direction also must be indicated in the previous section.

Draw North Arrow (Recommended) - To determine the direction of north, point the line of sight in the source layout sketch in the direction of the actual emission point, place the compass next to the circle and draw an arrow in the circle parallel to the compass needle. A map (plant layout) may also be used to determine direction north

Sun's Location (Recommended) - It is important to verify this parameter before making any opacity readings. The sun's location should be within the 140° sector indicated in the layout sketch; this confirms that the sun is within the 140° sector to the observer's back.

To draw the sun's location, point the line of sight in the source layout sketch in the direction of the actual emission point, place a pen upright along the "sun location line" until the

shadow of the pen falls across the observer's position Then draw the sun at the point where the pen touches the "sun location line "

G COMMENTS Includes all implications, deviations, disagreement with plant personnel and/or problems of a factual nature that have bearing on the opacity observations and that cannot be or have not been addressed elsewhere on the form

Comments

Comments (May be required) - Note all implications, deviations, disagreements with plant personnel, or problems of a factual nature that cannot be or have not been addressed elsewhere on the form Examples of points to be included in this section are:

- Changes in ambient conditions from the time of the start of readings
- Changes in plume color, behavior, or other characteristics
- Changes in observer position and reasons for the change, a new form should also be initiated in this case so that a new source layout sketch may be drawn
- Difficulties encountered in plant entry
- Conditions that might interfere with readings or cause them to be biased.
- Drawing of unusual stack configuration (to show multiple stacks or stack in relation to roof line)
- Suspected changes to the emissions or process during observation.
- Unusual process conditions
- Additional source identification information
- Type of plant (if not specified elsewhere)
- Reasons for missed readings
- Other observers present

H COMPANY ACKNOWLEDGEMENT Company acknowledgement of, but not necessarily agreement with, the opacity observations stated on the form

I have received a copy of these opacity observations	
Signature	
Title	*Date*

Signature (Recommended) - This space is provided for the signature of a plant official who acknowledges that he/she has received a copy of the observer's opacity readings. His/her signature does not in any way indicate that he/she or the company concurs with those readings

Title (Recommended) - Include the acknowledging official's company title

Date (Recommended) - The company official should enter the date of acknowledgment.

I DATA SET Opacity readings for the observation period, organized by minute and second This section also includes the actual date and start and stop times for the observation period

Observation date					*Start time*			*Stop time*	
M \ s	*0*	*15*	*30*	*45*	*M \ s*	*0*	*15*	*30*	*45*
1					*31*				
2					*32*				
29					*59*				
30					*60*				

Observation Date (Required) - Enter the date on which the opacity observations were made

Start Time, Stop Time (Required) - Indicate the times at the beginning and the end of the actual observation period The times may be expressed in 12-hour or 24-hour time (i e , 8.35 a m or 0835), however, 24-hour time tends to be less confusing

Data Set (Required) - Spaces are provided for entering an opacity reading every 15 s for up to a 1-hour observation period The readings should be in percent opacity and made to the nearest 5 percent The readings are entered from left to right for each numbered minute, beginning at the upper left corner of the left-hand column, labeled row "M 1" (minute 1) and column "s 0" (0 seconds) The next readings are entered consecutively in the spaces labeled M 1, s 15, M 1, s 30; M 1, s 45, M 2, s 0, M 2, s 15, etc

If, for any reason, a reading is not made for a particular 15-second period, that space should be skipped and an explanation should be provided in the comments section Also a dash (-) should be placed in the space which denotes that the space is not just an oversight

J DATA REDUCTION Basic analysis of the opacity readings to allow preliminary compliance appraisal in accordance with EPA Reference Method 9

Average opacity for highest period	*Number of readings above % were*
Range of opacity readings	
Minimum	*Maximum*

Average Opacity for the Highest Period (Required) - Enter the average of the sum of the highest 24 consecutive readings (6-minute set). In other words, identify the 24 consecutive readings that would sum to the greatest value and then divide this value by 24 to get the average opacity for that set of readings. *Note:* The average should not include a time lapse for which a valid reading could have been taken but was not (see Section 3 12 6).

Number of Readings Above . % Were . (Recommended) - Indicate an optional frequency count of the opacity readings above a particular value The value is chosen according to the opacity standard for the emission point and is generally the actual value of the standard

Method 9 does *not* specify the use of frequency counting to reduce data, but many States use it to determine compliance with their time exemption opacity standards For example, a State regulation might specify that opacity of a specific type of emission source is not to exceed 20 percent for more than 3 minutes in an hour If more than 12 readings out of 240 exceed 20 percent in an hour-long observation period, that State may consider that source out of compliance For example,

14 readings out of 240 readings (1 hour) are above 20 percent opacity
14 x 15 s per reading = 210 s
= 3 5 minutes of readings above the standard

Range of Opacity Readings (Required) - Enter the highest and lowest opacity readings taken during the specified observation period.

K OBSERVER DATA Information required to validate the opacity data

Observer's name (print)	
Observer's signature	*Date*
Organization	
Certified by	*Date*
Verified by	*Date*

Observer's Name (Required) - Print observer's entire name
Observer's Signature/Date (Recommended) - Self-explanatory
Organization (Required) - Provide the name of the agency or company that employs the observer.

Certified By (Recommended) - Identify the agency, company, or other organization that conducted the "smoke school" or VE training and certification course where the observer obtained his/her most current certification.
Date (Required) - Provide the date of the most current certification
Verified By (Recommended) - The actual signature of someone who has verified the opacity readings and calculations, usually the observer's supervisor, or the individual who is responsible for his/her work
Date (Recommended) - Provide the date of verification.

4.3.3 *Facility Operating Data* - It is strongly recommended that a VE inspection/observation conclude with a source inspection if opacity values are in excess of the standard. The observer would first follow the plant entry procedure in Subsection 4 1 and then follow the indicated procedure to obtain facility operating data.

After the VE determination, it is recommended that the following source information be determined:

1 Were the plant and the source of interest operating normally at the time of the VE evaluation?
2. Are there any control devices associated with the source?
3. Were the control devices operating properly?
4 Have there been any recent changes in the operation of the process or control devices?
5. Have any malfunctions or frequent upsets in the process or control devices been noted and reported (if required by the agency)?
6. Is the plant operator aware of excessive visible emissions and have any corrective steps been taken to alleviate the problems?
7. Are there any other sources of visible emissions in close proximity to the source in question that may interfere with reading the plume opacity or contribute to the appearance of the plume?

4.3.4 *Photographs* - It is suggested that photographs be taken before and after the observation is made, not during the observation period Conditions should be recorded as they existed at the time of the observation. The use of a 35-mm camera is recommended to ensure good photographs

Each photograph should be identified with the date and time, the source, and the position from which the photograph was taken

4.4 *Special Observation Problems*
The VE observer constantly should be aware that his/her observations may be used as the basis of a violation action and subject to questioning as to the reliability of the observations. Therefore, he/she must also be aware that under some conditions or situations it may be difficult or impossible to conduct a technically defensible visible emissions observation

This section discusses some of the most prevalent difficult conditions or special problems associated with the visible emission observation. Each discussion is directed toward defining the problem, indicating how it might invalidate readings taken, and addressing possible solutions and/or ways to minimize the invalidating effects

Not all of these discussions offer a complete solution for a particular problem; thus, it is important for the individual observer to keep in mind the purpose of the visible emission observation when considering exactly what action to take when faced with a special problem.

4.4.1 *Positional Requirements* - Valid VE evaluations can be conducted only when the sun is properly positioned at the observer's back. Failure to adhere to this positioning can result in significant positive bias caused by forward light scatter in opacity readings. Because of this overriding constraint, some times and locations make it difficult for the observer to meet other opacity reading criteria, e.g., reading the narrow axis of a rectangular stack, reading a series of stacks across a short axis to prevent multiple plume effects, and obtaining a contrasting background Plant topography also may generate constraints that restrict viewing positions to one or more locations The observer will be aided in determining the best observation location by following the criteria listed below

1. Make sure that the emission point is north of the observation point.
2. Obtain a clear view of the emission point with no interfering plumes
3 Be sure that rectangular stacks are read across the narrow axis and multiple stacks are read perpendicular to the line of stacks
4. Minimize the slant angle by moving a sufficient distance from the stack or to an elevated position (see Subsection 4.4 4).
5 Find a contrasting background or a clear sky background.
6. Finally, determine the best time of day for observations based on the daily sun tracks at that location

Collaborative studies of the performances of trained observers have indicated that, with the exception of the positive bias caused by having the improper sun angle, visible emission observation biases tend to be negative. Thus, if viewing conditions are not ideal and a negative bias (lower value) results, opacity readings may not provide the true measure of plume opacity required to correlate to mass emissions or control equipment efficiency. However, readings that indicate a violation can be regarded as the minimum opacity; therefore, documentation of the violation is valid.

In situations where the observer must make plume opacity readings when all the criteria for correct viewing cannot be met, all extenuating circumstances must be documented on the VE evaluation form

4.4.2 *Multiple Sources/Multiple Stacks* - An observer is sometimes compelled to evaluate a stack that discharges emissions from more than one source or to evaluate a single source that has more than one emission point

In the case where one stack serves more than one emission source, the observer may be able to isolate the emissions from one source as a result of intervals of operation, or by requesting the facility's cooperation in temporarily shutting down the other source(s) Otherwise, the observer should proceed with the VE observation and document the situation completely on the VE evaluation form

In the case of multiple emission points for a single source (e g., in positive-pressure baghouses and multiple vents in roof monitors), Section 2.1 of Method 9 directs the

observer to read multiple stacks independently if it is possible to do so while meeting sun position requirements. If it is necessary to get an overall reading for the group of stacks, the following set of formulas can be used to calculate this reading from the individual opacity values

$$1 - \frac{O_1}{100} = T_1$$

$$1 - \frac{O_2}{100} = T_2$$

$$1 - \frac{O_N}{100} = T_N$$

$$T_1 \times T_2 \times .. \; T_N = T_T$$

$$100 \times (1 - T_T) = O_T$$

where
O_1 = % opacity of 1st plume
O_2 = % opacity of 2nd plume
O_N = % opacity of nth plume
T_1 = Transmittance of 1st plume
T_2 = Transmittance of 2nd plume
T_N = Transmittance of nth plume
T_T = Total transmittance
O_T = % total opacity

4.4.3 High Winds - Occasionally the crosswind conditions are unfavorable during field observations of plume opacity. When the winds are strong enough to shear the emissions at the stack outlet, it is difficult for the observer to make an accurate and fair VE observation. Strong crosswinds can have several effects on the plume:

1. The plume becomes essentially flattened and is no longer conical in shape thus the path length and apparent opacity increases
2. The plume is torn into fragments and becomes difficult to obtain a representative reading
3. The plume becomes diluted, and the apparent opacity is lowered

The observer can compensate somewhat for the effect of flattening by reading the plume downwind of the stack, after it has reformed into a cone. The dilution effect of high winds, which lowers the apparent opacity, presents more of a problem Because of the negative bias introduced, the effectiveness of Method 9 as a control tool under these conditions is diminished If a violation is still observed under these conditions, it should be considered valid. It is recommended that whenever feasible, VE observations be suspended until the wind-caused interferences have abated.

4.4.4 Poor Lighting - Poor lighting conditions for VE observations usually involve one or more of the following (1) a totally overcast sky, (2) early morning or late afternoon hours, or (3) nighttime Each of these three lighting conditions has the same net effect on the plume; they differ slightly only in the cause of the poor illumination When the amount of available sunlight is below a certain level, the contrast between a white plume and the background decreases. Therefore, readings are not recommended in either the early morning hours (at or approaching dawn) or late afternoon hours (at or approaching dusk)

Nighttime viewing obviously represents the most severe of poor lighting conditions. Some agencies have attempted, with mixed results, to use night vision devices (light intensification scopes) for plume viewing and testing in the dark Others have achieved better results by placing a light behind the emissions, which provides a very high contrast background. For this method, it is important to select a source of light of moderate strength that does not cause the iris of the eye to close.

4.4.5 Poor Background - The color contrast between the plume and the background against which it is viewed can affect the appearance of the plume as viewed by an observer Field studies have corroborated predictions of the plume opacity theory by demonstrating that a plume is most visible and has the greatest apparent opacity when viewed against a contrasting background.

Consistent with these findings is the fact that with a high contrast background, the potential for positive observer bias is the greatest However, field trials consisting of 769 sets of 25 opacity readings each have shown that for more than 99 percent of the sets, the positive observer error was no greater than 7 5 percent opacity.[2]

Also consistent with these findings is the fact that as the contrast between the plume and its background *decreases,* the apparent opacity decreases; this greatly increases the chance for a negative observer bias Under these conditions, the likelihood lessens of a facility being cited for a violation of an opacity standard because of observer error.

When faced with a situation where there is a choice of backgrounds, the observer should always choose the one providing the highest contrast with the plume because it will permit the most accurate opacity reading However, if a situation arises where other constraints make it impossible to locate an observation point that provides a high contrast background, the observer may read against a less contrasting one with confidence that a documented violation should be legally defensible.

4.4.6 Reduced Visibility - Environmental factors at the time of observation also are of concern to the visible emissions observer. Environmental considerations include rain, snow, or other forms of precipitation, and photochemical smog buildup, fog, sea spray, high humidity levels, or any other cause of haze. These environmental factors create a visual obscuration that can increase the apparent opacity of the plume, but more commonly reduce the background contrast and thus decrease the apparent opacity.

In recognition of the problems that could result from reduced visibility caused by environmental factors, the amended Method 9 (November 12, 1974) states, in paragraph 2.1 of the Procedures Section: "The qualified observer shall stand at a distance sufficient to provide a clear view of the emissions ..." A "clear view" must be interpreted as a view free from obstacles or interferences. Most problems caused by reduced visibility can be alleviated simply by making the observations on another day.

4.4.7 Tall Stacks/Slant Angle - When an observer's distance from the stack approaches 1/4 mile (approximately 1300 feet, or a little over four football fields), the ambient light scattering may begin to have an adverse effect on the contrast between the plume and the background. Also, if the sky is overcast or hazy on the day of observation, the farther the observer is from the emission point, the more the haze interferes with the view of the plume and hence, the less reliable the readings.

On the other hand, the recommendation that the observer stand at least three stack heights from the stack being observed is intended to ensure that the width of the plume as it is viewed is approximately the same as it is at the stack outlet. As the observer gets closer to the stack and the viewing (slant) angle

increases, the observed path length also increases; this causes the observed opacity to increase because the observer is reading through more emissions. These relationships are shown in Figure 4.8 At an observer distance of three stack heights, which corresponds to a slant angle of 18°, the deviation of observed opacity from actual opacity decreases to 1 percent opacity, which is considered acceptable (see Section 3.12.6).

The three-stack-heights relationship only occurs if the observer and the base of the stack are in the same horizontal plane. If the observer is on a higher plane than the base of the stack, then the minimum distance for proper viewing can be reduced to *less* than three stack heights; conversely, if the observer's plane is lower than that of the stack base, then the minimum suggested distance will be *greater* than three stack heights (see Figure 4 8) The real determining factor is the slant angle To assure no more than a 1 percent opacity deviation of observed opacity from actual opacity, the observer must have a visual slant angle of 18° or less.

4.4.8 Steam Plumes - Under certain conditions, water vapor present in an effluent gas stream will condense to form a visible water droplet or "steam" plume Because the NSPS (specifically Method 9) and almost all SIP's exclude condensed, uncombined water vapor from opacity regulations, the VE observer must be careful that he/she does not knowingly read a plume at a point where condensed water vapor is present and record the value as representative of stack emissions.

Knowledge of the kind of process that generates the emissions being read and simple observation of the resultant plume almost always allows the observer to determine if a steam plume is present. Steam plumes are commonly associated with processes or control equipment that introduce water vapor into the gas stream. These sources include

- Fuel combustion,
- Drying operations,
- Wet scrubbers,
- Water-induced gas cooling prior to an emissions control device, and
- Water-induced chemical reaction cooling.

Also, observation of steam plumes will reveal that they are usually very white, billowy, and have an abrupt point of dissipation. At the point of dissipation, the opacity generally decreases *rapidly* from a high value (usually 100%) to a low value Depending on the moisture and temperature conditions in the stack and in the ambient air, steam plumes may be either "attached" or "detached." An attached steam plume forms within the stack and is visible at the exit; a detached steam plume forms downwind of the stack exit and does not appear to be connected to the stack. In cases when it is not clear whether a steam plume is present or when an observer would like to predict the formation of a steam plume, the stack gas conditions may be used in conjunction with the ambient relative humidity to make the prediction (see Section 3.12 6)

When a steam plume *is* present, the particulate plume is read at a point where 1) no condensed water vapor exists, and 2) the opacity is the greatest. In the case of a detached steam plume, this point is usually at the stack exit, prior to the water vapor condensation, in the case of an attached steam plume, it is usually slightly downwind of the point of steam plume dissipation (for examples, see Figure 4.7) The observer should always carefully document the point chosen

4.4.9 Secondary Plume Formation - Some effluent gas streams contain species that form visible mists or plumes by a physical and/or chemical reaction that occurs either at some point in the stack or after the emissions come in contact with the atmosphere This situation is known as secondary plume formation Examples of such secondary plume formation include

- A change in the physical state of a compound condensing from a gas into a liquid, such as vaporized hydrocarbon condensing into an aerosol or a solid.
- A physiocochemical reaction between two or more gaseous (or in some cases, liquid) species in a plume, such as the condensation of ammonia, sulfur dioxide, and water vapor to form

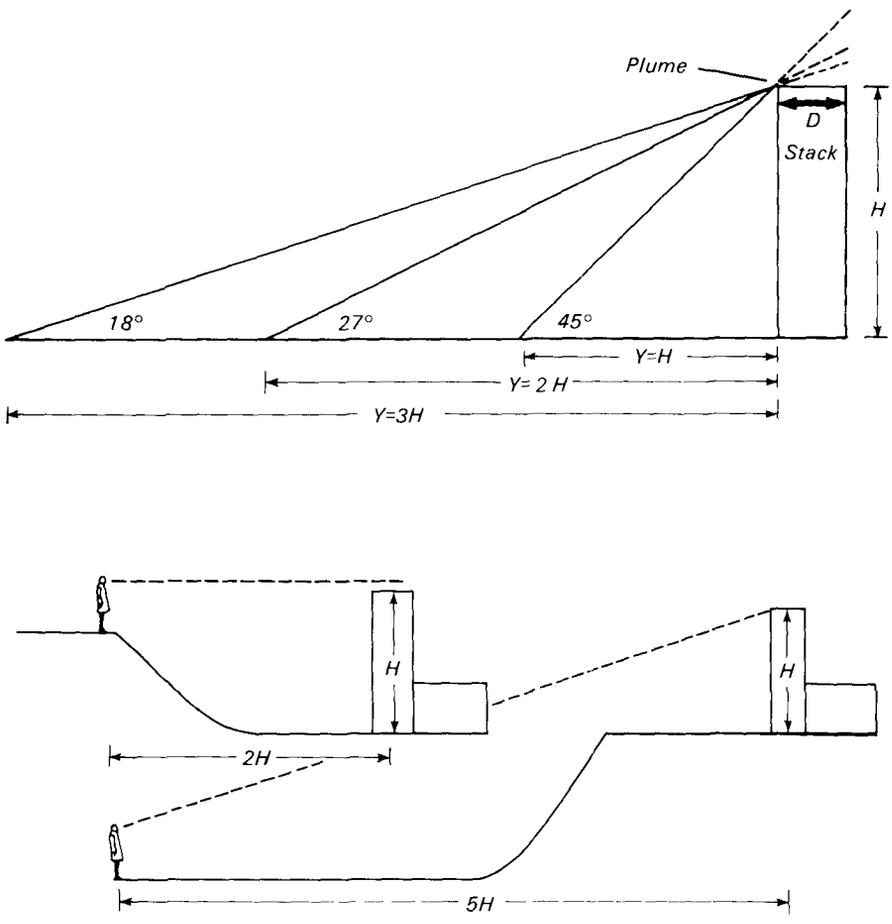


Figure 4.8. *Observer distance, observed path length relationships*

particulate ammonium sulfite or the condensation of sulfur trioxide and water vapor to form sulfuric acid mist
- A physiocochemical reaction between species in a plume and species in the atmosphere, such as the formation of N_2O_3

Secondary plumes are sometimes found in the following processes (with these suspected secondary reactions)·
- Coal- and oil-fired cement kilns ($SO_3 + H_2O \rightarrow H_2SO_4$ mist) or [$NH_3 + SO_2 + H_2O \rightarrow (NH_4)_2 SO_3$]
- Fossil-fuel-fired steam generators ($SO_2 + H_2O \rightarrow H_2SO_4$ mist)
- Sulfuric acid manufacturing ($SO_3 + H_2O \rightarrow H_2SO_4$ mist)
- Plywood and particleboard wood heating (organic vapor → organic mist)
- Glass manufacturing (inorganic vapor → organic aerosol)

As in the case of steam plumes, secondary plumes can be attached or detached, depending on the specific condensation reaction and the ambient conditions. For example, a secondary plume will be attached if a reaction between plume species occurs in the stack and the stack temperature is sufficiently low to cause condensation of the reaction products to a visible liquid or solid phase A detached secondary plume will be evident when the reaction does not occur until the gas stream comes in contact with the atmosphere. The degree of detachment depends on the ambient conditions, the degree of mixing between the effluent and the atmosphere, and the specific reaction(s) involved

Secondary plumes may occur with or without an accompanying steam plume, and it is important that the observer be able to distinguish between the two Unlike steam plumes, secondary plumes are often persistent (they do not dissipate rapidly), are usually bluish white (due to the fine particles present), and are grainy rather than billowy

To read a secondary plume, the observer must locate the densest point of the plume where water vapor is not evident and make the readings at that point This point may occur in several different areas, depending on the type of secondary plume An attached secondary plume will usually be read at the stack exit if an attached *steam* plume is not present, if an attached steam plume *is* present, the secondary plume must be read at the point of steam dissipation A detached secondary plume will usually be read slightly downwind of the area of formation, assuming there is no interfering condensed water vapor Under some conditions, a secondary plume may not fully condense until some distance downstream of the point of formation, in this case, the observer simply looks for the densest area of the plume and makes the reading at that point It is especially important in reading a secondary formation plume to describe fully the point at which the reading was taken and the exact appearance of the plume. (Refer to Figure 4 7 for one example of where to read a secondary plume.)

4.4.10 *Fugitive Emissions* - Fugitive emissions are those emissions that do not emanate from a conventional smoke stack or vent Examples of these nonconventional emissions include·
- Dusty or unpaved roads
- Stock or raw material piles under windy conditions or when moved by machinery
- Conveyor belts, pneumatic lifts, clamshells, and draglines
- Cutting, crushing, grinding, and sizing of minerals or other materials
- Plowing, tilling, and bulldozing
- Open incineration
- Demolition activities
- Roof monitors or building vents, especially in foundries, iron and steel facilities, and related industries

Because of the irregular shape of their emission point or area, conducting a conventional Method 9 test on fugitive emissions may appear difficult, however, it usually involves only relatively minor adjustments Commonly used procedures for observation of fugitive emissions are listed below

1. If possible, isolate the particular emission from other emissions by choosing an appropriate position for observation
2. Adhere to the lighting requirements of Method 9 by keeping the sun in the 140° sector to the observer's back
3. Also adhere to Method 9 in selecting a position with regard to wind direction and a contrasting background
4. Whenever possible, select the shortest path length through the plume
5. Before taking readings, view the emission for several minutes to determine its characteristics Changes that may occur in the airborne particulate pattern over time are important to note and to consider in selecting a viewing point
6. Select the line of sight and the viewing point in the emissions so that, on the average, the densest part of the emissions will be observed It is recommended that all subsequent readings in a data set be taken at the same relative position to the emission source
7. The configuration of the emission point or area may necessitate taking readings at a point downwind where the emissions have assumed a more conventional plume shape
8. If the plume cannot be viewed through a nearly perpendicular angle, corrections may be necessary

4.4.11 *Intermittent Sources* - Some sources release visible emissions intermittently rather than continuously, e g., coke ovens, batch operations, single chamber incinerators, malfunctioning control equipment (in rapping, bag shaking, etc), boilers during soot blowing, and process equipment during startup

Intermittent emissions may have a high opacity for a short time and a low or negligible opacity at other times This high-low cycle may be repeated at fairly regular intervals If a source is in violation (or in continuous compliance) of the applicable standard over the 6-minute averaging time required by Method 9, it does not pose a problem to the visible emissions observer If the pollutant-emitting operational cycle of a source is less than 6 minutes in duration, however, that source may be out of compliance only for a portion of each 6-minute averaging period, which will make it difficult or impossible to document a violation if the data is to be reduced to a 6-minute average

If the source is not covered by a NSPS or a State Implementation Plan that specifies the explicit use of Method 9 or another specified modification to Method 9, another technique for reading intermittent emissions of less than a 6-minute duration is to use Method 9 procedures but reduce the averaging time to about 3 minutes This reduction will allow the observer to tally the number of 3-minute violations that occur Analysis of many data sets has confirmed that using this method sacrifices little or no accuracy

In all cases where sources are not subject to NSPS or other federally promulgated standard, the existing State regulations and specified opacity observation methods (if any) must be used. Two other techniques that have been used to document intermittent emissions are the "stopwatch" technique (measuring the total accumulated time that the opacity exceeds the applicable standard) and the time-aggregate data reporting technique (taking readings every 15 seconds, tallying the number of readings exceeding the standard, and multiplying this number by 15 seconds to determine the amount of time the source is out of compliance during the observation period) Many State agencies use these latter techniques, and have adopted their methods in their SIP rules and regulations. EPA currently has studies underway to evaluate the accuracy and reliability of these nonaveraging techniques

Table 4.2. *Activity Matrix for Visible Emission Determination*

Activity	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Perimeter survey	*Completed perimeter survey*	*Prior to, following, and during (if warranted) the VE determination*	*N/A*
Plant entry	*Observer should follow protocol as suggested in Subsec 4.2 and adhere to confidentiality of data*	*Entry prior to taking VE readings only if necessary, entry after VE readings to provide plant representative with data and/or to obtain necessary plant process data*	*N/A*
VE Determination			
1 Position	*In accordance with Subsec 4.3.1*	*Take a position for observation as described in Subsec 4 3.1 and document on data form*	*Follow instructions under special problems (Subsec 4.4) when a proper position cannot be assumed*
2. Observations	*Taken in accordance with Subsec 4 3.1*	*Make VE determination as described in Subsec 4.3.1*	*As above*
3. Field data: VE observation form	*Completed data form*	*Complete data form as per instructions and examples in Subsec 4.3.2*	*Complete missing data (if possible) or give rationale for incomplete data*
4. Facility operating data	*Pertinent process data obtained*	*After VE observations, obtain facility data per Subsec 4.3.3*	*Data must be obtained as soon as possible after VE observation*
Special observation problems	*N/A*	*Refer to Subsec 4.4 when conditions do not permit VE observation under proper position, etc.*	*N/A*

N/A = not applicable.

5.0 Postobservation Operations

Table 5.1 at the end of this section summarizes the quality assurance activities for postobservation operations. These activities include preparation of reports and data summaries and validation.

5.1 Data Summary

The opacity observations are recorded on data forms such as those shown in Figures 4 1 and 4 2. Figure 5.1 is a summary data form for manual calculations This form and the calculation procedures are discussed in detail in Section 3 12 6. It is recommended, however, that a computer be used when reducing large quantities of data and to avoid calculation errors.

5.2 Reporting Procedures

Recording opacity observation data on a three-part form is most convenient One part can be given to the appropriate facility personnel immediately following the on-site field observation if this is the agency policy or procedure, one part should be given to the Agency, and one part should be maintained in the observer's file. The data form should be completed on-site, and it should be signed by the observer, the facility representative (if applicable), and the data validator. All corrections must be initialed The file copy should be signed by the data validator

Inspection forms alone may not be adequate for documenting an enforceable violation and can be supplemented by a narrative report. It is recommended that a summary report be made containing the following information:

1. Name and location of facility, date and time of inspection, name of inspector, and name of company official(s) contacted.
2. Brief description of the specific process information gathered,

Company Admiral Power Plant Date 15 July 1982 Location 112 Ocean Rd., Admiral City, Va.
Start time 1330 Emission point Oil Fired Boiler

Start no	Total opacity	Average opacity	Start no.	Total opacity	Average opacity	Start no	Total opacity	Average opacity	Start no.	Total opacity	Average opacity	Start no	Total opacity	Average opacity	Start no	Total opacity	Average opacity
1	885	36.8	37			73			109			145			181		
2	885	36.8	38			74			110			146			182		
3	880	36.6	39			75			111			147			183		
4	860	35.8	40			76			112			148			184		
5	840	35.0	41			77			113			149			185		
6	845	35.2	42			78			114			150			186		
7			43			79			115			151			187		
8			44			80			116			152			188		
9			45			81			117			153			189		
10			46			82			118			154			190		
11			47			83			119			155			191		
12			48			84			120			156			192		
13			49			85			121			157			193		
14			50			86			122			158			194		
15			51			87			123			159			195		
16			52			88			124			160			196		
17			53			89			125			161			197		
18			54			90			126			162			198		
19			55			91			127			163			199		
20			56			92			128			164			200		
21			57			93			129			165			201		
22			58			94			130			166			202		
23			59			95			131			167			203		
24			60			96			132			168			204		
25			61			97			133			169			205		
26			62			98			134			170			206		
27			63			99			135			171			207		
28			64			100			136			172			208		
29			65			101			137			173			209		
30			66			102			138			174			210		
31			67			103			139			175			211		
32			68			104			140			176			212		
33			69			105			141			177			213		
34			70			106			142			178			214		
35			71			107			143			179			215		
36			72			108			144			180			216		

Maximum average 36.8 % Start number of six minute average 1
Number of nonoverlapping averages in excess of standard 3 Listing start number of these averages 1, 12, 80, 175
Calculated by V.E. Proffit Date 16 JULY 1982 Reviewed by T.M. REVIEWER Date 17 JULY 1982

Figure 5.1 Visible emission summary data sheet

particularly any unusual occurrences.

3 Description of the equipment that was inspected and its operating mode at the time of inspection
4 Notation of any excessive emissions seen and corresponding data from opacity continuous emissions monitor if available.
5. Explanation of excessive emissions, if available, and corrective actions being taken
6 Summary of emission points *not* in compliance.
7 Recommendations for followup action.

One copy of the report, an updated plot plan, photographs, and other pertinent data should be placed in the Agency file Whenever a violation is noted, it is EPA policy to notify the facility of the alleged violation and to permit them to review the evidence against them in a meaningful way The importance of a good file cannot be overstated This file represents the official Agency documentation of compliance history, the latest information on the source's operation and compliance status The file also provides the means of communicating source conditions to other staff members A thorough and accurate historical record on source inspections and opacity readings is essential to good operation and any necessary compliance/enforcement actions

5.3 Data Validation

All opacity observation data obtained for compliance determination should be validated by senior staff assigned this responsibility Data validation procedures are described in References 16 and 17. These data should be checked to the extent possible for their completeness, the correctness of source, the emission point and description, the background, and the process and control equipment in use The calculation of the average opacities and highest average opacity also should be checked All calculation checks should agree within acceptable roundoff errors. If possible, any questionable data should be reviewed with the observer Ideally the data validation should occur as soon as possible after the observations are recorded so that questions may be resolved Any other calculations made for the purpose of supporting the data (e g , the effect of angle of observation on the observed opacity) should also be verified *Note.* Any corrections in the data must be forwarded to all interested parties so that they may correct their records (a data form should have been given to them after the opacity observations were completed)

5.4 Equipment Check

A check of the equipment following the opacity observations helps to ensure the quality of the data Any indication of equipment damage/malfunction should be recorded on an equipment log and noted for purposes of data validation The malfunctioning equipment should be repaired, adjusted, or replaced so that the equipment will be available for subsequent on-site field observations

Table 5.1. *Activity Matrix for Postobservation Operations*

Activity	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Data summary	*Completed data form*	*See Subsec 3 12 6 for instructions for calculations*	*Complete the data summary*
Reporting procedures	*Completed report and data forms*	*Use 3-part form as suggested in Subsec 5 2*	*Complete the necessary data forms and reporting procedure*
Data validation	*All checks should agree within acceptable roundoff error*	*Make data validation check as soon as possible after VE observation*	*Forward all corrections of the data/calculations to the interested parties*
Equipment check	*All equipment/apparatus should be checked for satisfactory operation after each VE observation day*	*Check equipment for damage/malfunctions*	*Note on equipment log and repair, adjust or replace the equipment*

6.0 Calculations

Three types of calculations are described in this section (1) the calculation of the average opacity for the specified time period (usually 6 min, or 24 observations recorded at 15-s intervals), (2) the calculation of the path length through the plume (seldom needed), and (3) the prediction of steam plume formation (seldom needed). In the first calculation, the 6-min running (or rolling) averages may be required To minimize errors in the calculations, another individual should check all calculations for each VE determination for compliance If a difference greater than a typical roundoff error is detected, the corrections should be made and initialed by the one making the correction. Table 6.3 at the end of this section summarizes the quality assurance activities for these calculations.

6.1 Calculation of Average Opacity

Figure 6 1 shows actual opacity data taken at one company (unspecified) for two 6-min periods *Note:* Any corrections made by an observer must be initialed and the corrected value used in the computation of an average The calculations can be checked by obtaining the row and column subtotals, the totals of these subtotals must be identical.

Running 6-min averages are calculated from data on Figure 6.2 and reported as described below Running averages can include a time-lapse break in opacity readings when caused by an element that makes taking a valid reading difficult (e g , fugitive emissions, improper background, or process shutdown). Running averages should not contain time-lapse breaks in the readings as a result of the observer's desire not to take visible emission data for personnel reasons when conditions exist that would allow the observer to take valid opacity data (e g., eye strain or no desire to continue readings) Figure 6.3 is included to provide an easy reference between the VE reading time on Figure 6 1 and the start number on Figure 6.2 The start numbers are used to find the corresponding observation time for the beginning of the calculated six minute average

Determination of the running average is generally performed by computer or by a hand calculator The main purpose of the calculations is to determine the number of 6-min periods in excess of the standard and the greatest value for any 6-min period It is also suggested, but not required, that the opacity readings be plotted on a graph showing percent opacity versus time, with a straight line connecting each subsequent reading.

6.1.1 Use of Computer for Calculations - It is highly recommended that a computer be used to calculate and plot data Programming will vary with the language used by the particular computer, but the basic principle is as follows

Input.

1 Enter all VE readings with their corresponding start number or identifying start time

Computation:

1. The first average opacity reading is obtained by averaging the first 24 opacity readings.
2 Each succeeding running average is obtained from the previous one by adding the next observation reading and subtracting the first observation in the series and then dividing by 24 (assuming 6-min running average).

Printout

1. The computer should print all VE readings with their corresponding number or time This printing will ensure that all readings have been entered properly
2. The computer should search all averages and print the highest average opacity and its corresponding number or time interval
3 Starting at the first interval, the computer should search for all nonoverlapping 6-minute periods in excess of the standard Each interval's average opacity value and corresponding number or time should be printed out
4 Finally the computer should plot VE readings versus time intervals. If the computer has a plotter, it should be used If not, the values can be plotted without connecting lines If desired, the computer can bracket intervals in excess of the standard.

6.1.2 Use of Hand Calculator for Calculations - When a hand calculator is used, the calculation procedures are the same as those for the computer, except that they must be performed manually All data should be recorded on the VE Summary Data Sheet (see Figure 6 2) if desired To avoid calculating average opacity values that are less than the standard, the following procedure can be used. The total value for the 24 readings should be calculated first, and the total opacity should be entered at Start no 1

Each succeeding total value can be obtained and recorded by adding the difference between the value dropped and the one added. These calculations can be performed easily without a calculator If desired, the average opacity reading could then be calculated only for those totals that exceed the total allowable opacity limit (e g , 20% x 24 = 480). Therefore, a total opacity of 480 or greater would be an exceedance of a 20 percent opacity standard Method 9 does, however, require that the accuracy of the method be taken into account when determining possible violations of applicable opacity standard

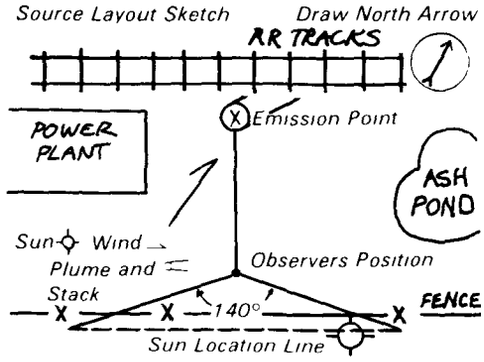
It is suggested that when the opacity standard has been exceeded for any 24 consecutive readings, the data be hand-plotted with each VE reading versus its time interval These plots fit best on graph paper scaled 10 lines to the inch Each 15-second reading can be plotted at 1/2 spacing, thereby allowing 20 readings per inch If desired, intervals of opacity in excess of the standards can be marked on this plot It is much easier to visualize a trend in opacity with time with such a graphical presentation than with tabulated numerical readings as shown in Figure 6 4

6.2 Calculation of Path Length Through the Plume

The observer should be located so that only one plume diameter is being sighted through In rare cases, the observer has no choice but to be relatively close to the stack so that the view is up through the plume rather than across it. In these cases, this extra width of plume should be

SOURCE NAME	ADMIRAL POWER PLANT
ADDRESS	112 OCEAN ROAD
CITY	ADMIRAL CITY
STATE	VA
ZIP	23451
PHONE	804-425-5101
SOURCE ID NUMBER	NEDS 45721
PROCESS EQUIPMENT	OIL FIRED BOILER
OPERATING MODE	BASE LOAD
CONTROL EQUIPMENT	ELECTROSTATIC PRECIPITATOR
OPERATING MODE	RAPPING
DESCRIBE EMISSION POINT	START BRICK STACK 25' DIA. STOP ✓
HEIGHT ABOVE GROUND LEVEL	START 100' STOP ✓
HEIGHT RELATIVE TO OBSERVER	START 100' STOP ✓
DISTANCE FROM OBSERVER	START 400' STOP ✓
DIRECTION FROM OBSERVER	START NNE STOP ✓
DESCRIBE EMISSIONS	START LOFTING PLUME STOP ✓
EMISSION COLOR	START GREY/WHITE STOP ✓
PLUME TYPE	CONTINUOUS ☑ FUGITIVE ☐ INTERMITTENT ☐
WATER DROPLETS PRESENT	NO ☑ YES ☐
IF WATER DROPLET PLUME	ATTACHED ☐ DETACHED ☐
POINT IN THE PLUME AT WHICH OPACITY WAS DETERMINED	START 10' ABOVE STACK EXIT STOP ✓
DESCRIBE BACKGROUND	START SKY STOP W/BROKEN CLOUDS
BACKGROUND COLOR	START BLUE STOP BLUE/WHITE
SKY CONDITIONS	START CLEAR STOP PARTLY CLOUDY
WIND SPEED	START 15mph STOP 20mph
WIND DIRECTION	START SW STOP ✓
AMBIENT TEMP	START 85°F STOP ✓
WET BULB TEMP	54°F
RH, percent	85%

Source Layout Sketch — Draw North Arrow



OBSERVATION DATE	START TIME	STOP TIME
15 JULY 1982	1330	1342

MIN \ SEC	0	15	30	45	MIN \ SEC	0	15	30	45
1	30	35	55	55	31				
2	55	50	40	30	32				
3	35	35	35	35	33				
4	30	35	35	35	34				
5	30	30	30	30	35				
6	35	35	35	35	36				
7	30	30	35	35	37				
8	35	40	60	55	38				
9	60	40	55	60	39				
10	50	45	35	30	40				
11	30	30	30	30	41				
12	30	30	30	30	42				
13					43				
14					44				
15					45				
16					46				
17					47				
18					48				
19					49				
20					50				
21					51				
22					52				
23					53				
24					54				
25					55				
26					56				
27					57				
28					58				
29					59				
30					60				

AVERAGE OPACITY FOR HIGHEST PERIOD 40%

NUMBER OF READINGS ABOVE 40 % WERE 11

RANGE OF OPACITY READINGS MINIMUM 30% MAXIMUM 60%

OBSERVER'S NAME (PRINT) V.E. PROFFIT

OBSERVER'S SIGNATURE V. E. Proffit — DATE 15 JULY 82

ORGANIZATION STATE AIR POLLUTION CONTROL BOARD

CERTIFIED BY EASTERN TECHNICAL ASSOC. — DATE 18 MAY 1982

VERIFIED BY RDA — DATE 15 AUG 1982

COMMENTS USES #6 OIL

I HAVE RECEIVED A COPY OF THESE OPACITY OBSERVATIONS

SIGNATURE William P. Jance

TITLE SHIFT MANAGER — DATE 7-15-82

Figure 6.1. Visible emission observation form

Visible Emission Summary Data Sheet

Company ADMIRAL POWER PLANT Date 15 JULY 1982 Location 112 OCEAN RD., ADMIRAL CITY

Start time 1330 Emission point OIL FIRED BOILER

Start no	Total opacity	Average opacity	Start no	Total opacity	Average opacity	Start no	Total opacity	Average opacity	Start no	Total opacity	Average opacity	Start no	Total opacity	Average opacity	Start no	Total opacity	Average opacity
1	885	36.8	37			73			109			145			181		
2	885	36.8	38			74			110			146			182		
3	880	36.6	39			75			111			147			183		
4	860	35.8	40			76			112			148			184		
5	840	35.0	41			77			113			149			185		
6	845	35.2	42			78			114			150			186		
7			43			79			115			151			187		
8			44			80			116			152			188		
9			45			81			117			153			189		
10			46			82			118			154			190		
11			47			83			119			155			191		
12			48			84			120			156			192		
13			49			85			121			157			193		
14			50			86			122			158			194		
15			51			87			123			159			195		
16			52			88			124			160			196		
17			53			89			125			161			197		
18			54			90			126			162			198		
19			55			91			127			163			199		
20			56			92			128			164			200		
21			57			93			129			165			201		
22			58			94			130			166			202		
23			59			95			131			167			203		
24			60			96			132			168			204		
25			61			97			133			169			205		
26			62			98			134			170			206		
27			63			99			135			171			207		
28			64			100			136			172			208		
29			65			101			137			173			209		
30			66			102			138			174			210		
31			67			103			139			175			211		
32			68			104			140			176			212		
33			69			105			141			177			213		
34			70			106			142			178			214		
35			71			107			143			179			215		
36			72			108			144			180			216		

Maximum average 36.8 % Start number of six minute average 1

Number of nonoverlapping averages in excess of standard 3 Listing start number of these averages 1, 12, 80, 175

Calculated by V.E. PROFFET Date 16 JULY 83 Reviewed by _____ Date 17 JULY 1982

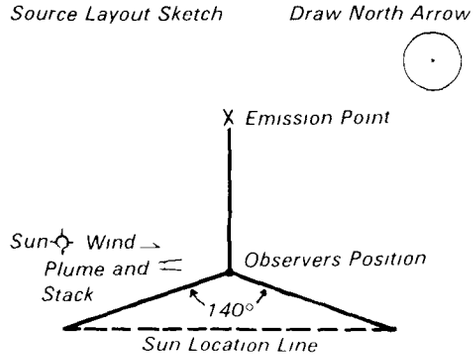
Figure 6.2. *Visible emission summary data sheet*

VISIBLE EMISSION OBSERVATION FORM

SOURCE NAME	OBSERVATION DATE	START TIME / STOP TIME
ADDRESS		
CITY	STATE	ZIP
PHONE	SOURCE ID NUMBER	
PROCESS EQUIPMENT	OPERATING MODE	
CONTROL EQUIPMENT	OPERATING MODE	
DESCRIBE EMISSION POINT START STOP		
HEIGHT ABOVE GROUND LEVEL START STOP	HEIGHT RELATIVE TO OBSERVER START STOP	
DISTANCE FROM OBSERVER START STOP	DIRECTION FROM OBSERVER START STOP	
DESCRIBE EMISSIONS START STOP		
EMISSION COLOR START STOP	PLUME TYPE CONTINUOUS ☐ FUGITIVE ☐ INTERMITTENT ☐	
WATER DROPLETS PRESENT NO ☐ YES ☐	IF WATER DROPLET PLUME ATTACHED ☐ DETACHED ☐	
POINT IN THE PLUME AT WHICH OPACITY WAS DETERMINED START STOP		
DESCRIBE BACKGROUND START STOP		
BACKGROUND COLOR START STOP	SKY CONDITIONS START STOP	
WIND SPEED START STOP	WIND DIRECTION START STOP	
AMBIENT TEMP START STOP	WET BULB TEMP	RH,percent

SEC / MIN	0	15	30	45	SEC / MIN	0	15	30	45
1	1	2	3	4	31	121	122	123	124
2	5	6	7	8	32	125	126	127	128
3	9	10	11	12	33	129	130	131	132
4	13	14	15	16	34	133	134	135	136
5	17	18	19	20	35	137	138	139	140
6	21	22	23	24	36	141	142	143	144
7	25	26	27	28	37	145	146	147	148
8	29	30	31	32	38	149	150	151	152
9	33	34	35	36	39	153	154	155	156
10	37	38	39	40	40	157	158	159	160
11	41	42	43	44	41	161	162	163	164
12	45	46	47	48	42	165	166	167	168
13	49	50	51	52	43	169	170	171	172
14	53	54	55	56	44	173	174	175	176
15	57	58	59	60	45	177	178	179	180
16	61	62	63	64	46	181	182	183	184
17	65	66	67	68	47	185	186	187	188
18	69	70	71	72	48	189	190	191	192
19	73	74	75	76	49	193	194	195	196
20	77	78	79	80	50	197	198	199	200
21	81	82	83	84	51	201	202	203	204
22	85	86	87	88	52	205	206	207	208
23	89	90	91	92	53	209	210	211	212
24	93	94	95	96	54	213	214	215	216
25	97	98	99	100	55	217	218	219	220
26	101	102	103	104	56	221	222	223	224
27	105	106	107	108	57	225	226	227	228
28	109	110	111	112	58	229	230	231	232
29	113	114	115	116	59	233	234	235	236
30	117	118	119	120	60	237	238	239	240

Source Layout Sketch Draw North Arrow



AVERAGE OPACITY FOR HIGHEST PERIOD	NUMBER OF READINGS ABOVE % WERE
RANGE OF OPACITY READINGS MINIMUM	MAXIMUM
OBSERVER'S NAME (PRINT)	
COMMENTS	OBSERVER'S SIGNATURE / DATE
	ORGANIZATION
I HAVE RECEIVED A COPY OF THESE OPACITY OBSERVATIONS SIGNATURE	CERTIFIED BY / DATE
TITLE / DATE	VERIFIED BY / DATE

Figure 6.3. Opacity data form with start numbers shown

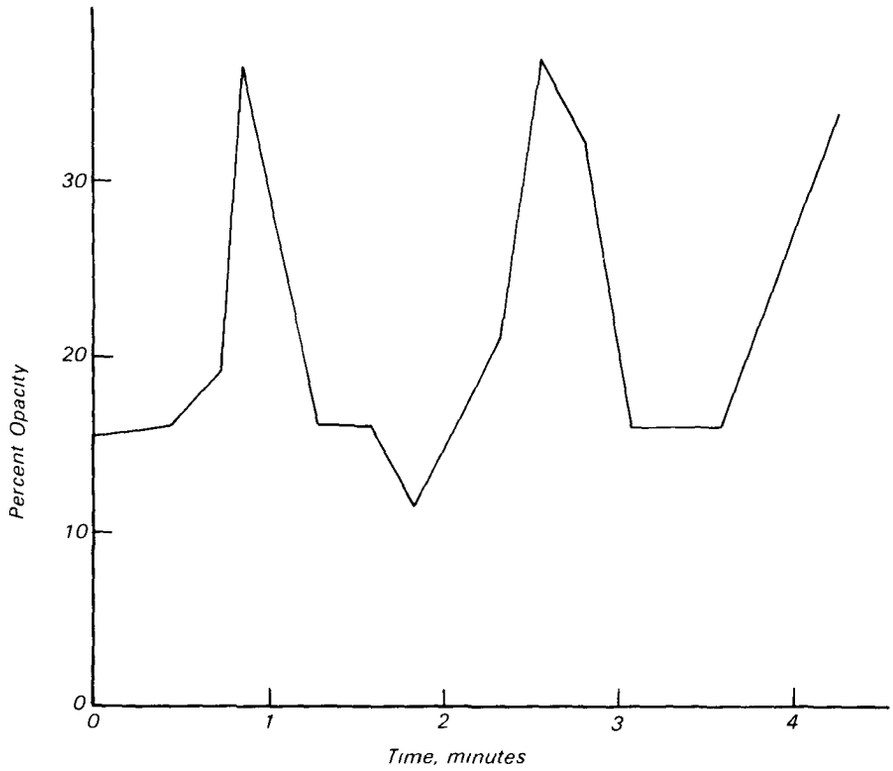


Figure 6.4. Plot opacity versus time

acknowledged and the individual data values may be adjusted mathematically in the final data report to show the increase in opacity reading due to the added path length These adjusted opacity readings should be used in determining averages in excess of the standard

The calculation of observed path length is shown in Appendix A of Reference 1 and is included here for the observer's convenience Figure 6 5 shows how the slant angle varies with distance from an elevated source. As an observer moves closer to the base of the stack, the angle of sight and the path length through the plume both increase; this causes the observed opacity to increase even though the cross-plume opacity remains constant This situation only applies when the opacity is read through a vertically rising plume and the observer is on the same plane as the base of the stack

The actual opacity may be calculated from the observed opacity, if the slant angle θ is known, or from the known height of the stack and the distance from the observer to the base of the stack.

Method 1 (when slant angle θ is known)

$$1 - \left(\frac{O_o}{100}\right) = T_o \qquad \text{Equation 6-1}$$

$$(1 - T_o^F) \times 100 = O_c$$

where

O_o = observed opacity in %
T_o = observed transmittance
F = cosine of θ
O_c = corrected opacity in %.

Method 2 (where distances are known)

$$F = \frac{Y}{\sqrt{H^2 + Y^2}} \qquad \text{Equation 6-2}$$

$$1 - \left(\frac{O_o}{100}\right) = T_o$$

$$(1 - T_o^F) \times 100 = O_c$$

where

O_o = observed opacity in %
T_o = observed transmittance
F = cosine of θ
O_c = corrected opacity in %
H = height of stack
Y = distance of observer from stack.

Note: Since the correction is a power function, the correction must be made on each opacity reading and the corrected values used for calculations, in lieu of the correction being conducted on the reduced (averaged) data

Table 6 1 presents the opacity corrected for slant angle or viewing angle θ versus the full range of opacity readings. For angles less than approximately 18° the adjustment is relatively insignificant.

6.3 Predicting Steam Plume Formation

The psychrometric chart can be used in conjunction with a simple

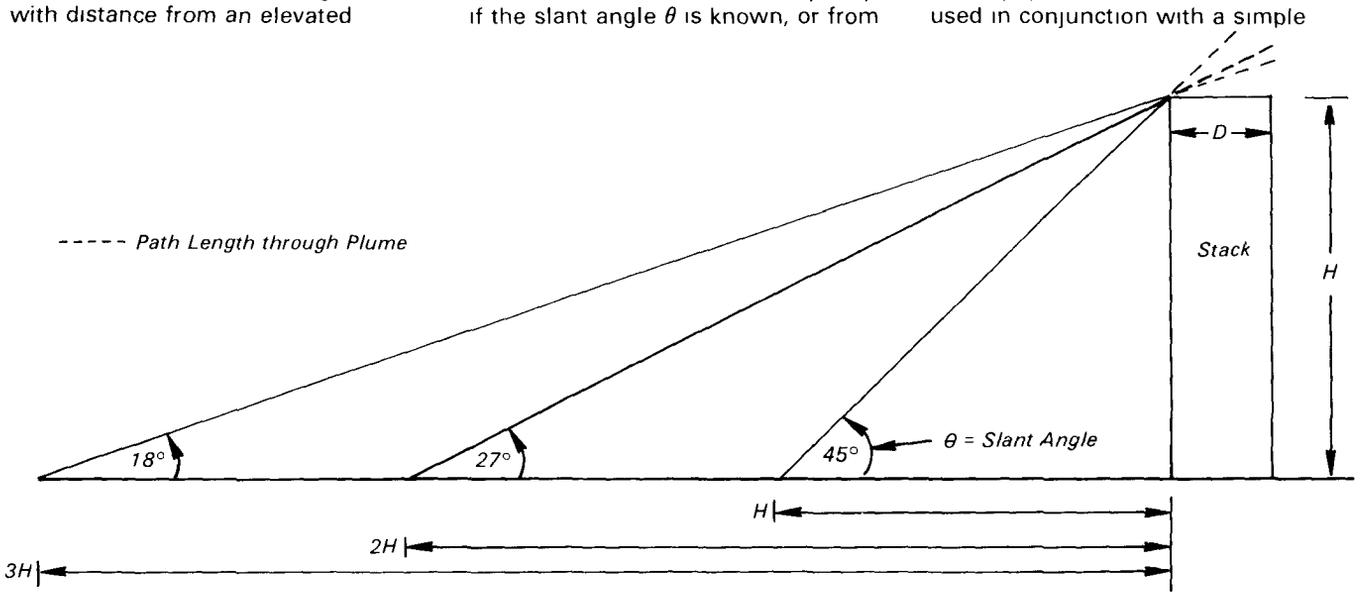


Figure 6.5. Variation of observation angle and pathlength with distance from an elevated source

Table 6.1. *Opacity Correction for Slant Angle*

Measured opacity, %	Slant angle θ, degrees 0	10	20	30	40	50	60
95	95	95	94	93	90	85	78
90	90	90	89	86	83	77	68
85	85	85	83	81	77	71	62
80	80	80	78	75	71	65	55
75	75	75	73	70	65	59	50
70	70	70	68	65	60	54	45
65	65	64	63	60	55	49	41
60	60	59	58	55	50	45	37
55	55	55	53	50	46	40	33
50	50	50	48	45	41	36	29
45	45	45	43	40	37	32	26
40	40	40	38	36	32	28	23
35	35	35	33	31	28	24	19
30	30	30	29	27	24	21	16
25	25	25	24	22	20	17	13
20	20	20	19	18	16	13	11
15	15	15	14	13	12	10	8
10	10	10	9	9	8	7	5
5	5	5	4	4	3	3	3
0	0	0	0	0	0	0	0

equation to predict the formation of a visible water vapor (steam) plume. The psychrometric chart is a graphical representation of the solutions of various equations of the state of air and water vapor mixtures (see Figure 6 6) Both the ambient and stack emission data points on the chart are referred to as their "state point" and represent one unique combination of the following five atmospheric properties.

Dry bulb temperature - The actual ambient temperature; represented by the horizontal axis

Wet bulb temperature - The temperature indicated by a "wet bulb" thermometer (a regular thermometer that has its bulb covered with a wet wick and exposed to a moving air stream); represented by the curved axis on the left side of the chart (saturation temperature)

Relative humidity - The ratio of the partial pressure of the water vapor to the vapor pressure of water at the same temperature; values are represented by the set of curved lines originating in the lower left portion of the chart.

Absolute humidity (humidity ratio) - The mass of water vapor per unit mass of air, expressed as grains per pound or pound per pound; represented by the vertical axes.

Specific volume - The volume occupied by a unit mass of air, expressed as cubic feet per pound; represented by the diagonal lines running from lower right to upper left. The relationships shown in the chart differ with changes in barometric pressure. The chart included in this section is for a barometric pressure of 29.92 inches of mercury. Therefore, with use of wet bulb dry bulb technique, if the actual pressure is less than about 29.5 inches of mercury, the humidity ratio should be calculated from the equation and not the chart.

Plotting the values for any two of the five atmospheric properties determines the values for the remaining three properties. For example, by using a sling psychrometer to measure the wet and dry bulb temperatures, one can determine the relative humidity, the absolute humidity, and the specific volume of the air.

To predict the occurrence of a visible steam plume, both the ambient air conditions and the stack gas conditions must be known or calculated and located on the psychrometric chart. If any portion of the line connecting the two points lies to the left of the 100 percent relative humidity line, it is an indication that the change of the exhaust gas from the stack state conditions to the ambient air state will be accompanied by the condensation of the water vapor present in the exhaust stream and a resultant visible steam plume.

Obtaining the state point for the ambient air conditions is relatively simple, as previously indicated, the wet and dry bulb temperatures, which will determine a unique state point, can be measured by using a sling psychrometer. Often the only data available for determining the state point of the stack gas are the dry bulb temperature of the exhaust gas stream and its moisture content.* However, a relationship exists between the moisture content and the humidity ratio (or absolute humidity), as shown in the following equation:

$$HR = \frac{0.62\,(MC)}{1 - MC} \quad \text{Equation 6-3}$$

where

HR = humidity ratio, in pound of water vapor per pound of dry air

MC = $\frac{\%}{100}$ moisture content, expressed as a decimal.

The following sample problem demonstrates the use of this equation

Given:

Ambient conditions
- Dry bulb temperature = 70°F
- Wet bulb temperature = 60°F
- Barometric pressure = 29.92 in. Hg

Effluent gas conditions
- Dry bulb temperature = 160°F
- Moisture content = $\frac{16.8\%}{100}$ = 0.168

Find.

Ambient relative humidity
Exhaust gas humidity ratio
Determine whether or not condensed water (steam plume) will form

Table 6.2. *Vapor Pressures of Water at Saturation*

Temp, °F	Water vapor pressure, in. Hg 0	1	2	3	4	5	6	7	8	9
30	0 1647	0.1716	0 1803	0 1878	0 1955	0 2035	0 2118	0.2203	0.2292	0.2383
40	0 2478	0.2576	0 2677	0 2783	0 2891	0 3004	0 3120	0 3240	0 3364	0 3493
50	0 3626	0 3764	0 3906	0.4052	0 4203	0 4359	0.4520	0 4586	0 4858	0.5035
60	0 5218	0 5407	0 5601	0 5802	0 6009	0 6222	0 6442	0.6669	0.6903	0 7144
70	0.7392	0 7648	0 7912	0 8183	0 8462	0 8750	0 9046	0 9352	0 9666	0 9989
80	1 032	1 066	1 102	1.138	1 175	1 213	1 253	1 293	1 335	1.378
90	1 422	1 467	1 513	1 561	1 610	1 660	1.712	1.765	1 819	1 875
100	1.932	1 992	2 052	2 114	2 178	2 243	2 310	2 379	2 449	2.521
110	2 596	2 672	2 749	2.829	2 911	2 995	3 081	3 169	3 259	3 351
120	3 446	3 543	3 642	3.744	3 848	3 954	4 063	4.174	4.289	4.406
130	4 525	4 647	4 772	4.900	5 031	5 165	5 302	5.442	5 585	5.732

*These are usually obtained from plant records or are estimated from recent source test data

Solution:

Plot ambient wet bulb and dry bulb temperatures (see Figure 6.5).

Ambient relative humidity = 55%

Exhaust gas humidity ratio = HR

$$HR = \frac{0.62\ (MC)}{1 - MC} = \frac{0.62\ (0.168)}{1 - 0.168} = 0.125 \text{ lb/lb dry air}$$

Plot humidity ratio and stack dry bulb temperature (see Figure 6 6) Connect the ambient state point and stack gas state point with a straight line (see Figure 6.5). The line crosses the 100 percent relative humidity line, thus, formation of a visible water vapor plume is probable.

When the wet bulb/dry bulb technique is used and the barometric pressure is less than 29.5 in. Hg, it is suggested that Equation 6-5 be used to calculate the moisture content (MC).

$$MC = \frac{V.P.}{P_{abs}} \qquad \text{Equation 6-5}$$

where

VP = Vapor pressure of H_2O using Equation 6-6

P_{abs} = Barometric pressure

$$VP = SVP - (3.57 \times 10^{-4})\ (P_{abs})\ (T_d - T_w)\ \left(1 + \frac{T_w - 32}{1571}\right) \qquad \text{Equation 6-6}$$

where

SVP = Saturated vapor pressure in in Hg at wet bulb temperature (taken from Table 6.2)

T_d = Temperature of dry bulb thermometer, °F

T_w = Temperature of wet bulb thermometer, °F

Table 6.3 *Activity Matrix for Calculations*

Calculation	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Average opacity	*Data in Fig 6.1 completed and checked to within roundoff error*	*For each compliance test, perform independent check of data form and calculations*	*Complete the data and initial any changes in calculations*
Running average opacity	*Data in Fig 6.2 completed and checked*	*As above*	*As above*
Path length through the plume	*No limits have been set*	*For each compliance test with the slant angle >18°, calculate using Eq. 6-1*	*Perform calculations*
Predicting steam plume	*No limits have been set*	*Use psychrometric chart and Equation 6-3*	*Perform calculations*

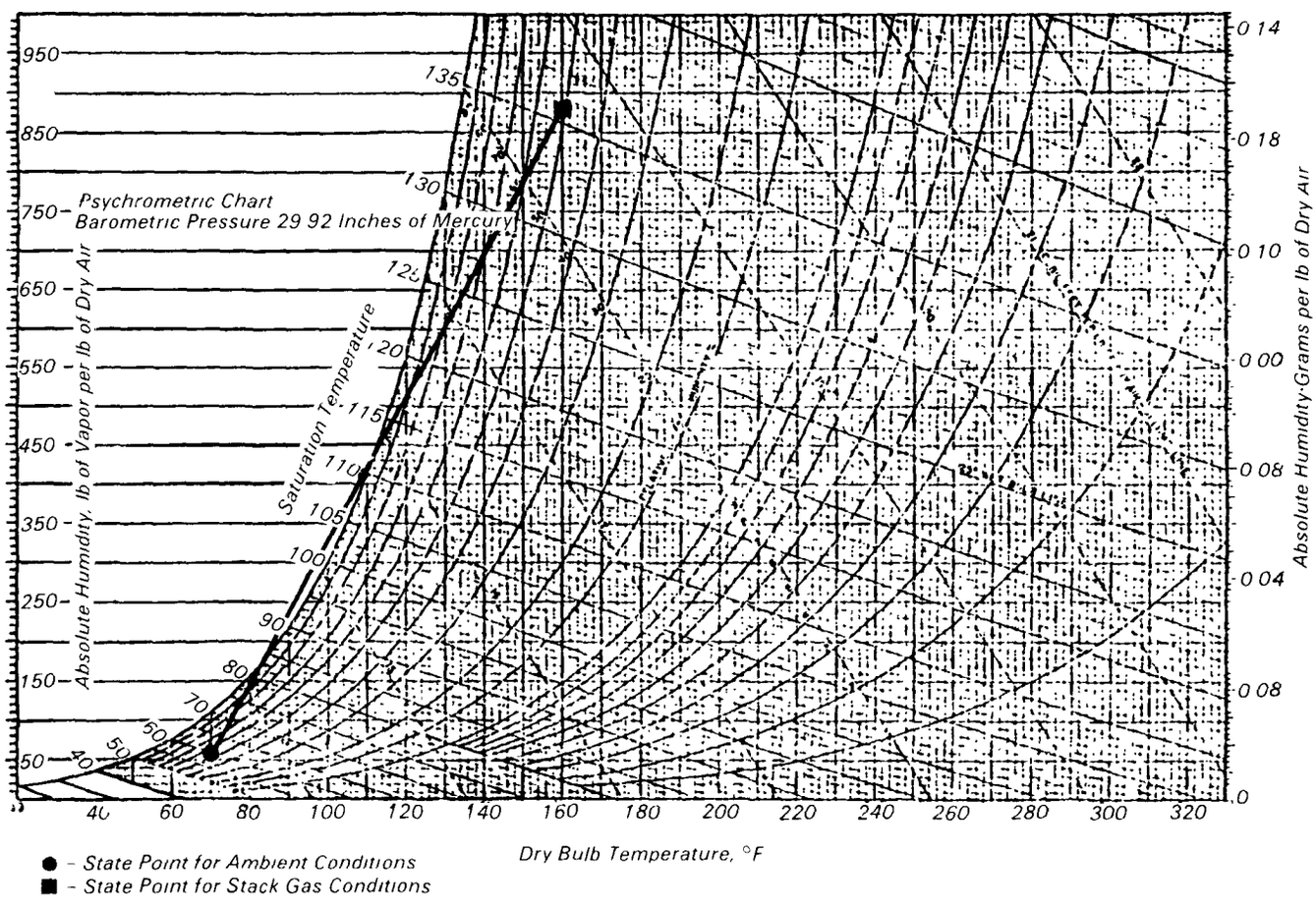


Figure 6 6 *Psychrometric chart for problem solution*

7.0 Auditing Procedures

An audit is an independent assessment of data quality Independence is achieved by using observers and data analysts other than the original observer/analyst Routine QA checks for proper observer positioning and documentation are necessary to obtain good quality data. Table 7.1 at the end of this section summarizes the QA activities for auditing

Two performance audits are recommended for VE readings

1. Audit of observer by having an experienced observer make independent readings
2. Audit of data forms and calculations

In addition, it is recommended that a systems audit be conducted by an experienced observer at the same time the performance audit of visible emissions is conducted. The two performance audits are described in Subsection 7 1 and the systems audit is described in Subsection 7 2

7.1 Performance Audits

Performance audits are quantitative evaluations of the quality of visible emission data.

7.1.1 Performance Audit of Visible Emissions - In this audit, an experienced observer goes with the observer being audited and both observers take the readings simulataneously (using the same time piece) and complete the data forms as independently as is practical The audit is intended for observers in their first year and observers who have not made opacity observation in the field in over a year The differences between the two readings serve as a measure of accuracy assuming the experienced observer reads the "true opacity " Because this assumption is not necessarily correct, the difference between the two readings is a combined measure of accuracy of both observers For a minimum of six minutes (24 readings), the average of the absolute differences should be less than 10 percent, and no individual differences should exceed 20 percent (The values of 10% and 20% suggested for the limits are the approximate results of combining the allowable errors of the two observers, e.g ,$\sqrt{(7.5)^2 + (7\ 5)^2}$ = 10 6%, and $\sqrt{15^2 + 15^2}$ = 21 2% This audit should be performed twice in a year for the first year of an observer and whenever conditions tend to warrant them thereafter Calculate %A using Equation 7-1.

$$\%A = |VE\ (observer) - VE\ (auditor)| \qquad \text{Equation 7-1}$$

where

VE (observer) = average and individual VE reading(s) of the observer being audited

VE (auditor) = average and individual VE reading(s) of the auditor

7.1.2 Performance Audit of Data Calculations - This audit is an independent check of all calculations performed for the summary VE report Every calculation should be checked within round-off error This audit should be conducted on at least 7 percent of the annual numbers of VE summary reports.

7.2 System Audit

A system audit provides an on-site qualitative inspection and review of the total inspection. This audit includes a check of the "Record of Visual Determination of Opacity," Figure 9 1 of Section 3 12 8, and the top portion of the "Observation Record," Figure 9.2 of Section 3.12.8. In addition, the auditor should assess the visible emission inspection technique used by the auditee. This portion of the system audit is best handled in conjunction with the performance audit described in the previous Subsection 7 1 1. Therefore, the frequency of the system audit should coincide with the frequency of the performance audits of visible emissions. Some observations to be made by the auditor are listed in Figure 7 1

Table 7.1. *Activity Matrix for Auditing Procedures*

Audit	*Acceptance limits*	*Frequency and method of measurement*	*Action if requirements are not met*
Performance audit of visible emissions	*Individual observations within ±20%, average (absolute) deviation within ±10%*	*At least two times during the first year; simultaneous observation and data recording*	*Review observation techniques*
Performance audit of data calculations	*Original and check calculations agree within round-off error*	*Seven percent of tests for compliance, perform independent check on all calculations*	*Check and correct all calculated results (averages)*
System audit	*Conduct observations as described in this section of the Handbook*	*At least two times during the first year; use audit checklist (Fig 7.1)*	*Explain to observer the deviations from recommended procedures; note the deviations on Fig 7 1*

Name of individual(s) audited Buff A. Low

Affiliation New York State Agency

Auditor name N. Jersey Affiliation Region II EPA

Date of audit 12·25·82 Auditor signature New Jersey

Yes	No	Comment	Operation
✓			1 Equipment satisfactory
✓			2 Data forms completed
✓			3 Post-notification (courtesy obligation) performed
✓			4 Correct identification of point of emissions
✓			5. Plume associated with process generation point
✓			6 Credentials okay
✓			7 Observer acted in professional and courteous manner
✓			8 Proper observer position
✓			9 Opacity readings complete
✓			10 Ancillary measurements available
✓		confidentially required	11 Camera used to validate sightings/source identification
✓			12 Facility personnel given a copy of raw data
		N/A	13 Mutiple sources/plumes/outlets
✓			14 Lighting conditions satisfactory
			15 Background conditions (raining, etc) satisfactory
✓			16 Slant angle recorded
		N/A	17 Fugitive emissions
✓			18 Time of day recorded
✓			19 Recertified within last 6 months

General comments:

Performance Audit of VE Readings Were Acceptable. However, All of the VE Readings were less than 20% in Opacity from the source.

Figure 7.1. *Method 9 checklist for auditors.*

8.0 Reference Method[a]

Method 9—Visual Determination of the Opacity of Emissions from Stationary Sources

Many stationary sources discharge visible emissions into the atmosphere; these emissions are usually in the shape of a plume This method involves the determination of plume opacity by qualified observers The method includes procedures for the training and certification of observers, and procedures to be used in the field for determination of plume opacity The appearance of a plume as viewed by an observer depends upon a number of variables, some of which may be controllable and some of which may not be controllable in the field Variables which can be controlled to an extent to which they no longer exert a significant influence upon plume appearance include. Angle of the observer with respect to the plume, angle of the observer with respect to the sun, point of observation of attached and detached steam plume, and angle of the observer with respect to a plume emitted from a rectangular stack with a large length to width ratio The method includes specific criteria applicable to these variables

Other variables which may not be controllable in the field are luminescence and color contrast between the plume and the background against which the plume is viewed These variables exert an influence upon the appearance of a plume as viewed by an observer, and can affect the ability of the observer to accurately assign opacity values to the observed plume Studies of the theory of plume opacity and field studies have demonstrated that a plume is most visible and presents the greatest apparent opacity when viewed against a contrasting background It follows from this, and is confirmed by field trials, that the opacity of a plume, viewed under conditions where a contrasting background is present can be assigned with the greatest degree of accuracy However, the potential for a positive error is also the greatest when a plume is viewed under such contrasting conditions Under conditions presenting a less contrasting background, the apparent opacity of a plume is less and approaches zero as the color and luminescence contrast decrease toward zero As a result, significant negative bias and negative errors can be made when a plume is viewed under less contrasting conditions. A negative bias decreases rather than increases the possibility that a plant operator will be cited for a violation of opacity standards due to observer error

Studies have been undertaken to determine the magnitude of positive errors which can be made by qualified observers while reading plumes under contrasting conditions and using the procedures set forth in this method. The results of these studies (field trials) which involve a total of 769 sets of 25 readings each are as follows:

(1) For black plumes (133 sets at a smoke generator). 100 percent of the sets were read with a positive error[1] of less than 7 5 percent opacity, 99 percent were read with a positive error of less than 5 percent opacity.
(2) For white plumes (170 sets at a smoke generator, 168 sets at a coal-fired power plant, 298 sets at a sulfuric acid plant), 99 percent of the sets were read with a positive error of less than 7 5 percent opacity; 95 percent were read with a positive error of less than 5 percent opacity.

The positive observational error associated with an average of twenty-five readings is therefore established. The accuracy of the method must be taken into account when determining possible violations of applicable opacity standards.

1. Principle and applicability.

1.1 Principle The opacity of emissions from stationary sources is determined visually by a qualified observer

1.2 Applicability. This method is applicable for the determination of the opacity of emissions from stationary sources pursuant to § 60.11(b) and for qualifying observers for visually determining opacity of emissions.

[1]For a set, positive error = average opacity determined by observers' 25 observations — average opacity determined from transmissometer's 25 recordings

2. Procedures.

The observer qualified in accordance with paragraph 3 of this method shall use the following procedures for visually determining the opacity of emissions:

2.1 Position. The qualified observer shall stand at a distance sufficient to provide a clear view of the emissions with the sun oriented in the 140° sector to his back Consistent with maintaining the above requirement, the observer shall, as much as possible, make his observations from a position such that his line of vision is approximately perpendicular to the plume direction, and when observing opacity of emissions from rectangular outlets (e.g. roof monitors, open baghouses, noncircular stacks), approximately perpendicular to the longer axis of the outlet. The observer's line of sight should not include more than one plume at a time when multiple stacks are involved, and in any case the observer should make his observations with his line of sight perpendicular to the longer axis of such a set of multiple stacks (e.g. stub-stacks on baghouses).

2.2 Field records. The observer shall record the name of the plant, emission location, type facility, observer's name and affiliation, and the date on a field data sheet (Figure 9-1). The time, estimated distance to the emission location, approximate wind direction, estimated wind speed, description of the sky condition (presence and color of clouds), and plume background are recorded on a field data sheet at the time opacity readings are initiated and completed.

2.3 Observations. Opacity observations shall be made at the point of greatest opacity in that portion of the plume where condensed water vapor is not present. The observer shall not look continuously at the plume, but instead shall observe the plume momentarily at 15-second intervals.

2.3.1. Attached steam plumes. When condensed water vapor is present within the plume as it emerges from the emission outlet, opacity observations shall be made beyond the point in the plume at which

Company _____
Location _____
Test Number _____
Date _____
Type Facility _____
Control Device _____

Hours of Observation _____
Observer _____
Observer Certification Date _____
Observer Affiliation _____
Point of Emissions _____
Height of Discharge Point _____

Clock Time	*Initial*			*Final*
Observer Location *Distance to Discharge*				
Direction from Discharge				
Height of Observation Point				
Background Description				
Weather Conditions *Wind Direction*				
Wind Speed				
Ambient Temperature				
Sky Conditions (clear, overcast, % clouds, etc)				
Plume Description *Color*				
Distance Visible				
Other Information				

Summary of Average Opacity

Set Number	*Time*	*Opacity*	
	Start—End	*Sum*	*Average*

Readings ranged from _____ *to* _____ *% opacity*

The source was/was not in compliance with _____ *at the time evaluation was made.*

Figure 9.1 *Record of Visual Determination of Opacity*

Page _____ *of* _____

condensed water vapor is no longer visible. The observer shall record the approximate distance from the emission outlet to the point in the plume at which the observations are made

2.3.2 Detached steam plume. When water vapor in the plume condenses and becomes visible at a distinct distance from the emission outlet, the opacity of emissions should be evaluated at the emission outlet prior to the condensation of water vapor and the formation of the steam plume.

2.4 *Recording observations.* Opacity observations shall be recorded to the nearest 5 percent at 15-second intervals on an observational record sheet (See Figure 9-2 for an example.) A minimum of 24 observations shall be recorded Each momentary observation recorded shall be deemed to represent the average opacity of emissions for a 15-second period.

2.5 *Data Reduction* Opacity shall be determined as an average of 24 consecutive observations recorded at 15-second intervals. Divide the observations recorded on the record sheet into sets of 24 consecutive observations. A set is composed of any 24 consecutive observations. Sets need not be consecutive in time and in no case shall two sets overlap. For each set of 24 observations, calculate the average by summing the opacity of the 24 observations and dividing this sum by 24 If an applicable

Company _____ Observer _____
Location _____ Type Facility _____
Test Number _____ Point of Emissions _____
Date _____

Hr	Min.	Seconds				Steam Plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	0							
	1							
	2							
	3							
	4							
	5							
	6							
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Figure 9.2 Observation Record

Page ____ of ____

standard specifies an averaging time requiring more than 24 observations, calculate the average for all observations made during the specified time period. Record the average opacity on a record sheet. (See Figure 9-1 for an example.)

3. Qualifications and testing.

3.1 Certification requirements. To receive certification as a qualified observer, a candidate must be tested and demonstrate the ability to assign opacity readings in 5 percent increments to 25 different black plumes and 25 different white plumes, with an error not to exceed 15 percent opacity on any one reading and an average error not to exceed 7.5 percent opacity in each category. Candidates shall be tested according to the procedures described in paragraph 3.2. Smoke generators used pursuant to paragraph 3.2 shall be equipped with a smoke meter which meets the requirements of paragraph 3.3.

The certification shall be valid for a period of 6 months, at which time the qualification procedure must be repeated by any observer in order to retain certification.

3.2 Certification procedure.

The certification test consists of showing the candidate a complete run of 50 plumes—25 black plumes and 25 white plumes—generated by a smoke generator. Plumes within each set of 25 black and 25 white runs shall be presented in random order. The candidate assigns an opacity value to each plume and records his observation on a suitable form. At the completion of each run of 50 readings, the score of the candidate is determined. If a candidate fails to qualify, the complete run of 50 readings must be repeated in any retest. The smoke test may be administered as part of a smoke school or training program, and may be preceded by training or familiarization runs of the smoke generator during which candidates are shown black and white plumes of known opacity.

3.3 Smoke generator specifications.

Any smoke generator used for the purposes of paragraph 3.2 shall be equipped with a smoke meter installed to measure opacity across the diameter of the smoke generator stack. The smoke meter output shall display instack opacity based upon a path length equal to the stack exit diameter, on a full 0 to 100 percent chart recorder scale. The smoke meter optical design and performance shall meet the specifications shown in Table 9-1. The smoke meter shall be calibrated as prescribed in paragraph 3.3.1 prior to the conduct of each smoke reading test. At the completion of each test, the zero and span drift shall be checked and if the drift exceeds ±1 percent opacity, the conditions shall be corrected prior to conducting any subsequent test runs. The smoke meter shall be demonstrated, at the time of installation, to meet the specifications listed in Table 9-1. This demonstration shall be repeated following any subsequent repair or replacement of the photocell or associated electronic circuitry including the chart recorder or output meter, or every 6 months, whichever occurs first.

Table 9-1. *Smoke Meter Design and Performance Specifications*

Parameter:	*Specification*
a. Light source	*Incandescent lamp operated at nominal rated voltage.*
b. Spectral response of photocell.	*Photopic (daylight spectral response of the human eye—reference 4.3).*
c. Angle of view	*15° maximum total angle.*
d. Angle of projection	*15° maximum total angle.*
e. Calibration error	*±3% opacity, maximum*
f. Zero and span drift.	*±1% opacity, 30 minutes.*
g. Response time	*≤5 seconds.*

3.3.1 Calibration. The smoke meter is calibrated after allowing a minimum of 30 minutes warmup by alternately producing simulated opacity of 0 percent and 100 percent. When stable response at 0 percent or 100 percent is noted, the smoke meter is adjusted to produce an output of 0 percent or 100 percent, as appropriate. This calibration shall be repeated until stable 0 percent and 100 percent readings are produced without adjustment. Simulated 0 percent and 100 percent opacity values may be produced by alternately switching the power to the light source on and off while the smoke generator is not producing smoke.

3.3.2 Smoke meter evaluation. The smoke meter design and performance are to be evaluated as follows:

3.3.2.1 Light source. Verify from manufacturer's data and from voltage measurements made at the lamp, as installed, that the lamp is operated within ±5 percent of the nominal rated voltage.

3.3.2.2 Spectral response of photocell. Verify from manufacturer's data that the photocell has a photopic response; i.e., the spectral sensitivity of the cell shall closely approximate the standard spectral-luminosity curve for photopic vision which is referenced in (b) of Table 9-1.

3.3.2.3 Angle of view. Check construction geometry to ensure that the total angle of view of the smoke plume, as seen by the photocell, does not exceed 15°. The total angle of view may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of view; d = the sum of the photocell diameter + the diameter of the limiting aperture; and L = the distance from the photocell to the limiting aperture. The limiting aperture is the point in the path between the photocell and the smoke plume where the angle of view is most restricted. In smoke generator smoke meters this is normally an orifice plate.

3.3.2.4 Angle of projection. Check construction geometry to ensure that the total angle of projection of the lamp on the smoke plume does not exceed 15°. The total angle of projection may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of projection; d = the sum of the length of the lamp filament + the diameter of the limiting aperture; and L = the distance from the lamp to the limiting aperture.

3.3.2.5 Calibration error Using neutral-density filters of known opacity, check the error between the actual response and the theoretical linear response of the smoke meter. This check is accomplished by first calibrating the smoke meter according to 3 3.1 and then inserting a series of three neutral-density filters of nominal opacity of 20, 50, and 75 percent in the smoke meter pathlength. Filters calibrated within ±2 percent shall be used. Care should be taken when inserting the filters to prevent stray light from affecting the meter. Make a total of five nonconsecutive readings for each filter. The maximum error on any one reading shall be 3 percent opacity.

3.3.2.6 Zero and span drift Determine the zero and span drift by calibrating and operating the smoke

generator in a normal manner over a 1-hour period The drift is measured by checking the zero and span at the end of this period

3.3.2 7 Response time Determine the response time by producing the series of five simulated 0 percent and 100 percent opacity values and observing the time required to reach stable response. Opacity values of 0 percent and 100 percent may be simulated by alternately switching the power to the light source off and on while the smoke generator is not operating.

4. References.

4.1 Air Pollution Control District Rules and Regulations, Los Angeles County Air Pollution Control District, Regulation IV, Prohibitions, Rule 50.

4.2 Weisburd, Melvin L Field Operations and Enforcement Manual for Air, U S. Environmental Protection Agency, Research Triangle Park, N C., APTD-1100, August 1972, pp 4.1-4.36.

4.3 Condon, E.U., and Odishaw, H., Handbook of Physics, McGraw-Hill Co., N Y , N Y , 1958, Table 3.1, p. 6-52.

9.0 References and Bibliography

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2. *Federal Register,* Volume 39, No. 219, November 12, 1974. Method 9 - Visual Determination of the Opacity of Emissions from Stationary Sources (Appendix A).
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12. Weir, A , Jr., D G. Jones, and L T Paypay. Measurement of Particle Size and Other Factors Influencing Plume Opacity. Paper presented at the International Conference on Environmental Sensing and Assessment, Las Vegas, Nevada, September 14-19, 1975
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14. U.S. Environmental Protection Agency. APTI Course 439 Visible Emissions Evaluation. Instructor Manual. EPA-450/3-78-105, 1978.
15. U.S. Environmental Protection Agency Guidelines for Evaluation of Visible Emissions EPA-340/1-75-007, 1975
16. U.S. Environmental Protection Agency. Screening Procedures for Ambient Air Quality Data EPA-450/2-78-037, July 1978.
17. Validation of Air Monitoring Data. EPA-600/4-80-030, June 1980.

10.0 Data Forms

Blank data forms are provided on the following pages for the convenience of the QA Handbook user No documentation is given on these forms because it would detract from their usefulness. Also, the titles are placed at the top of the figures, as is customary for a data form. These forms are not required format, but are intended as guides for the development of an organizations' own program. To relate the form to the text, a form number is also indicated in the lower right-hand corner (e.g., Form M9-1.1, which implies that the form is Figure 1.1. in Section 3.12.1 of the Method 9 Handbook) Any future revisions of this form can be documented by adding A, B, C (e g., 1 1A, 1.1B). The data forms included in this section are listed below.

Form	*Title*
1.2	Sample Certification Test Form
2 1	Procurement Log
4.1	Visible Emission Observer's Plant Entry Checklist
4.1	Visible Emission Observer's Plant Entry Checklist (Reverse Side)
4.2	Visible Emission Observation Form
4.2	Visible Emission Observation Form (Reverse Side)
5.1	Visible Emission Summary Data Sheet
6.2	Visible Emission Summary Data Sheet (same as Figure 5.1)
7 1	Method 9 Checklist for Auditors

Sample Certification Test Form

Affiliation _____ *Name* _____ *Run Number* _____

Course location _____ *Sunglasses* _____

Date _____ *Sky* _____ *Wind* _____

Distance and direction to stack _____

Reading number																						Error
1	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
2	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
3	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
4	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
5	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
6	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
7	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
8	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
9	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
10	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
11	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
12	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
13	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
14	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
15	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
16	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
17	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
18	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
19	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
20	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
21	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
22	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
23	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
24	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
25	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____

Deviation _____

Reading number																						Error
1	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
2	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
3	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
4	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
5	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
6	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
7	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
8	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
9	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
10	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
11	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
12	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
13	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
14	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
15	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
16	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
17	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
18	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
19	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
20	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
21	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
22	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
23	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
24	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____
25	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	____

Deviation _____

Procurement Log

Item description	*Quantity*	*Purchase order number*	*Vendor*	*Date*		*Cost*	*Disposition*	*Comments*
				Ordered	*Received*			

Visible Emission Observer's Plant Entry Checklist

Source name and address	*Observer* *Agency* *Date of VE observation*

Previous company contact (if applicable)

Title

Purpose of visit

Emission points at which VE observations to be conducted

Authority for entry (see reverse side)

Plant safety requirements

- ☐ *Hardhat*
- ☐ *Safety glasses*
- ☐ *Side shields (on glasses)*
- ☐ *Goggles*
- ☐ *Hearing protection*
  Specify _____
- ☐ *Safety shoes (steel-toed)*
- ☐ *Insulated shoes*
- ☐ *Gloves*
- ☐ *Coveralls*
- ☐ *Dust mask suggested*
- ☐ *Respirator(s)*
  Specify _____
- ☐ *Other*
- ☐ *Specify* _____

Company official contacted (on this visit)

Title

Visible Emission Observer's Plant Checklist (Continued)

Authority for Plant Entry: Clean Air Act, Section 114

(a)(2) the Administrator or his authorized representative upon presentation of his credentials -

(A) shall have a right of entry to, upon or through any premises of such person or in which any records required to be maintained under paragraph (1) of this section are located, and

(B) may at reasonable times have access to, and copy of any records, inspect any monitoring equipment or methods required under paragraph (1), and sample any emissions which such person is required to sample under paragraph (1).

(b) (1) Each State may develop and submit to the Administrator a procedure for carrying out this section in such State If the Administrator finds the State procedure is adequate, he may delegate to such State any authority he has to carry out this section.

(2) Nothing in this subsection shall prohibit the Administrator from carrying out this section in a State.
(c) Any records, reports or information obtained under subsection (a) shall be available to the public except that upon a showing satisfactory to the Administrator by any person that records, reports, or information, or particular part thereof, (other than emission data) to which the Administrator has access under this section if made public would divulge methods or processes entitled to protection as trade secrets of such person, the Administrator shall consider such record, report, or information or particular portion thereof confidential in accordance with the purposes of Section 1905 of Title 18 of the United States concerned with carrying out this Act or when relevant in any proceeding under this Act."

Confidential Information: Clean Air Act, Section 114 (see above) 41 ***Federal Register*** *36902, September 1, 1976*

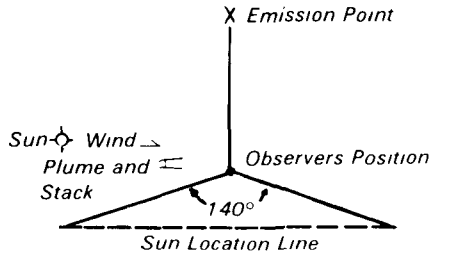
If you believe that any of the information required to be submitted pursuant to this request is entitled to be treated as confidential, you may assert a claim of business confidentiality, covering all or any part of the information, by placing on (or attaching to) the information a cover sheet, stamped or typed legend, or other suitable notice, employing language such as "trade secret," "proprietary," or "company confidential." Allegedly confidential portions of otherwise nonconfidential information should be clearly identified If you desire confidential treatment only until the occurrence of a certain event; the notice should so state Information so covered by a claim will be disclosed by EPA only to the extent, and through the procedures, set forth at 40 CFR, Part 2, Subpart B (41 ***Federal Register*** *36902, September 1, 1976.)*

If no confidentiality claim accompanies this information when it is received by EPA, it may be made available to the public by EPA without further notice to you

Visible Emission Observation Form

SOURCE NAME			OBSERVATION DATE				START TIME		STOP TIME	
ADDRESS			SEC / MIN	0	15	30	45	SEC / MIN	0	15	30	45
			1					31				
CITY	STATE	ZIP	2					32				
PHONE	SOURCE ID NUMBER		3					33				
PROCESS EQUIPMENT	OPERATING MODE		4					34				
CONTROL EQUIPMENT	OPERATING MODE		5					35				
DESCRIBE EMISSION POINT			6					36				
START	STOP		7					37				
HEIGHT ABOVE GROUND LEVEL	HEIGHT RELATIVE TO OBSERVER		8					38				
START STOP	START STOP		9					39				
DISTANCE FROM OBSERVER	DIRECTION FROM OBSERVER		10					40				
START STOP	START STOP		11					41				
DESCRIBE EMISSIONS			12					42				
START	STOP		13					43				
EMISSION COLOR	PLUME TYPE CONTINUOUS ☐		14					44				
START STOP	FUGITIVE ☐ INTERMITTENT ☐		15					45				
WATER DROPLETS PRESENT	IF WATER DROPLET PLUME		16					46				
NO ☐ YES ☐	ATTACHED ☐ DETACHED ☐		17					47				
POINT IN THE PLUME AT WHICH OPACITY WAS DETERMINED			18					48				
START	STOP		19					49				
DESCRIBE BACKGROUND			20					50				
START	STOP		21					51				
BACKGROUND COLOR	SKY CONDITIONS		22					52				
START STOP	START STOP		23					53				
WIND SPEED	WIND DIRECTION		24					54				
START STOP	START STOP		25					55				
AMBIENT TEMP	WET BULB TEMP	RH,percent	26					56				
START STOP			27					57				
			28					58				
			29					59				
			30					60				

Source Layout Sketch *Draw North Arrow*



AVERAGE OPACITY FOR HIGHEST PERIOD	NUMBER OF READINGS ABOVE % WERE
RANGE OF OPACITY READINGS MINIMUM	MAXIMUM
OBSERVER'S NAME (PRINT)	
COMMENTS	OBSERVER'S SIGNATURE / DATE
	ORGANIZATION
I HAVE RECEIVED A COPY OF THESE OPACITY OBSERVATIONS SIGNATURE	CERTIFIED BY / DATE
TITLE / DATE	VERIFIED BY / DATE

Visible Emission Observation Form

This form is designed to be used in conjunction with EPA Method 9, "Visual Determination of the Opacity of Emissions from Stationary Sources" Any deviations, unusual conditions, circumstances, difficulties, etc., not dealt with elsewhere on the form should be fully noted in the section provided for comments Following are brief descriptions of the type of information that needs to be entered on the form; for a more detailed discussion of each part of the form, refer to the "User's Guide to the Visible Emission Observation Form"

***Source Name** - full company name, parent company or division information, if necessary.*

***Address** - street (not mailing) address or physical location of facility where VE observation is being made*

***Phone** - self-explanatory*

***Source ID Number** - number from NEDS, CDS, agency file, etc*

***Process Equipment, Operating Mode** - brief description of process equipment (include ID no.) and operating rate, % capacity utilization, and/or mode (e g , charging, tapping)*

***Control Equipment, Operating Mode** - specify control device type(s) and % utilization, control efficiency*

***Describe Emission Point** - stack or emission point location, geometry, diameter, color, for identification,purposes*

***Height Above Ground Level** - stack or emission point height, from files or engineering drawings*

***Height Relative to Observer** - indicate vertical position of observation point relative to stack top*

***Distance From Observer** - distance to stack ±10%, to determine, use rangefinder or map*

***Direction From Observer** - direction to stack, use compass or map, be accurate to eight points of compass*

***Describe Emissions** - include plume behavior and other physical characteristics (e g , looping, lacy, condensing, fumigating, secondary particle formation, distance plume visible, etc)*

***Emission Color** - gray, brown, white, red, black, etc*

Plume Type:
Continuous - opacity cycle >6 minutes
Fugitive - no specifically designed outlet
Intermittent - opacity cycle <6 minutes

****Water Droplets Present** - determine by observation or use wet sling psychrometer, water droplet plumes are very white, opaque, and billowy in appearance, and usually dissipate rapidly*

****If Water Droplet Plume.***
Attached - forms prior to exiting stack
Detached - forms after exiting stack

****Point in the Plume at Which Opacity was Determined** - describe physical location in plume where readings were made (e g , 4 in above stack exit or 10 ft after dissipation of water plume)*

***Describe Background** - object plume is read against, include atmospheric conditions (e g , hazy)*

***Background Color** - blue, white, new leaf green, etc*

***Sky Conditions** - indicate cloud cover by percentage or by description (clear, scattered, broken, overcast, and color of clouds)*

***Windspeed** - use Beaufort wind scale or hand-held anomometer; be accurate to ±5 mph*

***Wind Direction** - direction wind is **from**; use compass; be accurate to eight points.*

***Ambient Temperature** - in °F or °C.*

****Wet Bulb Temperature** - the wet bulb temperature from the sling psychrometer*

****Relative Humidity** - use sling psychrometer; use local U.S Weather Bureau only if nearby*

***Source Layout Sketch** - include wind direction, associated stacks, roads, and other landmarks to fully identify location of emission point and observer position*

***Draw North Arrow** - point line of sight in direction of emission point, place compass beside circle, and draw in arrow parallel to compass needle*

***Sun Location Line** - point line of sight in direction of emission point, place pen upright on sun location line, and mark location of sun when pen's shadow crosses the observers position*

****Comments** - factual implications, deviations, altercations, and/or problems not addressed elsewhere*

***Acknowledgment** - signature, title, and date of company official acknowledging receipt of a copy of VE observation form*

***Observation Date** - date observations conducted*

***Start Time, Stop Time** - beginning and end times of observation period (e g , 1635 or 4 35 p m)*

***Data Set** - percent opacity to nearest 5%, enter from left to right starting in left column*

***Average Opacity for Highest Period** - average of highest 24 consecutive opacity readings*

***Number of Readings Above (Frequency Count)** count of total number of readings above a designated opacity*

Range of Opacity Readings:
Minimum - lowest reading
Maximum - highest reading

***Observer's Name** - print in full*

***Observer's Signature, Date** - sign and date after performing final calculations*

***Organization** - observer's employer*

***Certifier, Date** - name of "smoke school" certifying observer and date of most recent certification*

***Verifier, Date** - signature of person responsible for verifying observer's calculations and date of verification*

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*Required by Reference Method 9, other items suggested

**Required by Method 9 only when particular factor could affect the reading

Visible Emission Summary Data Sheet

Company _____ *Date* _____ *Location* _____

Start time _____ *Emission point* _____

Start no	Total opacity	Average opacity	Start no	Total opacity	Average opacity	Start no	Total opacity	Average opacity	Start no	Total opacity	Average opacity	Start no	Total opacity	Average opacity	Start no	Total opacity	Average opacity
1			37			73			109			145			181		
2			38			74			110			146			182		
3			39			75			111			147			183		
4			40			76			112			148			184		
5			41			77			113			149			185		
6			42			78			114			150			186		
7			43			79			115			151			187		
8			44			80			116			152			188		
9			45			81			117			153			189		
10			46			82			118			154			190		
11			47			83			119			155			191		
12			48			84			120			156			192		
13			49			85			121			157			193		
14			50			86			122			158			194		
15			51			87			123			159			195		
16			52			88			124			160			196		
17			53			89			125			161			197		
18			54			90			126			162			198		
19			55			91			127			163			199		
20			56			92			128			164			200		
21			57			93			129			165			201		
22			58			94			130			166			202		
23			59			95			131			167			203		
24			60			96			132			168			204		
25			61			97			133			169			205		
26			62			98			134			170			206		
27			63			99			135			171			207		
28			64			100			136			172			208		
29			65			101			137			173			209		
30			66			102			138			174			210		
31			67			103			139			175			211		
32			68			104			140			176			212		
33			69			105			141			177			213		
34			70			106			142			178			214		
35			71			107			143			179			215		
36			72			108			144			180			216		

Maximum average _____ *% Start number of six minute average* ____/ ___

Number of nonoverlapping averages in excess of standard _____ *Listing start number of these averages* _____

Calculated by _____ *Date* _____ *Reviewed by* _____ *Date* _____

Quality Assurance Handbook M9-5.1 and M9-6.2

Method 9 Checklist for Auditors

Name of individual(s) audited _____

Affiliation _____

Auditor name _____ *Affiliation* _____

Date of audit _____ *Auditor signature* _____

Yes	*No*	*Comment*	*Operation*
___	___	_____	*1 Equipment satisfactory*
___	___	_____	*2 Data forms completed*
___	___	_____	*3 Post-notification (courtesy obligation) performed*
___	___	_____	*4 Correct identification of point of emissions*
___	___	_____	*5 Plume associated with process generation point*
___	___	_____	*6 Credentials okay*
___	___	_____	*7 Observer acted in professional and courteous manner*
___	___	_____	*8 Proper observer position*
___	___	_____	*9 Opacity readings complete*
___	___	_____	*10 Ancillary measurements available*
___	___	_____	*11 Camera used to validate sightings/source identification*
___	___	_____	*12 Facility personnel given a copy of raw data*
___	___	_____	*13 Mutiple sources/plumes/outlets*
___	___	_____	*14 Lighting conditions satisfactory*
___	___	_____	*15 Background conditions (raining, etc) satisfactory*
___	___	_____	*16 Slant angle recorded*
___	___	_____	*17 Fugitive emissions*
___	___	_____	*18 Time of day recorded*
___	___	_____	*19 Recertified within last 6 months*

General comments:

*U.S. Government Printing Office: 1991 — 548-187/40519