Section 3.0

GENERAL ASPECTS OF QUALITY ASSURANCE FOR STATIONARY SOURCE EMISSION TESTING PROGRAMS

OUTLINE

SUMMARY

Section 3.0 provides guidelines for quality assurance in performance of emission testing of stationary sources by federally prescribed procedures. The guidelines may be applied to all categories of sources commonly monitored.

The purpose of emission testing (also called "source sampling" or "stack sampling") is to extract from the stack or duct a sample that is representative of emissions from that source during a time period in which the process is under a desired operating condition. The sampling methods prescribed by Federal agencies are for specific substances and types of sources, and are designed to provide representative and reliable data. Since the Federal New Source Performance Standards are promulgated from data obtained by these methods, adherence to these standard procedures for sampling and analysis is essential.

Although personnel engaged in emission testing learn to perform these tests routinely, some of the procedures may not be readily understood by laymen who are involved in hearings or litigations concerning an emission source. When an enforcement agency must rely on results of emissions testing, the test results may be subjected to the requirements of legal rules of evidence. Emissions monitoring personnel, therefore, should not only follow standard testing procedures but should also document each step of the test by maintaining complete and accurate records.

The following guidelines for assurance of high quality emissions test data are presented in four major phases: planning the test program, performing the test, chain-of-custody procedure, and establishing the traceability of calibration gases. Specific method descriptions are given in subsequent sections of this Handbook.

GENERAL QUALITY ASSURANCE GUIDELINES

1.0 PLANNING THE TEST PROGRAM

Although a detailed and specific plan will be developed for each test program, the factors discussed here apply to all cases and provide a basis for formulation of a test plan.

The reason for conducting the emission test must first be carefully determined. Data may be required to check for compliance with a specific regulation, to measure process stream losses, or to obtain engineering data for designing control equipment. The guidelines presented in this Handbook are designed to provide more accurate data regardless of the test purpose. The test methods discussed here are those used to determine compliance with U.S. EPA emission regulations. These methods can also be used in other applications, but caution must be exercised against overloading the equipment due to higher pollutant concentrations or introducing interferences.

For compliance testing, the first planning step is to determine the applicable emission control regulation. Since most control regulations designate specific process conditions to be monitored and recorded as part of a valid emission test, a thorough understanding of the regulation is a prerequisite to formulating the sampling plan. Monitoring personnel may become familiar with specific industry operations and the required test data through inspection manuals published by EPA.

1.1 Preliminary Plant Survey

The next step in developing the test program is a preliminary survey of the process and the test site. Except in the most routine cases, an on-site inspection or presurvey should be performed to determine process information, emission parameters, and locations of sampling points. The presurvey may be made by telephone, particularly when the monitoring personnel have had experience with the specific industry/process.

Considerable information concerning the process to be monitored may be gained in advance of the on-site survey by consulting a registration form or permit application pertaining to the plant operations. These forms provide valuable data on process throughput, emission factors, material balances, types and sizes of fans and motors, and similar items. From these data, one can often estimate gas flow rates and compositions of effluents. For testing of new sources, the plant's construction permit may provide a guide to locations of test ports and scaffolding.

A further step in preparing for the on-site survey is to assemble the equipment that may be required to obtain preliminary data such as:

1. A 10°-to-650°C (50°-to-1200°F) dial thermometer, 30-cm (12-in.) stem.
2. Velocity meter (velometer, Pitot tube, or anemometer).
3. A 15-m (50-ft) tape measure.
4. Set of basic shop tools.
5. Polaroid type camera.
6. Gas absorption colorimetric indicator tubes for SO_2, CO, NO_x, HC, etc.
7. Survey data forms.
8. Safety equipment (hardhats, safety shoes, goggles, etc.).

1.2 Process Information

One plant employee should be designated as the personal contact for monitoring personnel. This person should understand the process thoroughly and must have authority to obtain information and to elicit the cooperation of other plant personnel. A member of the staff of the plant manager or the plant engineer is often an appropriate contact.

The on-site survey is greatly facilitated by use of a survey form that lists the process parameters. Figures 1.1 and 1.2 are example forms for use in the presurvey of combustion and incineration sources. These forms are general guides; in

Type of Heat Exchanger

	Primary	Standby
Coal fired	☐	☐
Oil fired	☐	☐
Gas fired	☐	☐

If multiple fired, check appropriate boxes

Rated input capacity ________ Btu/h
Maximum operating rate ________ Btu/h
Rated steam output ________ lb/h @ ________ Btu/lb steam
Maximum steam output ________ lb/h @ ________ Btu/lb steam
Furnace volume, width ____ ft × depth ____ ft × height ____ ft = ____ ft^3
Operating schedule ____ h/day ____ days/wk ____ wk/yr

Coal Firing

Type of firing ☐ Grate Type ____________
☐ Spreader stoker
☐ Pulverized coal ☐ Dry bottom ☐ Wet bottom
☐ Cyclone

	Yes	No
Fly ash reinjection		
Soot blowing		
Continuous	☐	☐
Intermittent	☐	☐

Time interval between blowing ____ min
Duration ____ min
Outside coal storage ☐ Yes ☐ No
Maximum amount stored outside ____ tons
Outside storage sprayed ☐ Yes ☐ No

Coal consumption	Range	Average
Ash	____% to ____%	____%
Sulfur	____% to ____%	____%
Btu/lb as fired	____ to ____	____

Fuel consumption records kept ☐ Yes ☐ No
For stoker system, Coal size ____
For pulverized coal and cyclone system,
Firing method ☐ Front wall
☐ Front wall - rear wall
☐ All wall
☐ Tangential
☐ Other Type ____________

Oil Firing

Firing method ☐ Front wall
☐ Front wall - rear wall
☐ All wall
☐ Tangential
☐ Cyclone
☐ Other Type ____________

Type of fuel ☐ No. 1
☐ No. 2
☐ No. 4
☐ No. 5
☐ No. 6
☐ Other Type ____________

Figure 1.1. Example of a presurvey data form for fossil fuel-fired steam generators.

Facility name ____________________
Facility address ____________________
Name of plant contact ____________________
Source code number ____________________
Unit designation ____________________
Design charge rate ____________________
Actual charge rate ____________________
Inspection date ____________________

A. Pre-entry Observations

Time ________________

Stack plume (use EPA plume observation procedures)

Opacity regulation ☐ In compliance ☐ Not in compliance

Weight scales ☐ Operating ☐ Not operating

Trucks weighed and recorded before dump ☐ Yes ☐ No
Trucks weighed and recorded after dump ☐ Yes ☐ No

B. Control Equipment

1) Electrostatic precipitator

Section					
Primary current, A					
Primary voltage, V					
Secondary current, mA					
Secondary voltage, kV					
Spark rate, spk/min					

2) Scrubber

Module					
Liquid flow, gal/min					
Pressure across scrubber, in. H_2O					

3) Fabric filter

Compartment	
Pressure drop across fabric filter, in. H_2O	

Additional observations:

(continued)

Figure 1.2. Example of a presurvey data form for municipal incinerators.

Figure 1.2 (continued)

C. Control Panel

Time ____________________

Secondary chamber temperature ________ °F
APC device entry temperature ________ °F
Underfire air draft ________ in. H_2O
Overfire air draft ________ in. H_2O
O_2 analyzer ________ %
CO_2 analyzer ________ %
CO analyzer ________ %
Grate speed ____________ (indicate units)
Refuse measuring sensors ____________ (indicate units)

D. Incinerator

Time ____________________

	Satisfactory	Unsatisfactory
Charge cranes	☐	☐
Furnace grates (if visible)	☐	☐
Residue removal system (including quenching)	☐	☐

E. Records

Temperature charts (dated and filed by incineratory personnel)

	Satisfactory	Unsatisfactory
Secondary chamber	☐	☐
APC device entry gas	☐	☐

Hours of operation ________________________________
Charging rate, T/h ________________________________
Daily collection, T/day ____________________________

many cases, additional information will be available and should be noted for possible future use.

When possible, the normal operation of a process should be determined during the survey. If a process varies with time over a defined cycle, monitoring personnel should determine the variation in emission parameters during the cycle as a basis for deciding whether to sample during part of a cycle, during an entire cycle, or during several cycles. If the process involves steady-state operation, the level of operation to be sampled should be determined. The applicable control regulations may indicate the process operating conditions required for emissions tests. Most regulations require sampling at rated capacity. Any seasonal variations in process conditions should be noted, as should variations in feed stream composition or control device operation.

1.2.1 Stack Information - The sampling site and the number of traverse points designated will affect the quality of the sample extracted. Site selection should be simple for new installations, since in most states one of the requirements for obtaining a permit to construct is the installation of an acceptable sampling site. For new and existing installations, acceptability of the sampling procedure is generally determined by the distances from the nearest upstream and downstream disturbances (obstruction or change in direction) to gas flow. The minimum requirements for an acceptable sampling procedure are in Method 1, and are summarized herein.

In addition to flow considerations, accessibility and safety are important. Clearance for the probe and sampling apparatus, availability of electricity, exposure to weather or excessive heat, presence of toxic or explosive gases, and other safety factors must be considered in selecting a site.

Detailed information is needed regarding the gas stream parameters at the sampling site, especially in the sampling of atypical processes. Figure 1.3 lists the stack data needed to

Stack (Vent) Number ___________		
Parameter	Value	Comments
Process vented		
Platform height, ft		
Platform width, ft		
Platform length, ft		
Inside diameter, in. at port		
Wall thickness, in. at port		
Material of construction		
Ports: a. Existing		
b. Size opening		
c. Distance from platform		
Straight distance before ports, ft		
Type of restriction before ports		
Straight distance after ports, ft		
Type of restriction after ports		
Environment at sampling site		
Work space area		
Ambient temperature, °F		
Average Pitot reading, in. H_2O and range in Δp		
Stack gas velocity, ft/min		
Stack gas flow, ft^3/min		
Moisture, % by volume		
Stack gas temperature, °F		
Particulate loading, gr/scf		
Particle size		
Gases present		
Stack pressure, in. H_2O		
Water sprays prior to site		
Dilution air prior to site		
Elevator to site?		
Available electricity and distance, ft		

(21

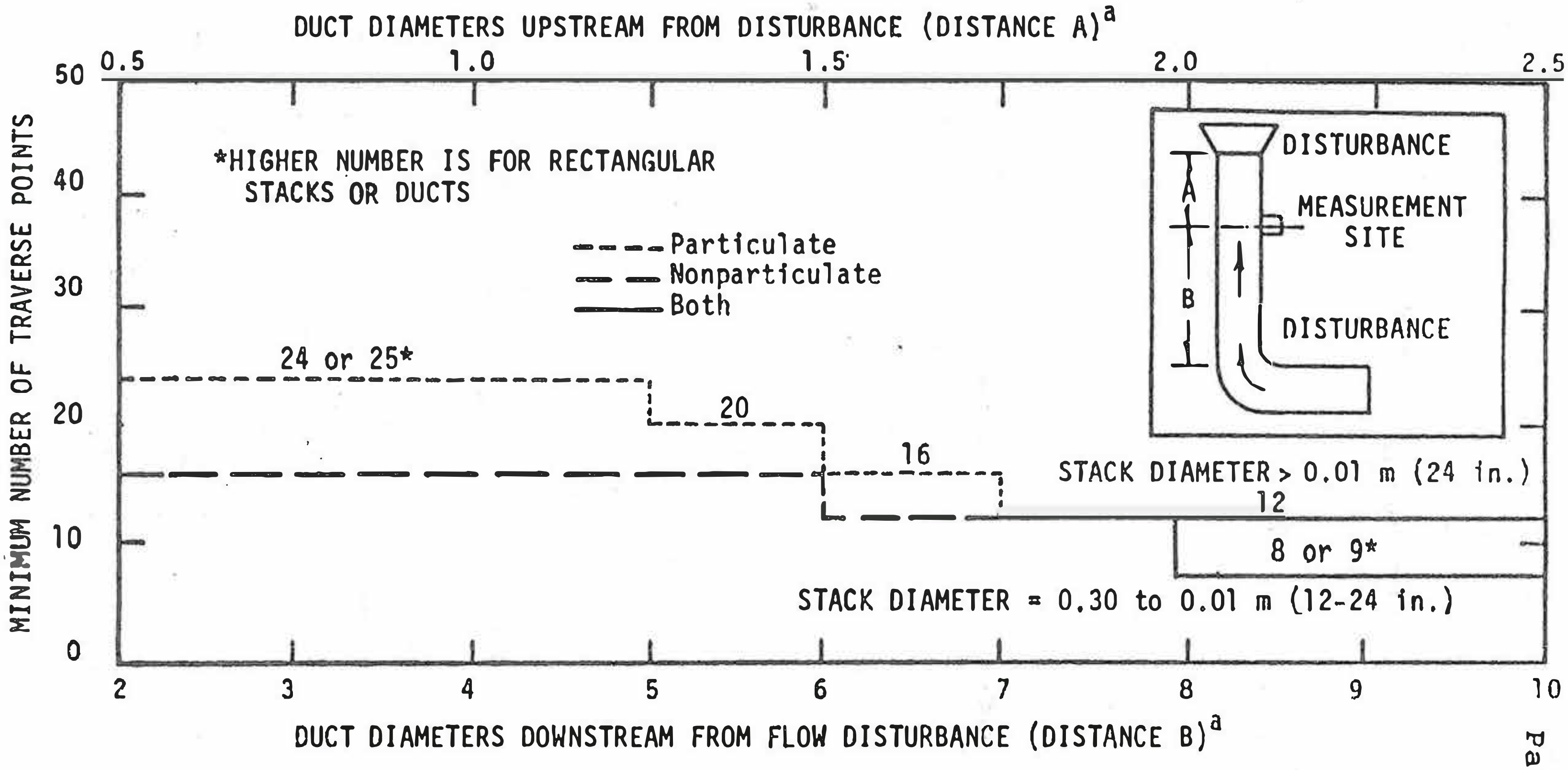
Figure 1.3. Stack and gas stream data requirements.

determine the required probe lengths and any change in sampling equipment. Most of the data can be obtained or checked from plant blueprints or engineering drawings, material-balance calculations, process instrumentation readings, or from comparable data obtained for similar processes. When no data can be obtained from these or other sources, exit gas parameters may be determined by inserting a velocity probe (Pitot tube, anemometer, or velometer) and a thermometer into the duct at or near the test site to determine approximate velocity and temperature. Color-change-type gas indicator tubes and a squeeze bulb sampler can be used to determine approximate concentrations of a wide variety of gases, and are useful if estimates based on process parameters cannot be made. These can also be used for ambient air sampling to determine any potential employee exposure problems.

1.2.2 Location of Sampling Points - As mentioned earlier, emission tests are based on the assumption that the sample obtained at a given point is representative of the concentration at that point. Therefore, a system in which concentrations are nonuniform with respect to the stack cross-sectional area will require more sampling points than will a system with uniform concentrations. Usually, gaseous concentrations are fairly uniform across a duct's cross section, and a single sampling point is sufficient. To obtain representative gas velocities and particulate concentrations, traversing of the duct cross-sectional area is required, as described in the Reference Methods 1 and 2.

Figure 1.4 can be used as a basis for determining the number of sampling points required for representative sampling of a given system for particulate and nonparticulate emissions. First, measure the distances (in duct diameters) from the sampling port to the nearest upstream and downstream disturbances, and determine the corresponding number of traverse points for each distance (Figure 1.4). Select either the higher of the two numbers of traverse points or a greater even value. For round ducts, select a number that is a multiple of four, and place half of these points along each of two diameters that are at right

Revision based on the August 30, 1983 Federal Register (48 FR 45034)



[a] From point of any type of disturbance (bend, expansion, contraction, etc.)

Figure 1.4. Minimum number of traverse points for velocity (Particulate and Nonparticulate) traverse.

angles to each other. The exact sample point locations for round ducts can then be determined by using the percentage of stack diameter from the duct's inside wall to the traverse point, as shown in Table 1.1. Duct diameters should be checked along two directions. If the two measurements are similar, use an average value. If they are not similar, use each separate diameter in determining point locations. Figure 1.5 may be used for calculating the distances to each traverse point by multiplying the percentage from Table 1.1 by the stack diameter. The total distance to the point from the outside of the stack or port is obtained by adding the port length and stack wall thickness to the calculated point location. No sampling point should be either <1 in. from an inner wall for stacks >24 in. in diameter, or <0.5 in. (or a distance equal to the sampling nozzle diameter from the wall) in stacks <24 in. in diameter.

For rectangular ducts, an equivalent diameter is calculated from the following equation to determine the distance to disturbances in terms of duct diameters:

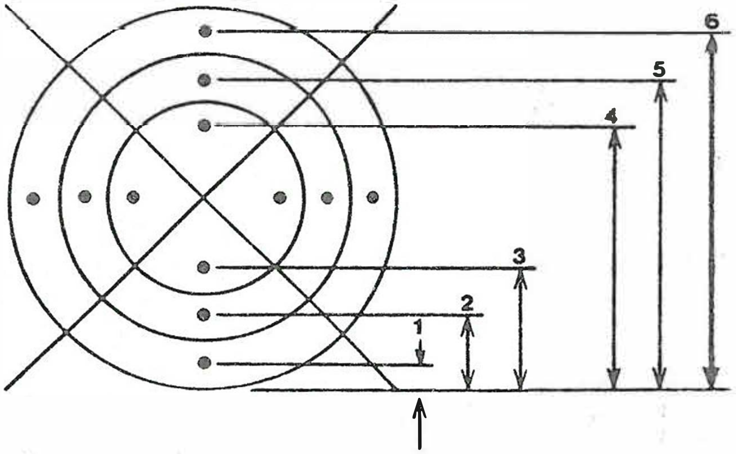
$$\text{Equivalent diameter} = 2\left[\frac{\text{length} \times \text{width}}{\text{length} + \text{width}}\right].$$

The minimum number of traverse points is then determined in the same manner as it is for circular stacks, with the use of Figure 1.4. The rectangular cross section is then divided into equal rectangular areas, according to the values in Table 1.2. Studies referenced in Method 1 show that velocity measurement data quality is not significantly increased by traversing 48 points versus 24 points for acceptable flow conditions. The studies also show that four traverse points along a line generally are representative of that traverse line. These two determinations allowed EPA to reduce the number of traverse points required for velocity measurement (as shown in Figure 1.4) and to require a more even matrix arrangement of sample points in a

Table 1.1. LOCATION OF TRAVERSE POINTS IN CIRCULAR STACKS

Example Showing Circular Stack Cross Section Divided Into 12 Equal Areas With Location of Traverse Points Indiciated

Traverse point	Distance, % of diameter
1	4.4
2	14.6
3	29.6
4	70.4
5	85.4
6	95.6



Percent of Stack Diameter From Inside Wall to Traverse Point

Traverse point number on a diameter[a]	Number of traverse points on a diameter [b]											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.2	2.6	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.6	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.6	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.4	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.4	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.6	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.4	36.6	28.3	23.6	20.4	18.0	16.1
8				96.8	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.2	23.0
10					97.4	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.8	67.7
15								95.1	89.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										96.1	91.3	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.9	94.5
23												96.8
24												98.9

[a] Points numbered from outside wall toward opposite wall.

[b] The total number of points along two diameters would be twice the number along a single diameter.

Plant ____________________

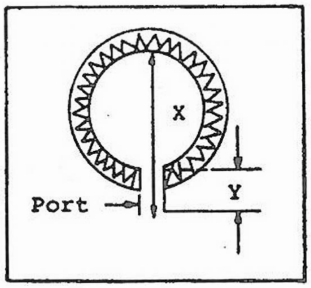
Date ____________________

Sampling location ____________________

Inside of far wall to outside of port (distance, X) ____________________

Inside of near wall to outside of port (distance, Y) ____________________

Stack I.D. (distance X-distance Y) ____________________



SCHEMATIC OF SAMPLING LOCATION

1 Traverse point number	2 Percent of stack I.D.	3 Stack I.D. inches	4 Product of Columns 2 and 3 (to nearest 1/8 in.)	5 Distance Y	6 Traverse point location from outside of port (sum of columns 4 & 5)

Figure 1.5. Traverse point location calculation form for round ducts.

Table 1.2. LAYOUT OF CROSS-SECTIONAL SUBAREAS IN RECTANGULAR DUCTS

Number of traverse points[a]	Subarea layout matrix
9	3 × 3
12	4 × 3
16	4 × 4
20	5 × 4
25	5 × 5
30	6 × 5
36	6 × 6
42	7 × 6
49	7 × 7

[a] From Figure 1.4.

square or rectangular duct (as shown in Table 1.2). For small ducts requiring many points, a slot may have to be cut into one side of each duct with a sliding port to accommodate all of the points. The sampling points should be located at the center of each equal area, according to Figure 1.6. Many studies have been conducted on the Pitot tube and Method 1. See References 1 through 14.

The calculation and marking of sampling points on the probe or Pitot tube are very critical. If marked incorrectly, the sample probe may hit the opposite stack wall, and the emission results will probably be nonrepresentative.

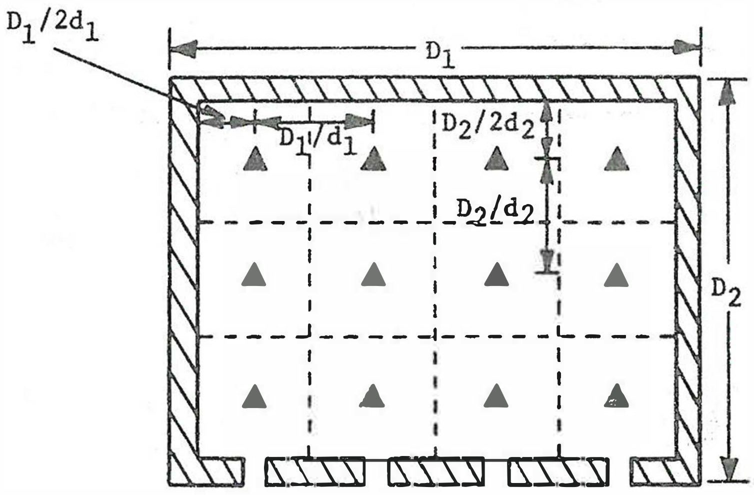
1.2.3 Cyclonic Gas Flow - Location of a suitable sampling site for velocity measurement or for particulate and mist determinations requires that the gas flow be essentially parallel to the stack walls. If there is a possibility of cyclonic or nonparallel flow as determined by observation of the duct system, checks with a Pitot tube and draft gauge (see Section 3.1, Method 2) should be made as follows:

1. Connect an acceptable type-S Pitot tube to a manometer, and leak check as described in Section 3.1, Method 2. Carefully zero the manometer and insert the Pitot tube so that the planes of the face openings are perpendicular to the stack area cross-sectional plane--that is, parallel to the expected gas flow. The Pitot tube is thus 90° from its usual position.

2. Traverse the stack area by measuring the velocity head at each sampling point with the Pitot tube in this position. Keep the sampling port opening sealed with a rag or sponge while traversing. Temperature need not be measured at this time.

3. When the gas flow is exactly parallel to the stack walls and therefore parallel to the Pitot tube face openings, no reading will be obtained on the manometer. If a reading is obtained, rotate the Pitot tube around its longitudinal axis until a zero reading is indicated on the manometer.

4. Record the angle of rotation (starting with 0° in the Pitot tube's initial position), required to obtain a zero manometer reading. Record data on the Method 2 gas velocity and volume data form (Figure 1.7).



where:

▲ = sampling point

d_1 = number of areas across flue width

d_2 = number of areas across flue perpendicular to width

Figure 1.6. Example showing rectangular stack cross section divided into twelve equal areas, with a traverse point at the centroid of each area.

Plant and city	Run date

Sampling location	Clock time

Run number	Operator	Amb. temp., °F	Bar. press., in. Hg	Static press., in. H_2O

Molecular wt.	Stack inside dimension, in.		Pitot tube (Cp)
	Diam. or side 1	side 2	

Field data

Traverse point number	Position, in.	Velocity head (Δp_s), in. H_2O	Stack temp., °F	Cyclonic flow determination	
				Δp_s at 0° reference	Angle (α) which yields a null Δp
				Average angle (α)[a]	

[a] Average of (α) must be < 10 degrees to be acceptable.

Figure 1.7. Method 2 gas velocity and volume data form.

5. Obtain an arithmetic average of the angles of rotation at each traverse point, including angles of 0° (Figure 1.7). If the average angle of rotation is $\leq 10°$, the gas flow conditions at the sampling site are acceptable. If the average angle is $>10°$, the flow conditions are not acceptable; another test site must be found, the flow pattern must be modified by installing flow straighteners or consult the administrator.

To facilitate measurement of Pitot tube rotation, a number of devices can be made, depending on the ingenuity of the user. Fabrication of a protractor that will fit over the sampling port along with a movable indicating arm clamped to the Pitot tube will provide a measurement of the angle of rotation. A level indicator (available at most hardware stores) calibrated in 5-degree increments can also be mounted on the Pitot tube and used to measure rotation.

The preferred device is a degree indicating level (available at most hardware stores) with 1° increments which can be mounted on the end of the pitot tube (Figure 1.8). Its alignment with the head of the pitot tube can be checked by one of two methods. (1) The use of two indicating levels, one at the front and one at the end or (2) by placing the pitot on a stable surface then place the indicating level at the front and then the end and compare readings. The readings do not have to be the same. The differential, using the front as the reference, or true value can be subtracted or added to the corresponding angular determinations of stack flow.

<u>References</u>

1. 40 CFR 60, July 1, 1978

2. Determination of the Optional Number of Traverse Points: An Analysis of Method 1 Criteria. Final Report, EPA Contract No. 68-01-3172. Entropy Environmentalists, Inc., April 1977.

3. Hansen, H.A., R.I. Davis, et al. Particulate Sampling Strategies for Large Power Plants Including Nonuniform Flow. EPA-600/2-76-120, June 1976.

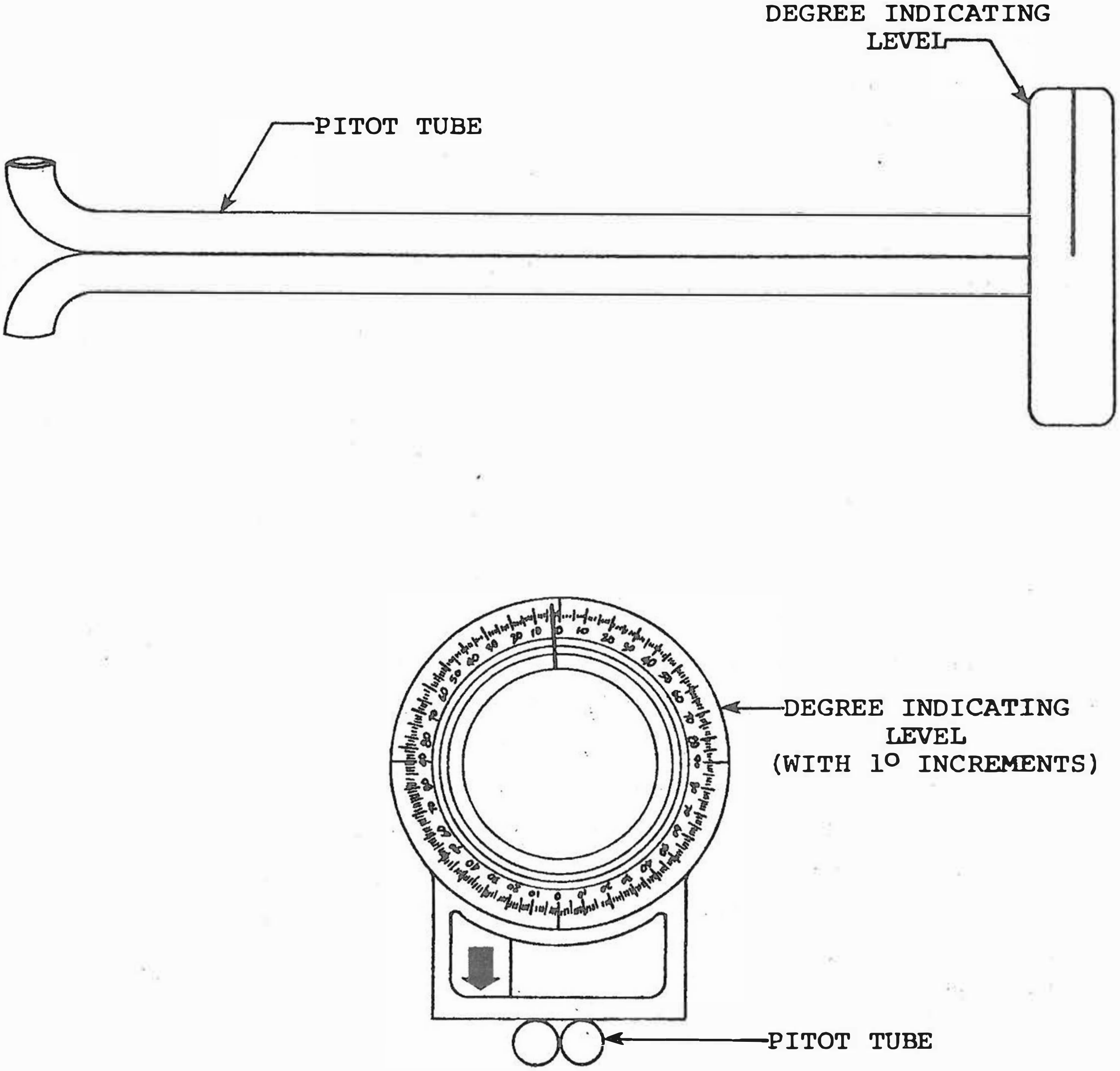


Figure 1.8. Angle determination with a degree indicating level.

4. Smith, Franklin, Denny E. Wagoner, et al. Guidelines for Development of a Quality Assurance Program: Volume I - Determination of Stack Gas Velocity and Volumetric Flow Rate (Type-S Pitot Tube). EPA-650/4-74-005-a, February 1974.

5. Source Sampling Reference Manual - Supplemental Training Material for Technical Workshop on Evaluating Performance Tests. EPA, Division of Stationary Source Enforcement, January 1977.

6. Stack Sampling Technical Information: A Collection of Monographs and Papers (Vols. II, IV). EPA-450/2-78-042-b,d, October 1978.

7. Standards of Performance for New Stationary Sources - A Compilation. EPA Contract No. 68-01-4147. PEDCo Environmental, Inc., Cincinnati, OH, November 1977.

8. Williams, J.C., III and F. R. DeJarnette. A Study on the Accuracy of Type-S Pitot Tube, EPA-600/4-77-030, June 1977.

9. Folson, R. G. Review of the Pitot Tube. Trans. ASME, 78, 1447-1459, 1956.

10. Ower, E. and F. C. Johansen. Design of Pitot-Static Tubes. R and M, No. 981, British A.R.C., 1925.

11. Merriam, K. F., and E. R. Spaulding. Comparative Tests of Pitot Static Tubes. NACA TN 546, 1935.

12. Vollaro, R. F. Use of Type-S Pitot Tubes for the Measurement of Low Velocities. U.S. Environmental Protection Agency, Research Triangle Park, N.C. In-house Report, January 19, 1977.

13. Vollaro, R. F. A Survey of Geometric and Aerodynamic Factors Which Can Affect Type-S Pitot Tube Accuracy. U.S. Environmental Protection Agency, Research Triangle Park, N.C., In-house Report, February 17, 1978.

14. Leland, B. J., J. L. Hall, A. W. Joensen, and J. M. Carroll. Correction of S-Type Pitot-Static Tube Coefficients When Used for Isokinetic Sampling from Stationary Sources. ES&T, 11, 694-700, 1977.

2.0 GENERAL FACTORS INVOLVED IN STATIONARY SOURCE TESTING

It is essential to the production of valid test data that the emissions measurement program be performed by qualified personnel using proper test equipment. Although the sampling team chief need not be a professional engineer, the chief must be specially trained in source sampling and must be experienced in field test procedures. If the sampling results are used in legal proceedings, the team chief may be called as a witness. Monitoring of a single sampling station usually requires two persons; monitoring of two stations usually requires a minimum of three. In all cases, there should be an adequate staff to perform the level of sampling required.

Similarly, valid emission tests require the use of appropriate and properly functioning test equipment, which consists basically of process-measuring devices such as scales for weighing fuel or raw materials and orifices and gauges for measuring material flows and temperatures. Process-weight regulations may require the use of scales which can be properly serviced and calibrated only by trained personnel. The scale manufacturer usually provides this service. A stamp affixed to the scale by the service crew should note the date of calibration or inspection.

Sampling equipment, such as flow meters and gauges, must be properly calibrated and maintained. As standard practice, the monitoring team should check and record the dates of calibration or servicing. Gas-sampling equipment that requires maintenance and calibration includes the Pitot tube, manometers, thermometers, flow meters, and dry gas meters. Because calibration and maintenance of these instruments is subject to close scrutiny in legal proceedings, written records are required.

Emphasis is placed upon these standard practices as means of ensuring the validity of results. Deviations from standard procedures must be kept to a minimum and applied only when they are absolutely necessary to obtain representative samples. For compliance testing, deviations from standard procedures may be used only with approval of the regulatory agency. Any changes in methodology must be based on sound engineering judgment and must be thoroughly documented.

The following procedures merit particular attention.

1. Locating the sampling site,
2. Determining the number of sampling points in the duct,
3. Using recommended sampling equipment and calibration methods,
4. Determining gas velocities,
5. Maintaining isokinetic sampling conditions for particulates,
6. Handling the sample and maintaining records, and
7. Sample analysis.

The remainder of this section describes procedures for stack sampling; source sampling tools and equipment; identification and handling of samples; laboratory analysis; use of the sampling data; and preparation of reports.

2.1 <u>Source Sampling Tools and Equipment</u>

The needs for specific tools and equipment will vary from test to test. A listing of the most frequently used tools and equipment given below is to serve as a checklist; this equipment is useful, but not mandatory.

1. <u>Equipment transportation</u>
    a. Lightweight handtruck to transport cases.
    b. A 1.2-cm (0.5 in.) continuous filament nylon rope with a snatch block for raising and lowering equipment on stacks and roofs.
    c. Tarpaulin or plastic to protect equipment in case of rain; sash cord 0.63 cm (1/4 in.) for securing equipment and tarpaulin.
    d. One strong metal or wooden box for transporting small items up and down the stack.
2. <u>Safety equipment</u>
    a. First-aid kit.
    b. Safety harness with nylon and steel lanyards and large throat snaphooks for use with lanyards for hooking over guardrails or safety lines on stacks.

c. Earplugs, H_2O, and quick-energy food.

d. A fail-safe hook for use with harness when climbing ladders having safety cables.

e. Hardhats with chinstraps and winter liners; gas masks, safety glasses, and/or safety goggles.

f. Protective clothing including suits for both hot and cold weather, both asbestos and leather gloves, and steel-toed shoes.

g. Steel cable 0.5 cm (3/16 in.) cable clips, and turnbuckles for installing a safety line or for securing equipment to the stack structure.

3. Tools and spare parts

a. Electric and power equipment:

(1) Circular saw,
(2) Variable voltage transformer,
(3) Variable speed electrical drill and bits,
(4) Ammeter-voltmeter-ohmeter (VOM),
(5) Extension cords (light, #14 Awg; 2 @ 25 ft, 2 @ 50 ft),
(6) Two 3-wire electric adapters,
(7) 3-wire electric triple taps,
(8) Thermocouple extension wire,
(9) Thermocouple plugs,
(10) Fuses,
(11) Electric wire,
(12) Jigsaw, and
(13) Small space heater for cold weather.

b. Tools:

(1) Tool boxes (1 large, 1 small),
(2) Screwdriver sets (1 flat blade, 1 Philips), and
(3) Two C-clamps (6 in., 3 in.).

c. Wrenches:

(1) Open-end set (1/4 in. - 1 in.),
(2) Adjustable (12 in., 6 in.),
(3) A chain wrench,
(4) A 12-in. pipe wrench, and
(5) An Allen wrench set.

d. Miscellaneous:

(1) Silicone sealer,
(2) Silicone vacuum grease,
(3) Pump oil,
(4) Manometers (gauge oil),
(5) Antiseize compound, (e.g., high temperature graphite)
(6) Pipe fittings,
(7) Dry cell batteries,
(8) Flashlight,
(9) Valves,
(10) Thermometers (dial, 6 in. - 36 in., a remote-reading type),
(11) Vacuum gauge,
(12) Short SS-tubing (1/4 in., 3/8 in., 1/2 in.),
(13) Heavy duty wire (telephone type),
(14) Adjustable packing gland,
(15) Nails,
(16) Spare swagelocks,
(17) Hammer,
(18) Hanging lamp, and
(19) Two-by-four's.

4. <u>Data recording</u>

a. Data forms or data notebook.

b. Carbon paper.

c. Slide rule or electronic calculator.

d. Psychrometric charts.

e. Combustion nomographs (Reference 1).

f. Pencils and pens.

2.2 Standard Data Forms

Recorded test data are part of the physical evidence in legal proceedings. Standardized forms are used to ensure that all required information is obtained. Example forms for use in the field, in the laboratory, and for calculations are included in later sections. The field form used when taking the sample identifies the process tested; date and time; location of test station; sampling personnel; and the person who records the data. Ink should always be used to record the data. In the event of error, the data-taker crosses through the erroneous value with a single line, records the correct value above it, and initials the change.

2.3 Identification of Sampling Materials

All samples must be marked to ensure positive identification throughout the test and analysis procedures. The legal rules of evidence require systematic identification of samples at all points in their processing. Valid testimony requires that a laboratory analyst be able to relate the analytical data to a specific sample by number. Analysts also must provide positive identification of filters. All identifying marks on the filters should be made before weighing. The filters should be serially numbered to ensure their unique identification. The ink used for marking must be indelible and unaffected by gases, temperatures, or other conditions to which it is subjected. If an agency specifies another method of identification, that method must be positive and must not impair the capacity of the filter to function.

Finally, the monitoring personnel must provide unique identification for each container to preclude the possibility of interchange. The number of the container is recorded on the field form and on the analysis data form so that it is associated with the sample throughout testing and analysis. See Section 3.0.3 for further details concerning the uses of source samples as evidence.

2.4 Reference

Smith, Walter S., and D. James Groves. Stack Sampling Nomographs for Field Estimations. Entropy Environmentalists, Inc., Research Triangle Park, North Carolina.

3.0 CHAIN-OF-CUSTODY PROCEDURE FOR SOURCE SAMPLING

As part of the overall quality assurance activities associated with the collection and analysis of source samples, particular attention should be directed to the handling of the sample and the analysis report.

Source test results, or possibly even the sample itself, may be used to prove the compliance status of a facility. However, test results and samples will not be admitted as evidence unless it can be shown that they accurately represent the conditions that prevailed at the time the test was conducted. This requires that:

1. the sample be collected properly,
2. the sample be handled properly,
3. the sample be analyzed in accordance with documented test procedure, and
4. the test report be prepared completely and accurately and then filed in a secure place.

Failure to comply with these requirements may void the results of a test or, at least, diminish the credibility of the test report.

3.1 Sample Collection

Proper sampling requires the use of the correct method, the equipment designated by the method, and competent personnel. Prior to the test date, the tester should determine that the proposed test methods comply with the appropriate testing regulations; in some instances, it may be necessary to deviate from the proposed methods. For example, the only reasonable sample site may be too close to an elbow or a duct obstruction. In such cases, the tester should make an engineering analysis of the use of the test site and then proceed only after obtaining the approval of the regulatory authority. This determination should be recorded in the field notes. An after-the-fact site analysis may suffice in many instances, but good quality assurance techniques dictate that this analysis be made prior to spending the many man-hours required to extract the sample. Once the test method is selected, preparations for the test should be made according to documented guidelines.

3.1.1 Preparations - When conducting the test, it is necessary that the sample be extracted in a manner to ensure that it represents the actual conditions at the time of the test. This means that the process is operating in its mode specified by the applicable control regulation, the extracted sample typifies the stack gas conditions, and the instruments used in the sampling are properly calibrated and maintained.

Because the results of source tests are being used increasingly as proof of compliance, the pretest preparation and post-test scrutiny are becoming more sophisticated. Thus, steps need to be taken prior to the actual test to ensure the integrity of the test data.

In many cases, reagents or filters are prepared prior to sampling and become an integral part of the sample itself. A record should list the date, the person by whom it was prepared, and the location of these items at all times from preparation until actual use for sampling. Since these items become a part of the sample itself, it is necessary that their integrity be maintained from preparation through analysis. For example, a bulk quantity of solution may be prepared and transported to the field where the specified amount is used in accordance with the test method. The bulk solution ultimately becomes an integral part of several samples during the sampling process. For this reason, one member of the sampling crew generally serves as sample custodian and should be responsible for entering information on sample preparation items in the field notebook. However, as long as proper records are kept, more than one individual may serve in this capacity. This serves as a written record for the sampling crew and also fulfills chain-of-custody procedures.

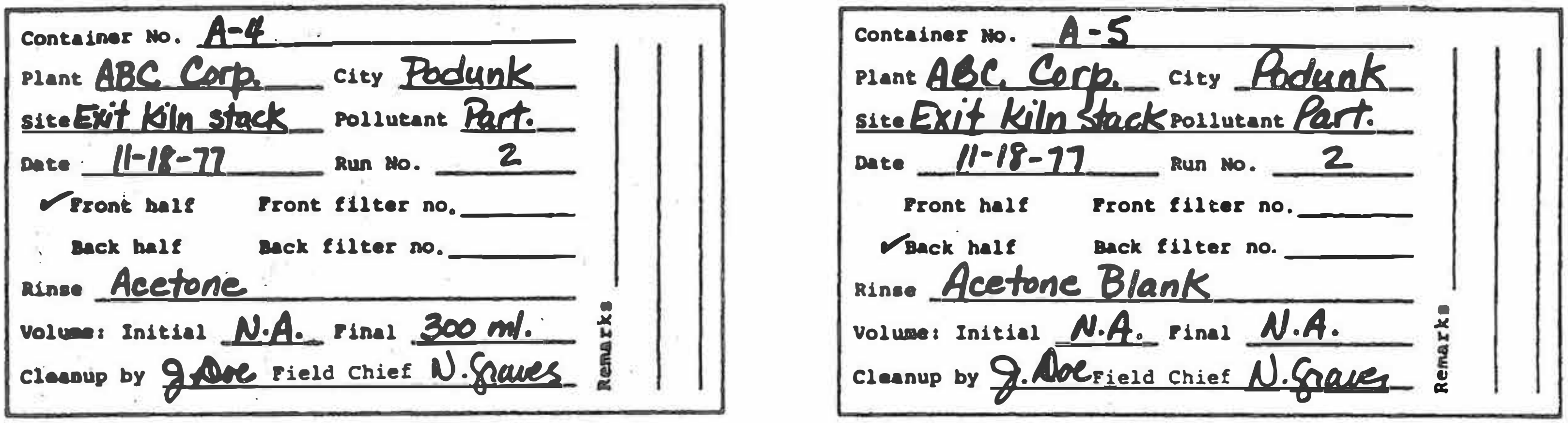
3.1.2 Sample Handling - Once the sample is procured it should be handled in such a way as to ensure that there is no contamination and that the sample analyzed is actually the sample taken under the conditions reported. For example, each sample should be kept in a secure place between the time it is extracted and the time it is analyzed. If further analysis may be required, the sample should be returned to a secure place. It is always best to keep a sample secure up to the time it is discarded. These security measures should be documented by a written record signed by the handlers of the sample.

Identification - Care should be taken to mark the samples to ensure positive identification throughout the test and analysis procedures. The evidence used in legal proceedings requires positive procedures for identification of samples used in analyses as the basis for future evidence. An admission that the laboratory analyst could not be positive whether sample No. 6 or sample No. 9 was analyzed could destroy the validity of the entire test report.

Positive identification also should be provided for the filters used in any specific test before taring. If ink is used for marking, it must be indelible and unaffected by the gases and temperatures to which it will be subjected. Other methods of identification can be used, if they provide a positive means of identification and do not impair the function of the filter.

Finally, each container should have a unique identification to preclude the possibility of interchange. Grease pencils may be used for this purpose. A better method, however, is to affix an adhesive-backed label to the container. The number of the container should be recorded on the analysis data form. Figure 3.1 shows how a standardized identification sticker can be used for each of the four containers needed to collect a sample for EPA Test Method 5.

Contamination and Tampering - To reduce the possibility of invalidating the results, all components of the sample should be carefully removed from the sampling train and placed in nonreactive containers. The best method of sealing depends on the container. Place containers in a place of limited access (i.e., locked van or locked sample box). This will preclude accidental opening of the container and should be a sufficient safeguard if

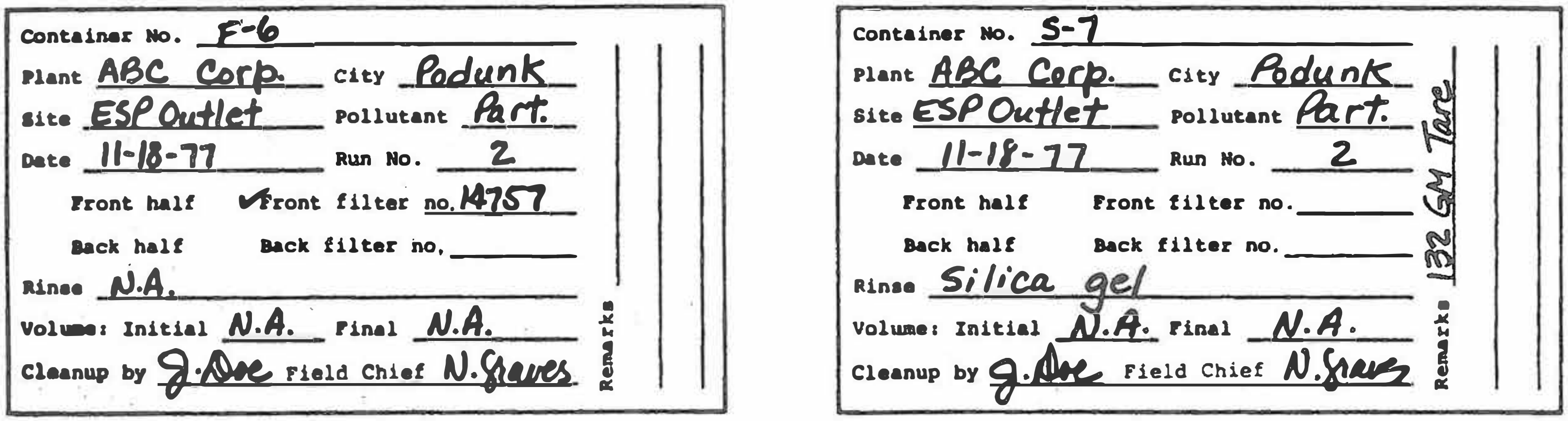


Container No. A-4
Plant ABC Corp. City Podunk
Site Exit kiln stack Pollutant Part.
Date 11-18-77 Run No. 2
✓Front half Front filter no. ______
Back half Back filter no. ______
Rinse Acetone
Volume: Initial N.A. Final 300 ml.
Cleanup by J. Doe Field Chief N. Graves
Remarks

PROBE RINSINGS

Container No. A-5
Plant ABC Corp. City Podunk
Site Exit kiln stack Pollutant Part.
Date 11-18-77 Run No. 2
Front half Front filter no. ______
✓Back half Back filter no. ______
Rinse Acetone Blank
Volume: Initial N.A. Final N.A.
Cleanup by J. Doe Field Chief N. Graves
Remarks

ACETONE BLANK



Container No. F-6
Plant ABC Corp. City Podunk
Site ESP Outlet Pollutant Part.
Date 11-18-77 Run No. 2
Front half ✓Front filter no. 14757
Back half Back filter no. ______
Rinse N.A.
Volume: Initial N.A. Final N.A.
Cleanup by J. Doe Field Chief N. Graves
Remarks

FILTER

Container No. S-7
Plant ABC Corp. City Podunk
Site ESP Outlet Pollutant Part.
Date 11-18-77 Run No. 2
Front half Front filter no. ______
Back half Back filter no. ______
Rinse Silica gel
Volume: Initial N.A. Final N.A.
Cleanup by J. Doe Field Chief N. Graves
Remarks 132 GM Tare

SILICA GEL

Figure 3.1 - Typical labels used for samples collected for a source test of particulate matter using EPA Test Method 5.

all other aspects of the chain-of-custody procedure are observed. However, if there is any possibility of temporary access to the samples by unauthorized personnel, the sample jars and containers should be sealed with a self-adhesive sticker that has been signed and numbered by the test supervisor or other responsible person. This sticker should adhere firmly to ensure that it cannot be removed without destruction. The samples should then be delivered to the laboratory for analysis. It is recommended that this be done on the same day that the sample is taken. If this is impractical, all of the samples should be placed in a carrying case or other place of limited access (preferably locked) for protection from breakage, contamination, and loss.

In transporting the sample to the laboratory, it is important that precautions be taken to eliminate the possibility of tampering, accidental destruction, and physical and/or chemical damage to the sample. This practical consideration should be dealt with on a case-by-case basis. For example, samples obtained from a rock crusher are nonreactive but those from an asphalt saturator may be reactive, and gaseous samples may decay or react.

The person who has custody of the samples should be able to testify that no one tampered with them. Any handling of samples by unauthorized persons can result in contamination. For example, a curious person with a cigarette in his mouth may open a sample; the smallest ash dropping into the container could make a significant difference in the analysis. Security should be continuous. If the samples are put in a truck, lock it. In the laboratory, the samples should be kept in a secure place.

To ensure that none of the sample is lost in transport, mark all liquid levels on the side of the container with a grease pencil. Thus any major losses that occur will be readily ascertainable.

<u>Chain-of-Custody</u> - The chain-of-custody is perhaps the most critical part of the test procedure. The chain-of-custody is necessary to make a prima facie showing of the representativeness

of the sample. Without it, one cannot be sure that the sample analyzed was the same as the one purported to be taken at a particular time. The samples should be handled only by persons associated in some way with the test. A general rule to follow is "the fewer hands the better", even though a sealed sample may pass through a number of hands without affecting its integrity. Ideally, all sample containers should be transported from the site to the vehicle and from the vehicle to the laboratory by the same person.

It is generally impractical for the analyst to perform the field test. For this reason, each person should remember from whom the sample was received and to whom it was delivered. This requirement is best satisfied by having each recipient sign the data form for the sample or set of samples. Figure 3.2 shows a form for particulate samples which may be used to establish the chain-of-custody from the test site to the laboratory. This form is designed for tests performed by EPA Method 5. Note that the silica gel was weighed in the field. If for some reason this is not done, the silica gel must be returned with the other containers, and an appropriate notation made under "Remarks". Figure 3.3 shows another form which may be used. A form of this type should accompany the samples at all times from the field to the laboratory. All persons who handle the samples should sign the form. It is important to realize that the chain-of-custody procedures do not stop with the sample analysis. If the sample must be kept for future analysis, it should be kept in a secure storage area. Figures 3.2 and 3.3 reflect this.

3.2 Sample Analysis

For source samples to provide useful information, laboratory analyses should meet the following requirements:

1. Equipment should be adequate for proper analysis;
2. Personnel should be qualified to make analysis;
3. Analytical procedures should be in accordance with accepted good practice; and

Plant ABC Corp., Podunk, Ohio Sample date 11-17-77
Sample location kiln exit stack Run number 2
Sample recovery by John Doe Recovery date 11-18-77
Filter number(s) 14757

Moisture

Impingers			**Silica gel**					
Final volume (wt)	380	ml (g)	Final wt.	268	g	—	g
Initial volume (wt)	300	ml (g)	Initial wt.	250	g	—	g
Net volume (wt)	80	ml (g)	Net wt.	18	g	—	g

Total moisture 98 g
Color of silica gel pink and blue
Description of impinger water cloudy

Recovered Sample

Filter container number F-6 Sealed ✓
Description of particulate on filter gray

Acetone rinse container number A-4 Liquid level marked ✓
Acetone blank container number A-5 Liquid level marked ✓
Samples stored and locked N/A
Remarks transported directly to lab.

Date of laboratory custody 11-18-77
Laboratory personnel taking custody Jim Smith
Remarks

Figure 3.2. Chain-of-custody receipt form for source sample.

Plant ABC Corp., Podunk, O.

Sample number	Number of container	Description of samples
2	A-4 A-5 F-6	Acetone Rinse Acetone Blank Filter # 14757

Person responsible for samples J. Doe	Time 4:30 p.m.	Date 11-18-77

Sample number	Relinquished by	Received by	Time	Date	Reason for change of custody
2	J. Doe	Jim Smith	5:00 p.m.	11-18-77	put in sample locker
	Jim Smith	W. Frank	10:15 a.m.	11-20-77	Run analysis
	W. Frank	Jim Smith	4:30 p.m.	11-20-77	put in sample locker

Figure 3.3. Chain-of-custody receipt form - general form.

4. Records should be complete and accurate.

The first three requirements are discussed elsewhere in this handbook and need no further elaboration.

Complete and accurate records generally take the form of a laboratory notebook. Where practical, standard preprinted forms should be used. Do not discard these records, since it is possible that they will be needed in the future to substantiate the final report. Figures 3.4 and 3.5 are examples of standardized forms that can be used in the laboratory. Note that the entries on these forms must agree with those shown on the container labels (Figure 3.1) and on the chain-of-custody receipt form (Figures 3.2 and 3.3).

3.3 Field Notes

Manual recording of data is required for source tests. Standardized forms should be utilized to ensure that all necessary data are obtained. These forms should be designed to clearly identify the process tested, the date and time, the test station location, the sampling personnel, and the person who recorded the data. During the actual test period, the meter readings, temperature readings, and other pertinent data should be recorded in the spaces immediately upon observation. These data determine the accuracy of the test and should not be erased or altered. Any error should be crossed out with a single line; corrected value should be recorded above the crossed-out number.

Do not discard the original field records even if they become soiled. For neatness, the field data may be transcribed or copied for inclusion in the final report, but the originals should be kept on file. Copies are not normally admissible as evidence, but since the records may be subpoenaed, it is important that all field notes be legible.

3.4 The Report as Evidence

In addition to samples and field records, the report of the analysis itself may serve as material evidence. Just as the procedures and data leading up to the final report are subject to

Plant ABC CORP., PODUNK, OHIO Run number 2

Sample location KILN EXIT STACK

Density of acetone (ρa) 0.790 g/ml

Sample type	Container number	Liquid level marked	Container sealed
Acetone blank	A-5	✓	✓
Acetone rinse	A-4	✓	✓
Filter(s)	F-6		✓

Acetone rinse volume (Vaw) 300 ml

Acetone blank residue concentration (Ca) 2.1×10^{-3} mg/g

Wa = Ca Vaw ρa = (2.1×10^{-3}) (300) (.790) = 0.5 mg

Date and time of wt. 11-20-77; 9:00 AM Gross wt. 5210.8 mg

Date and time of wt. 11-21-77, 8:25 AM Gross wt. 5210.6 mg

Average gross wt. 5210.7 mg

Tare wt. 5108.6 mg

Less acetone blank wt. (Wa) 0.5 mg

Weight of particulate in acetone rinse 101.6 mg

Filter number(s) 14757

Date and time of wt. 11-20-77; 9:10 AM Gross wt. 652.8 mg

Date and time of wt. 11-21-77; 8:15 AM Gross wt. 652.6 mg

Average gross wt. 652.7 mg

Tare wt. 450.0 mg

Weight of particulate on filter(s) 202.7 mg

Weight of particulate in acetone rinse 101.6 mg

Total weight of particulate 304.3 mg

Remarks

Signature of analyst

Signature of reviewer Jim Smith

Figure 3.4. Standard form for laboratory analysis of sample (EPA Test Method 5).

Plant ABC Corp, Podunk, Ohio Blank number A-5

Sample location kiln exit stack

Liquid level at mark ✓ Container sealed ✓

Density of acetone (ρa) 0.790 mg/ml

Acetone blank volume (Va) 300 ml

Date and time of wt. 11-20-77; 8:15 a.m. Gross wt. 5080.8 mg

Date and time of wt. 11-20-77; 3:20 p.m. Gross wt. 5080.6 mg

Average gross wt. 5080.7 mg

Tare wt. 5080.2 mg

Weight of blank (ma) 0.5 mg

$$Ca = \frac{ma}{Va\ \rho a} = \frac{(\ 0.5\ )}{(300)\ (790)} = 0.0021\ \text{mg/g}$$

Remarks

Signature of analyst W. Frank

Signature of reviewer Jim Smith

Figure 3.5. Standard form for laboratory analysis of acetone blank.

the rules of evidence, so is the report itself. Written documents, generally speaking, are considered hearsay and are not admissible as evidence without a proper foundation. A proper foundation consists of testimonies from all persons having anything to do with the major portions of the test and analysis. Thus the chief of the field team, the cleanup man, all persons having custody of the samples, and the laboratory analyst would be required to lay the foundation for introduction of the test report as evidence.

Legal rules recognize that a record of events is the result of input from many persons who have no reason to lie and that introduction of all these persons as witnesses in onerous. These rules recognize the complexity and mobility of our society and are relatively liberal. Indeed, in many cases the trial judge will require the parties to verify the authenticity of source test reports during the pretrial proceedings. However, the party against whom the report is offered still has the right, with reasonable cause, to cross-examine the test participants. In this area, the trial judge may exercise discretion.

The relaxed attitude toward reports of experiments made by persons in the regular course of activity greatly simplifies the introduction of the report as evidence. Only the custodian of the report (usually the supervisor or the test team) need testify.

To ensure compliance with legal rules all test reports should be filed in a secure place by a custodian having this responsibility. Although the field notes and calculations are not generally included in the summary report, this material may be required at a future date to bolster the acceptability and credibility of the report as evidence in an enforcement proceeding. Therefore, the full report--including all original notes and calculation forms--should be kept in the file. Signed receipts for all samples should also be filed with the test data.

The original of a document is the best evidence and a copy is not normally admissible as evidence. Microfilm, snap-out carbon copies, and similar contemporary business methods of producing copies are acceptable in many jurisdictions if the unavailability of the original course is adequately explained and if the copy was made in the ordinary course of business.

In summary, although all the original calculations and test data need not be included in the final report, they should be kept in the files. It is a good rule to file all reports together in a secure place.

5.0 SPECIFIC PROCEDURES TO ASSESS ACCURACY OF REFERENCE METHODS USED FOR STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

On May 30, 1979, the EPA Administrator stated in a memo "the EPA must have a comprehensive quality assurance (QA) effort to provide for the generation, storage, and use of environmental data which are of known quality." The memo further stated that participation in the QA effort was mandatory for all EPA supported or required monitoring activities. In a subsequent memo (dated June 14, 1979), it was stated that the mandatory QA program included all EPA grants, contracts, cooperative agreements, and interagency agreements. On November 24, 1980, the EPA Administrator approved a strategy to implement the QA program. As part of this strategy, each Project Officer must develop and obtain approval for a QA Project Plan if he/she determines the project will result in "environmentally related measurements." All source emission tests conducted for compliance or enforcement purposes are considered "environmentally related measurements." Guidelines for the development of a QA Project Plan are discussed in Section 1.4.23 and Appendix M of Volume I of this Handbook. The most important part of any QA Project Plan is a description of specific procedures to routinely assess and document data precision, accuracy, and completeness of specific measurement parameters involved.

The purpose of this Section is to briefly describe specific procedures to routinely assess and document the accuracy of reference and alternative methods for source test data under SPNSS (Standards of Performance for New Stationary Sources). Procedures for assessment of precision and completeness are not given because compliance or enforcement tests are short-term (only a few hours duration) and additional duplicate tests to obtain precision data are costly. Accuracy is determined from results of performance audits (i.e., measurements made by the routine operator or analyst). The routine operator or analyst must not know the concentration or value of the audit standard used, and the results must be submitted to an immediate supervisor or QA coordinator who does know the audit value.

Audit samples must have known or true values. They must be prepared with materials similar to field samples and/or calibration standards. Meticulous procedures and programs must also be established to ensure audit sample values (1) are correct as stated, (2) remain stable until used, (3) are properly coded and recorded, and (4) are of the proper concentration range to be audited.

Since a high degree of experience and planning is required for audit sample preparation, and EPA has mandated that quality assurance be an integral part of the agency measurement programs, the EPA's Environmental Monitoring Systems Laboratory (EMSL) in Research Triangle Park, North Carolina has been delegated the responsibility for preparation of audit samples and materials for air measurements. Federal, State, and local agency personnel can obtain audit samples and materials for any enforcement and compliance measurement program directly from the Quality Assurance Coordinator in each EPA Regional Office unless otherwise directed in the following Reference Method subsections. When audit materials are unavailable from EPA or needed for nonagency use, commercial suppliers should be sought. Table 5.1 lists the address and telephone number for the Quality Assurance Coordinator in each of the ten EPA Regional Offices.

Several of the EPA Reference Methods have no performance audits because (1) they are specification methods or (2) no reliable or low cost procedures are currently available. The EPA Reference Methods for which audits are recommended are shown in Table 5.2 with their corresponding subsection number.

The specific assessment procedure for each promulgated Reference Method is approximately three pages in length. This brief description of the assessment procedure includes the following:

1. Method description.

2. References for details on the method.

3. Performance audit program to assess the accuracy of sampling and analytical procedures.

4. Recommended frequency for performance audits of compliance and enforcement tests. A frequency less than that recommended for enforcement purposes may be acceptable when testing for other purposes.

5. Recommended standards and levels for establishing audit values.

6. Procedure to calculate accuracy.

7. Availability of audit materials.

8. Cost of the recommended audit.

The philosophy of these assessments is that relative error calculations will be made of the accuracy (1) to determine errors in the testers'/analysts' techniques and systems, (2) when possible, to correct errors in these techniques and systems, and (3) for interpretation of the final reported emission test results by the data user. The reported emissions test data should not be corrected on the basis of these relative error calculations.

The general approach that has been developed for these audits follow those already described in the Reference Methods

TABLE 5.1. REGIONAL QUALITY ASSURANCE COORDINATORS (AIR)

Quality Assurance Coordinator (Air)
Central Regional Laboratory
Environmental Services Division
US EPA, Region 1
60 Westview Street
Lexington, MA 02173
FTS: 861-6700; COML: 617-861-6700

Quality Assurance Coordinator (Air)
Environmental Services Division
USEPA, Region 2
Edison, NJ 08837
FTS: 340-6766; COML: 201-321-6766

Quality Assurance Coordinator (Air)
Environmental Services Division
USEPA, Region 3
841 Chestnut Building, 8th Floor
Philadelphia, PA 19107
FTS: 597-6445; COML: 215-597-6445

Quality Assurance Coordinator (Air)
Environmental Services Division
USEPA, Region 4
College Station Road
Athens, GA 30613
FTS: 250-3390; COML: 404-546-3390

Quality Assurance Coordinator (Air)
Environmental Services Division
USEPA, Region 5
536 South Clark Street
Chicago, IL 60605
FTS: 353-9317; COML: 312-353-9317

Quality Assurance Coordinator (Air)
Environmental Services Div.
US EPA, Region 6
First International Bldg.
1201 Elm Street
Dallas, TX 75270
FTS: 729-0728,
COML: 214-767-0728

Quality Assurance Coordinator (Air)
USEPA, Region 7
25 Funston Road
Kansas City, KS 66115
FTS: 926-3881;
COML: 913-236-3881

Quality Assurance Coodinanator (Air
Environmental Services Div.
1860 Lincoln Street
Denver, CO 80295
FTS: 776-5064;
COML: 303-564-5064

Quality Assurance Coordinator (Air)
USEPA, Region 9
215 Fremont Street
San Francisco, CA 94105
FTS: 454-7480;
COML: 415-974-0922

Quality Assurance Coordinator (Air)
Environmental Services Div.
US EPA, Region 10
1200 Sixth Ave.,
Mail Stop 337
Seattle, WA 98101
FTS: 399-1675;
COML: 206-442-1675

TABLE 5.2. EPA REFERENCE METHODS INCLUDED IN SECTION 3.0.5

Method number	Description	Subsection number
2	Volumetric Flow Rate	5.1
3	Carbon Dioxide and Oxygen	5.2
5, 5A, & 5D	Particulate Matter	5.3
6, 6A, & 6B	Sulfur Dioxide	5.4
7, 7A, 7C, & 7D	Oxides of Nitrogen	5.5
8	Sulfuric Acid and Sulfur Dioxide	5.6
10	Carbon Monoxide	5.7
11	Hydrogen Sulfide	5.8
12	Inorganic Lead	5.9
13A & 13B	Total Fluoride	5.10
15	Hydrogen Sulfide, Carbonyl Sulfide, and Carbon Disulfide	5.11
16	Hydrogen Sulfide, Methylmercaptan, Dimethyl Sulfide, and Dimethyl Disulfide	5.12
16A	Alternate Method for TRS	5.13
17	Instack Filterable Particulate	5.14
18	VOC, General GC Method	5.15
19	Sulfur Dioxide Removal Efficiency and Particulate, Sulfur Dioxide, and Nitrogen Oxide	5.16
20	Nitrogen Oxide, Sulfur Dioxide, and Oxygen for Stationary Gas Turbines	5.17
25	Total Gaseous Nonmethane Organics	5.18
25A & 25B	Total Gaseous Organics	5.19

for EPA Methods 6 and 7 (see Reference 1) and/or Method 18 (see Reference 2). These audit procedures require the tester/analyst to provide the auditor with the audit results, either prior to the field sample analysis or prior to including the field sample results in the test report. When large relative errors are identified, the tester/analyst is allowed to correct his system. If possible, this is accomplished prior to the taking of the field samples or performing the final analysis on the field samples; this approach works quite well when the auditor is present for an on-site analysis. However, in the absence of the auditor the tester/analyst must telephone the auditor with results of the audit sample analysis in order to make necessary corrections prior to analyzing the field samples. If the auditor feels that is unwarranted, or if the tester/analyst does not wish to take the possible opportunity to correct an error in the system and/or techniques, the audit sample(s) would then be prepared and analyzed in the same manner and at the same time as the field samples. The approach of notifying the auditor prior to field sample analysis can provide the source and agency with a greater chance of more accurate data, may require the rejection of less test results, and may improve the techniques and system of the tester and/or analyst.

For compliance determination, the audit sample values should be within the range of the allowable emission limit. The audit sample concentration or value should be within 40 to 200 percent of the value of interest for audits containing a single audit sample. For audits containing two audit samples, the low concentration sample should be between 25 and 100 percent of the value of interest and the high concentration between 100 and 250 percent.

5.1 Method 2 (Stack Gas Velocity and Volumetric Flow Rate)

5.1.1 Method Description - Method 2 is applicable for measurement of the average velocity of a gas stream and for quantifying gas flow. This procedure is not applicable at measurement sites which fail to meet the criteria of Method 1. Also, the Method cannot be used for direct measurement in cyclonic or swirling gas streams. Method 1 shows how to determine cyclonic or swirling flow conditions. Therefore, when unacceptable conditions exist, alternative procedures subject to the approval of the Administrator, U.S. Environmental Protection Agency, must be employed to make accurate flow rate determinations; examples of such alternative procedures are: (1) to install straightening vanes; (2) to calculate the total volumetric flow rate stoichiometrically; or (3) to move to another measurement site at which the flow is acceptable.

The average gas velocity in a stack is determined from the gas density and from measurement of the average velocity head with a Type S (Stauscheibe or reverse type) pitot tube.

Section 3.1.10 of this Handbook contains a detailed description of Method 2 (40 CFR 60, Appendix A, Method 2).

5.1.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

5.1.2.1 Sampling Accuracy - When an inclined manometer that meets the specifications shown in Section 2.2 of Method 2 is used to measure the velocity pressure of the stack gas velocity, no audit is recommended. When another differential pressure gauge is used (e.g., Magnahelic^R gauge), the gauge should be assessed for accuracy against an inclined manometer for each test series. The auditor should use an inclined manometer that meets the specifications shown in Section 2.2 of Method 2, Appendix A, 40 CFR 60.

The following items are provided as guidance for a proper audit and should be performed only when a differential pressure gauge other than an inclined manometer is used. When an inclined manometer that meets the specifications in Method 2 is used as the differential pressure gauge, no audit is recommended.

1. The pitot tube/differential pressure system should have been leak checked, leveled and zeroed.

2. After the velocity measurement system has been checked and prepared for testing, the differential pressure gauge should be audited by attaching an inclined manometer and "T" connections and tubing to the measurement system as explained in Method 2, Subsection 3.1.2 of this Handbook. The tubing may be slipped over the end of the pitot tube if a leakless connection can be made.

3. Prior to the testing series, the differential pressure gauge's accuracy must be checked at a value close to the average Δp obtained from the preliminary velocity traverse. Check both the negative and positive side. The readings should agree within 5 percent. If this agreement cannot be met, try to determine the problem and repeat the audit.

4. The auditor should compute the % relative error (RE) for each of the audits:

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Pressure measured by differential pressure gauge, in. H_2O, and
C_A = Pressure measured by inclined manometer, in. H_2O.

5. When the initial and repeat audit does not meet the 5 percent relative error, the auditor may take actions deemed appropriate, or may inform the tester that if the post-test calibration of the differential pressure gauge does not meet the 5 percent agreement, the test may be voided.

6. The calculated RE should be included in the emission test report as an assessment of the accuracy of Method 2.

The difference between the measured values is used to assess the sampling accuracy. The significance of the error in the final velocity measurement will be the square root of $1 + \frac{RE}{100}$.

5.1.2.2 Analytical Accuracy - No analysis is in this Method.

5.1.3 Audit Frequency - When Method 2 is used for SPNSS purposes, the following audit frequency is recommended for the compliance and enforcement test. No audits are recommended for sampling or analysis if an inclined manometer is used that meets the specifications of Method 2. If a differential pressure gauge other than an inclined manometer is used, the gauge should be audited prior to the field test series (one audit per entire test series). An additional audit should be performed when (1) the differential pressure gauge is replaced or (2) the differential pressure gauge is altered to the point that the mechanical workings may be changed. A lesser frequency may be accepted when Method 2 is used for other applications depending on the purpose of the test.

5.1.4 Availability of Audit Materials - The inclined manometers are available commercially. The purchaser should ensure that the manometer meets the specifications explained in Method 2, Subsection 2.2.

5.1.5 Cost of Audit - The audit for Method 2 should require less than one additional technical hour of effort to complete. This would generally represent less than 10 percent of the total effort to conduct, calculate, and report the Method 2 testing.

5.2 Method 3 (Carbon Dioxide and Oxygen)

Method 3 should be audited using the quality assurance requirements in Method 3 (see Reference 3 for details).

5.2.1 Method Description* - This Method is used for determining CO_2 and O_2 concentrations > 0.2 percent by volume and for calculating excess air and the dry molecular weight of gas streams from combustion sources. The Method may also be applicable to other processes where it has been determined that compounds other than CO_2, O_2, CO, and nitrogen (N_2) are not present in concentrations sufficient to affect the results. Section 3.2.11 of this Handbook contains a detailed description of Method 3 (Method 3 is found in 40 CFR 60, Appendix A). Limitations to the use of Method 3 are cited in the NOTE below.

5.2.2 Audits to Assess Accurcy of Sampling and Analytical Procedures -

5.2.2.1 Sampling Accuracy - No audit is recommended for sampling procedures at this time .

5.2.2.2 Analytical Accuracy - If the data are to be used only for molecular weight determination, no audit is recommended for the analytical procedures. If the data are to be used for excess air determination, concentration correction or F-factor calculation, an audit is recommended. This is the same audit that is suggested by EPA Reference Method 3. No additional requirements were included.

Although in most instances only CO_2 or O_2 is required, it is recommended that both CO_2 and O_2 be measured to provide a check on the quality of the data. The following performance audit is suggested.

*NOTE: Since the Method for validating CO_2 and O_2 analyses is based on combustion of organic and fossil fuels and dilution of the gas stream with air, this Method does not apply to sources that (1) remove CO_2 or O_2 through processes other than combustion, (2) add O_2 (e.g., oxygen enrichment) and N_2 in proporations different from that of air, (3) add CO_2 (e.g., cement or lime kilns), or (4) have no fuel factor, F_o, values obtainable (e.g., extremely variable waste mixtures). This Method validates the measured proportions of CO_2 and O_2 for the fuel type, but the Method does not detect sample dilution resulting from leaks during or after sample collection. The Method is applicable for samples collected downstream of most lime or lime flue-gas desulfurization units as the CO_2 added or removed from the gas stream is not significant in relation to the total CO_2 concentration. The CO_2 concentrations from other types of scrubbers using only water or basic slurry can be significantly affected and would render the F_o check minimally useful.

Calculate a fuel factor, F_o, using the following equation:

$$F_o = \frac{20.9 - \%O_2}{\%CO_2}$$

where:

$\% O_2$ = Percent O_2 by volume (dry basis).
$\% CO_2$ = Percent CO_2 by volume (dry basis).
20.9 = Percent O_2 by volume in ambient air.

If CO is present in quantities measurable by this Method, adjust the O_2 and CO_2 values before performing the calculation for F_o as follows:

$$\%CO_{2(adj)} = \%CO_2 + \%CO$$
$$\%CO_{2(adj)} = \%O_2 - 0.5\ \%CO$$

where: %CO = Percent CO volume (dry basis).

Compare the calculated F_o factor with the expected F_o values. The following table may be used in establishing acceptable ranges for the expected F_o if the fuel being burned is known. When fuels are burned in combination, calculate the combined fuel F_d and F_c factors (as defined in EPA Reference Method 19) according to the procedure in Method 19 Section 5.2.3. Then calcuate the F_o factor as follows:

$$F_o = \frac{0.209\ F_d}{F_c}$$

where:

F_d and F_c have the units of scm/J or scf/million Btu; %H, %C, %S, %N, %O, and $\%H_2O$ are the concentrations by weight (expressed in percent) of hydrogen, carbon, sulfur, nitrogen, oxygen, and water from an ultimate analysis of the fuel; and GCV is the gross calorific value of the fuel in kJ/kg or Btu/lb and is consistent with the ultimate analysis. Follow ASTM 2015 for solid fuels, D 240 for liquid fuels, and D 1826 for gaseous fuels as applicable in determining GCV.

Fuel Type	F_o Range
Coal:	
Anthracite and lignite	1.016 - 1.130
Bituminous	1.083 - 1.230
Oil:	
Distillate	1.260 - 1.413
Residual	1.210 - 1.370

Fuel Type	F_o Range
Gas:	
Natural	1.600 - 1.836
Propane	1.434 - 1.586
Butane	1.405 - 1.553
Wood:	1.000 - 1.120
Wood bark:	1.003 - 1.130

Calculated F_o values beyond the acceptable ranges shown in this table should be investigated before accepting the test results. For example, the strength of the solutions in the gas analyzer and the analyzing technique should be checked by sampling and analyzing a known concentration, such as air; the fuel factor should then be reviewed and verified. An acceptability range of ±12 percent is appropriate for the F_o factor of mixed fuels with variable fuel ratios. The level of the emission rate relative to the compliance level should be considered in determining if a retest is appropriate, i.e., if the measured emissions are much lower or much greater than the compliance limit, repetition of the test would not significantly change the compliance status of the source and would be unnecessarily time-consuming and costly.

It should be noted that this audit only checks the accuracy relative to the ratio of CO_2 to O_2. If the sampling system had a leak, this check would not detect the bias in the results.

5.2.3 Audit Frequency - When Method 3 is used for SPNSS purposes, the following audit frequency is recommended for the compliance and enforcement test. An audit for accuracy should be conducted after each analysis. A lesser frequency may be acceptable when Method 3 is used for other applications depending on the purposes of the test (i.e., no audit would be recommended if the data are to be used only to determine stack gas molecular weight).

5.2.4 Availability of Audit Materials - No audit materials are required.

5.2.5 Cost of Audit - The audit of Method 3 is a calculation audit of the field sample analytical results. No additional samples or analysis is required. The audit for Method 3 should require less than one technical man hour of effort to complete. This effort would generally represent less than 10 percent of the total effort to conduct, calculate, and report Method 3 sampling and analysis.

5.3 Method 5, 5A and 5D (Particulate Matter)

Methods 5, 5A, and 5D should be audited using the quality assurance requirements in Method 5 (see Reference 4 for details).

5.3.1 Method Description - These Methods, when used in conjunction with Methods 1, 2, 3, and 4, are applicable for the determination of particulate emissions from stationary sources.

A gas sample is extracted isokinetically from the stack. Particulate matter is collected on an out-of-stack, glass fiber filter maintained at $120^\circ \pm 14^\circ C$ ($248^\circ \pm 25^\circ F$) for Methods 5 and 5D and $42^\circ \pm 10^\circ C$ ($108^\circ \pm 18^\circ F$) for Method 5A, or at another temperature specified by an applicable subpart of the standard or approved by the Administrator. The mass of particulate matter, which includes any material that condenses at or above the specified filter temperature, is measured gravimetrically after removal of uncombined water. Section 3.4.10 of this Handbook contains a detailed description of Method 5. Method 5 is found in 40 CFR 60, Appendix A. Method 5A can be found in the Federal Register Vol. 47, page 34137, August 6, 1982.

5.3.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

5.3.2.1 Sampling Accuracy - The audit procedure for the sampling phase is to determine the accuracy of the flow totalizing system (dry gas meter) which is described below in this subsection and the accuracy of any differential pressure gauge used to measure velocity that does not meet the specifications in Section 2.2 of Method 2, 40 CFR 60, Appendix A. The audit of the differential pressure gauge is described in Subsection 5.1.2 (Method 2) in this Section.

The audit of the flow totalizing system may be conducted by two methods. The first method compares it to the flow rate system (orificemeter) in the sample train as described in the Reference Method and described below. The second method is with the use of a calibrated orifice that has been certified by EPA.

The following items are provided to conduct a proper audit of the flow totalizing system using the flow rate system. Using the calibration data obtained during the calibration procedure described in Section 5.3 of Method 5, determine the $\Delta H_@$ for the metering system orifice. The $\Delta H_@$ is the orifice pressure differential that correlates to 0.75 cfm of air at $528^\circ R$ and 29.92 in. Hg in units of in. H_2O. The $\Delta H_@$ is calculated as follows:

$$\Delta H_{@} = 0.0319\ \Delta H \left(\frac{T_m}{P_{bar}}\right)\left(\frac{\theta^2}{Y^2\ V_m^2}\right)$$

where:

ΔH = Pressure drop reading from orifice meter, in. H_2O.
T_m = Absolute average dry gas meter temperature, ^{o}R.
P_{bar} = Barometric pressure, in. Hg.
θ = Total sampling time, min.
Y = Dry gas meter calibration factor, dimensionless.
V_m = Volume of gas sample as measured by dry gas meter, dcf.
0.0319 = $(0.0567\ \text{in. Hg}/^{o}R) \times (0.75\ \text{dscfm})^2$

Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (i.e., pump, volume meter, and orifice) at the $H_@$ pressure differential for 10 minutes. Record the volume collected, the dry gas meter temperatures and the barometric pressure. Calculate the average dry gas meter temperature. Calculate a dry gas meter calibration check value, Y_c, as follows:

$$Y_c = \frac{10}{V_m}\left|\frac{0.0319\ T_m}{P_{bar}}\right|^{1/2}$$

where:

Y_c = Dry gas meter calibration check value, dimensionless.
10 = 10 minutes of run time.

Compare the Y_c value with the dry gas meter calibration factor Y to determine that :

$$0.97Y < Y_c < 1.03Y\ .$$

If the Y_c value is not within this range, the volume metering system should be investigated before beginning the test and the audit repeated. If the initial and repeat audit do not agree with the range, the auditor may take actions deemed appropriate or inform the tester that if the post test calibration does not agree within the range stated by the Method, that the results may affect the acceptability of the test.

Alternatively, the dry gas meter may be audited using a calibrated flow orifice housed in a quick-connect coupling certified by the EPA. The following recommendations are provided as guidance:

1. Remove the calibrated orifice from its case and insert it into the gas inlet quick-connect coupling on the source

sampling meter box. Turn on the pump and adjust until 19 in. Hg vacuum is being pulled on the calibrated orifice based on the sampling meter box vacuum gauge.

2. Make the quality assurance check prior to the start of the field test. Record the initial and the final dry gas meter volumes, the dry gas meter inlet and outlet temperatures, the internal orifice pressure drop (ΔH), the ambient temperature, and the barometric pressure. The duration of the run should be slightly >15 min. The following procedure is recommended for each quality assurance run: 15 min. after a run is started, watch the dry gas meter needle closely. As the needle reaches the zero (12 o'clock) position stop the pump and stopwatch simultaneously. Record the dry gas meter volume and the time.

3. Calculate the corrected dry gas volume for the run using the equation below. Record the collected dry gas volume (V_m), the sampling time in decimal minutes, the barometric pressure (P_{bar}) the average temperature (T_m), the internal orifice pressure drop (ΔH) and the dry gas meter calibration factor (Y).

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m} \right) \left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} \right)$$

$$= K_1 V_m Y \left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m} \right)$$

where:

K_1 = 0.3858 °K/mm Hg for metric units, or
= 17.64 °R/in. Hg for English units.

The auditor should then calculate the percent relative error (RE) between the measured standard volume and the audit or given standard volume (calibrated orifice calculated volume). The percent relative error is a measure of the bias of the [illegible]ume measurement in the sampling phase of Method 5. Calcula[illegible] RE using the equation below.

$$RE = \frac{V_M - V_A}{V_A} \times 100$$

where:

V_M = Volume measured by the field crew, corrected to standard conditions, m^3, and
V_A = Audit or given volume of the audit device, corrected to standard conditions, m^3.

4. The results of the calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling phase of the Method 5 test.

Since the calibrated orifice is not a primary standard, the auditor should always have at least two orifices available. When the first orifice audit results deviate by more than ±10 percent, the second orifice should be used to validate this difference.

When a differential pressure gauge other than an inclined manometer is used for velocity pressure measurement, an audit to assess the accuracy of the velocity pressure measurement is recommended. The audit should follow the procedure and frequency as described for Method 2 in Subsection 5.1.

5.3.2.2 Analytical Accuracy - None recommended.

5.3.3 Audit Frequency - When Method 5, 5A or 5D is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters) and on all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when (1) a different flow totalizing system is used or (2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when (1) a different differential pressure gauge is used or (2) when repairs are made on the differential pressure gauge after auditing. A lesser frequency may be acceptable when Method 5 is used for applications other than compliance or enforcement.

5.3.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain certified calibrated orifices (when available) prior to each compliance or enforcement test. By contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 5 and sent to the USEPA for certification.

5.3.5 Cost of Audit - The audit of Method 5, 5A or 5D is an audit of the sampling phase. This audit should require less than two technical hours of effort to complete. This effort should generally represent less than 2 percent of the total effort to conduct, calculate, and report the Method 5 sampling and analysis.

5.4 Method 6, 6A, and 6B (Sulfur Dioxide)

Methods 6, 6A and 6B should be audited using the quality assurance requirements in Method 6. (See Reference 1 for details.)

5.4.1 Method Description - Method 6 is applicable to the determination of sulfur dioxide (SO_2) emissions from stationary sources. A gas sample is extracted at a constant rate from the sampling point in the stack. The SO_2 is separated from the sulfuric acid mist (including sulfur trioxide) and is measured by the barium-thorin titration method. The barium ions react preferentially with sulfate ions in solution to form a highly insoluble barium sulfate precipitate. When the barium has reacted with all sulfate ions, excess barium then reacts with the thorin indicator to form a metal salt of the indicator, resulting in a color change. Section 3.5.10 of this Handbook contains a detailed description of Method 6. Methods 6, 6A and 6B are found in 40 CFR 60, Appendix A.

5.4.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

5.4.2.1 Sampling Accuracy - No audit is recommended when the midget impingers are used. An audit to assess the accuracy of the flow measuring device (dry gas meter) is recommended when the standard size impingers (i.e., Method 5 or Method 8) are used. The audit of the flow measuring device with the use of a critical orifice is described in Subsection 5.3.2.

5.4.2.2 Analytical Accuracy - According to Method 6, when the Method is used for compliance testing, the analyst must analyze two audit samples along with the field samples. One of these samples should be at a low concentration (500 to 1000 mg SO_2/m^3 of gas sampled when a EPA specified aliquot of the audit sample is diluted to exactly 100 ml) and one at a high concentration (1500 to 2500 mg SO_2/m^3 when an EPA specified aliquot of the audit sample is diluted to exactly 100 ml). This is based on an emission standard of 1.2 lb of SO_2 per million Btu which would be about 1300 mg SO_2/m^3 at 35 percent excess air. The percent relative error (RE) of the audit samples is determined using the following equation. The calculated RE must be included in the emission test report as an assessment of the accuracy of the analytical phase of the Method 6 test.

$$RE = \frac{C_d - C_a}{C_a} \times 100$$

where:

C_d = Determined audit sample concentration, mg/m^3, and
C_a = Actual audit concentration, mg/m^3.

Method 6 states that the relative error (RE) should be less than 5 percent for both audit samples. When agreement is not met, the audit samples and field samples must be reanalyzed and the initial and reanalysis results included in the test report. Nonagreement on the initial and reanalysis results of the audit samples may void the test.

5.4.2.3 Combined Sampling and Analytical Accuracy - For Method 6B, a cylinder gas (SO_2/CO_2 in N_2) audit that addresses both sampling and analytical accuracy is also available (refer to Section 3.13.8 of this Handbook for details). It is recommended that this audit be conducted in addition to the required liquid sample audit when Method 6B is used for compliance testing.

5.4.3 Audit Frequency - When Method 6 or Method 6A is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the analytical procedures should be conducted simultaneously with the analysis of field samples. The analytical series may contain field samples from more than one stack or test. The audit samples should be analyzed concurrently with the field sample analysis. An additional audit must be conducted when the analyst, analytical reagents and/or analytical system is changed. If acceptable results have been obtained on an audit performed within 30 days of the date of the audit sample analysis and the above conditions are met, the agency may not require an audit. A lesser frequency may be acceptable when Method 6 is used for applications other than compliance and enforcement tests. Note: When Method 6B is used for compliance with 60.47a (f) of 40 CFR Part 60, Subpart Da, the analytical procedures must be audited on a monthly basis (provided the analytical system and analyst do not change). For the cylinder gas audit of Method 6B, audit procedures are shown in Section 3.13.8 of this Handbook.

5.4.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain SO_2 audit samples prior to each compliance or enforcement test, by contacting the Quality Assurance Coordinator (shown in Table 5.1) in his respective EPA Regional Office. The SO_2 audit samples are prepared by EPA's Environmental Monitoring Systems Laboratory at the Research Triangle Park, North Carolina. For purposes other than compliance and enforcement tests, audit samples may be prepared using primary standard grade ammonium sulfate by the procedure described in this Handbook for control sample preparation. For details, see Method 6, Section 3.5.5, Subsection 5.2.5.

5.4.5 Cost of Audit - The required audit for Methods 6, 6A and 6B is an audit of the analysis phase. The audit should require less than four technical hours of effort to complete. This effort would generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 6 sampling and analysis.

5.5 Methods 7, 7A, 7C, and 7D (Oxides of Nitrogen)

Methods 7, 7A, 7C, and 7D should be audited using the quality assurance requirements in Method 7. (See Reference 1 for details.)

5.5.1 Method Description - Methods 7, 7A, 7C, and 7D are applicable to the measurement of nitrogen oxides emitted from stationary sources. The range of the Methods has been determined to be 2 to 400 mg NO_x, expressed as NO_2, per dry standard cubic meter without having to dilute the sample. A gas sample is extracted from the sampling point in the stack. The sample is collected in an evacuated 2-liter round bottom borosilicate flask containing 25 ml of dilute sulfuric acid-hydrogen peroxide absorbing solution (7 and 7A) or in impingers containing alkaline-potassium permanganate solution (7C and 7D). The nitrogen oxides, except nitrous oxide, are measured colorimetrically for Method 7 and 7C, and by ion chromatography for Method 7A and 7D. Section 3.6 of the Handbook contains a detailed description of Method 7. Methods 7, 7A, 7C, and 7D are found in 40 CFR, 60 Appendix A.

5.5.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

5.5.2.1 Sampling Accuracy - No audit recommended.

5.5.2.2 Analytical Accuracy - According to Method 7, when the Method is used for compliance testing, the analyst must analyze two audit samples along with the field samples. One of the samples should be at a low concentration (250 to 500 mg NO_2/dsm^3 of gas sampled when an EPA specified aliquot of the audit sample is diluted to exactly 100 ml), and one at a high concentration (750 to 1500 mg NO_2/dsm^3 of gas sampled when an EPA specified aliquot of the audit sample is diluted to exactly 100 ml). This is based on an emission standard of 0.7 lb NO_2 per million Btu which would be about 750 mg/dsm^3 at 35 percent excess air.

The audit samples must be analyzed simultaneously with the field samples. The percent relative error (RE) of the audit samples is determined using the equation below. The RE results must be included with the emission test report as an assessment of the accuracy of the analytical phase during the Method 7 test.

$$RE = \frac{C_d - C_a}{C_a} \times 100$$

where:

C_d = Determined audit sample concentration, mg/m^3, and

C_a = Audit or given sample concentration, mg/m^3.

Method 7 states that the relative error (RE) should be less than 10 percent for both audit samples. When the argument is not met, the audit samples and field samples must be reanalyzed and the initial and reanalysis results included in the test report. Nonagreement on the initial analysis and reanalysis of the audit samples may void the test.

5.5.3 Audit Frequency - When Method 7 is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted simultaneously with the analysis of the field samples. The anlayses may contain samples from more than one stack or test. An additional audit must be conducted when the analyst, analytical reagents, and/or analytical system is changed. If acceptable results have been obtained on an audit performed within 30 days of the date of the audit sample analysis and the above conditions are not met, the agency may not require an audit. A lesser frequency may be acceptable when Method 7 is used for applications other than compliance and enforcement.

5.5.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain NO_2 audit samples prior to each compliance or enforcement test by contacting the Quality Assurance Coordinator (shown in Table 5.1) in their respective EPA Regional Office. The NO_2 audit samples are prepared by EPA's Environmental Monitoring Systems Laboratory at the Research Triangle Park, North Carolina. For purposes other than compliance and enforcement tests, audit samples may be prepared using potassium nitrate by the procedure described in this Handbook for control sample preparation. For details, see Method 7, Section 3.6.5, Subsection 5.2.2.

5.5.5 Cost of Audit - The audit for Method 7, 7A, 7C, or 7D is an audit of the analysis phase. This audit should require less than four technical hours of effort to complete. This effort would generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 7 sampling and analysis.

5.6 Method 8 (Sulfuric Acid and Sulfur Dioxide)

5.6.1 Method Description - This Method is applicable for the determination of sulfuric acid mist (including SO_3) emissions from stationary sources. A gas sample is extracted isokinetically from the stack. The sulfuric acid mist (including SO_3) and the SO_2 are separated; both fractions are then measured separately by the barium-thorin titration method. The barium ions react preferentially with sulfate ions in solution to form a highly insoluble barium sulfate precipitate. When the barium has reacted with all sulfate ions, the excess barium reacts with the thorin indicator to form a metal salt of the indicator and to give a color change. Section 3.7 of this Handbook contains a detailed description of Method 8. The Method can be found in 40 CFR 60, Appendix A.

5.6.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

5.6.2.1 Sampling Accuracy - The audit for the sampling phase is used to determine the accuracy of the flow totalizing system (dry gas meter) of the Method 8 sampling train and the differential pressure gauge used to measure the velocity when the gauge does not meet the specifications in Section 2.2 of Method 2 (40 CFR 60, Appendix A). The flow totalizing system should be audited using the same procedures and with the same frequency as described in detail for Method 5 in Subsection 5.3.2 of this Section. The differential pressure gauge should be audited using the same procedures and with the same frequency as described in detail for Method 2 in Subsection 5.1.2 of this Section.

5.6.2.2 Analytical Accuracy - The analytical procedures for both the sulfuric acid and sulfur dioxide should be audited using the procedure described for Method 6 in Subsection 5.4.2. An emission standard of 0.15 lb of sulfuric acid per ton of acid produced is about 100 mg/dsm^3 at 100 percent excess air, and 4.0 lb of SO_2 per ton of acid produced is about 2500 mg/dsm^3 at 100 percent excess air. Note: Separate audits are not necessary for both the sulfuric acid and sulfur dioxide. The single audit procedure will provide sufficient accuracy assessment for both pollutants.

5.6.3 Audit Frequency - When Method 8 is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters) and all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when (1) a different flow totalizing system is used or (2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when (1) a different differential pressure gauge is used or (2) repairs are made on the differential pressure gauge after auditing. An audit for accuracy of the analytical procedures should be conducted prior to the analysis of the field samples for every field test series. The analytical series may contain field samples from more than one stack or test. A lesser frequency may be acceptable when Method 8 is used for applications other than compliance and enforcement.

5.6.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain certified calibrated orifices (when available) prior to each compliance or enforcement source test. Orifices may be obtained by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 1 and sent to the USEPA for certification.

Agencies may obtain SO_2 audit samples prior to each compliance or enforcement test by contacting the Quality Assurance Coordinator (Table 5.1) in his respective EPA Regional Office. The SO_2 audit samples are prepared by EPA's Environmental Monitoring Systems Laboratory at the Research Triangle Park, North Carolina. For purposes other than compliance and enforcement tests, audit samples may be prepared using primary standard grade ammonium sulfate by the procedure described in this Handbook for control sample preparation. For details, see Method 6, Section 3.5.5, Subsection 5.2.5.

5.6.5 Cost of Audit - The audit for Method 8 is an audit of portions of both the sampling and analytical phases. These audits should require less than five technical hours of effort to complete. This effort would generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 8 sampling and analysis.

5.7 Method 10 (Carbon Monoxide)

5.7.1 Method Description - Method 10 is applicable to the determination of carbon monoxide (CO) from stationary sources. A gas sample is extracted from the stack either at a constant rate using a continuous sampling train (constant rate sampling) or at a rate proportional to the stack gas velocity using an integrated sampling train. The concentration of CO from both sampling methods is determined by a Luft-type nondispersive infrared (NDIR) analyzer. The Method is applicable to stationary sources when specified by a compliance regulation and/or when the CO concentration is $\geq$20 parts per million (ppm) for a 0-to-1000-ppm testing range. With this Method, interferences can result from substances with strong infrared absorption energies. Major interferences can be avoided using silica gel and Ascarite traps to remove H_2O and CO_2, respectively. If traps are used, the sample volumes must be adjusted to account for the CO_2 removed. Section 3.8 of this Handbook contains a detailed description of Method 10. The Method can be found in 40 CFR 60, Appendix A. Note: This audit is not applicable to 40 CFR 60, Subpart Z (Ferroalloy Production Facilities).

5.7.2 Audits to Assess Accuracy of Sampling and Analysis Procedures - The accuracy of the sampling and analytical procedure is assessed by conducting a cylinder gas audit. An audit cylinder of CO is needed. Use audit gas that has been certified by comparison with National Bureau of Standards (NBS) gaseous Standard Reference Materials (SRM) or NBS/EPA approved gas manufacturer's Certified Reference Materials (CRM) following EPA Traceability Protocol No. 1 for audit gases (Section 3.0.4 of this Handbook). CRM's may be used directly as audit gases; procedures for preparation of CRM's are described in Reference 6.

The audit sample concentration should be within the range of 40 to 200 percent of the applicable regulation. A typical standard of 0.050 percent would require an audit cylinder of 0.02 to 0.1 percent CO. Note: The audit gas must not be the gas used for normal calibration.

The following recommendations are provided as guidance for conducting a proper audit.

1. The analyzer should be at normal operating conditions. No adjustment must be made during the audit.

2. For a continuous sampling train, attach a manifold or vented bubbler to the probe tip. Be sure that the audit gas flow to the manifold is kept under a slight positive pressure at all times. For integrated sampling trains, fill a sample bag with the audit gas, and attach the bag to the analyzer.

3. Challenge the analyzer prior to the first sample

analysis and again after the last sample analysis.

4. Compute the percent relative error (RE) for the audit,

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by NDIR, ppm, and
C_A = Audit or given concentration of the audit sample, ppm.

5. An acceptable relative error of ±15% or ±50 ppm (whichever is greater) has been established for this method. These relative errors are based on the SO_2 and NO_x monitor's cylinder gas audits as described in Reference 7, and on the collaborative tests from Method 10 as described in Reference 8.

6. The results of the calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analysis phase of Method 10.

5.7.3 Audit Frequency - When Method 10 is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted after the NDIR calibration and prior to and at the conclusion of, the field sample analysis. A lesser frequency may be acceptable when Method 10 is used for applications other than compliance and enforcement.

5.7.4 Availability of Audit Materials - The given concentrations of CO cylinder gases used for audits of Method 10 must be both accurate and stable. Accurate and stable CO cylinder gases are available from several commercial cylinder gas manufacturers. They can be obtained by two methods:

1) Require the gas manufacturer to use Protocol 1 to establish the audit gas concentration. (The gas manufacturer should also be required to guarantee in writing that Protocol 1 was followed to certify the audit gas concentration.)

2) Obtain a CRM gas from a commercial gas manufacturer. A list of commercial gas manufacturers who have CO CRM gases approved for sale by NBS/EPA may be obtained by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: List of CRM Manufacturers

5.7.5 Cost of Audit - The audit of Method 10 is an audit of both the sampling and analysis phases. This audit should require less than four technical hours of effort to complete. This effort will generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 10 sampling and analysis.

5.8 Method 11 (Hydrogen Sulfide)

5.8.1 Method Description - This Method is applicable for the determination of hydrogen sulfide. The hydrogen sulfide is collected from the source in a series of midget impingers and reacted with acidified cadmium sulfate $CdSO_4$ to form cadmium sulfide (CdS). The precipitated CdS is then dissolved in hydrochloric acid to regenerate H_2S, which is absorbed in a known volume of iodine solution. The iodine consumed is a measure of the H_2S content of the gas. An impinger containing hydrogen peroxide is included to remove SO_2 as an interfering specie. The sampling and analytical procedures are not described in this Handbook. The promulgated Method is in the Federal Register. Vol. 43, page 1494, January 10, 1978 and 40 CFR, Appendix A.

5.8.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedure is assessed by conducting a cylinder gas audit. One audit cylinder of H_2S is needed. The audit cylinder will assess both the sampling and analytical procedures. The range of the audit gas should be within about 40 to 200 percent of the applicable standard. An emission standard of 0.016 percent H_2S would require an audit concentration between 64 to 320 percent H_2S. The following items are provided as guidance to conduct a proper audit.

1. The tester should attach a manifold system or vented bubbler to the sample train and keep the audit gas at a slightly positive pressure through the manifold to ensure that the audit sample is not diluted with ambient air. The vented H_2S should be discharged into a well ventilated area for safety reasons.

2. The tester should attach the manifold or bubbler to the sample train and sample the audit gas using the standard sampling procedures. The tester should ensure an undiluted transfer of audit gas to the sample train.

3. The tester should then recover and analyze the audit sample in the same manner and at the same time as the field samples. This requires an additional sample collection run and analysis to be performed.

4. Compute the percent relative error (RE) for the audit,

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 11, ppm H_2S, and
C_A = Audit or given concentration of the audit sample, ppm H_2S.

(2)

5. The results of the calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phase of the Method 11 test. An acceptable relative error has been established as ±15 percent for this Method. This relative error has been established based on the SO_2 and NO_x monitor's cylinder gas audits, as described in Reference 7, and on the collaborative tests, as described in Reference 9. Due to the cost of auditing and the analytical procedures for this Method, a single audit sample is recommended which is analyzed with the field samples.

5.8.3 Audit Frequency - When Method 11 is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted once during each field testing series and the collected audit sample analysed with the field samples. A lesser frequency may be acceptable when Method 11 is used for other applications, depending on the purpose of the test.

5.8.4 Availability of Audit Materials - Control agencies responsible for compliance and enforcement tests may obtain an audit cylinder of H_2S prior to each compliance or enforcement test by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

If an audit cylinder is unavailable, commercial manufacturers should be sought to obtain the desired audit gas.

5.8.5 Cost of Audit - The audit for Method 11 is an audit of both the sampling and analysis phase. This audit should require less than four technical hours of effort to complete. This effort will generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 11 sampling and analysis.

5.9 Method 12 (Inorganic Lead)

5.9.1 Method Description - This Method applies to the determination of inorganic lead (Pb) emissions. Particulate and gaseous Pb are withdrawn isokinetically from the source and collected on a filter and in dilute nitric acid. The collected samples are digested in acid solution and analyzed by atomic absorption spectrometry using an air acetylene flame. The sampling and analytical procedures are not described in this Handbook. The Method can be found in 40 CFR 60, Appendix A.

5.9.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

5.9.2.1 Sampling Accuracy - The audit for the sampling phase is to determine the accuracy of the flow totalizing system (dry gas meter) of the Method 12 sampling train and the differential pressure gauge used to measure the velocity when the gauge does not meet the specifications in Section 2.2 of Method 2 (40 CFR 60, Appendix A). The flow totalizing system should be audited using the same procedures and with the same frequency as described in detail for Method 5 in Subsection 5.3.2 of this Section. The differential pressure gauge should be audited using the same procedures and with the same frequency as described in detail for Method 2 in Subsection 5.1.2 of this Section.

5.9.2.2 Analytical Accuracy - The analytical procedures should be audited using two audit samples. The audit samples are glass fiber filters impregnated with lead nitrate. One audit sample should be at a low concentration (between 100 μg and 600 μg total weight of lead per audit sample) and one audit sample at a high concentration (between 900 μg and 2000 μg total weight of lead per audit sample). This requirement is based on emission standards of 0.4 mg/dsm^3 and 1.0 mg/dsm^3 corresponding to about 400 and 1000 μg of lead per sample. These audit samples should be prepared simultaneously with the field samples using the same procedures, but analyzed prior to the source test filter. The auditor should calculate the relative error (RE) of the audit samples using the equation below. The calculated RE should be included in the emission test report as an assessment of the accuracy of the analytical phase of the Method 12 test.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by the lab analyst, total μg lead per audit sample, and
C_A = Audit or given concentration of the audit sample (glass fiber filter), total μg lead per audit sample.

An acceptable relative error has been established as ±15 percent for this Method. The relative error was established based on the collaborative tests, as described in Reference 10.

5.9.3 Audit Frequency - When Method 12 is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters) and all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when (1) a different flow totalizing system is used or (2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when (1) a different differential pressure gauge is used or (2) repairs are made on the differential pressure gauge after auditing. An audit for accuracy of the analyses of the field sample should be conducted after the preparation of the calibration curve and just prior to the field sample analysis. The analyses may cover samples from more than one stack or test. A lesser frequency may be acceptable when Method 12 is used for applications other than compliance and enforcement.

5.9.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain lead audit samples (glass fiber filter strips impregnated with lead nitrate) and a certified calibrated orifice prior to each compliance or enforcement test by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 5 and sent to the USEPA for certification.

5.9.5 Cost of Audit - The audit for Method 12 is an audit of portions of both the sampling and the analysis phase. This audit should require less than five technical hours of effort to complete. This effort will generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 12 sampling and analysis.

5.10 Methods 13A and 13B (Total Fluoride)

5.10.1 Method Description - These Methods are applicable for the determination of fluoride emissions from stationary sources. Fluorocarbons, such as Freons, are not quantitatively collected or measured by these procedures. Both Methods withdraw gaseous and particulate fluorides from the source isokinetically using a sample train with water-filled impingers and filter(s). Method 13A determines the weight of total fluoride by the SPADNS Zirconium Lake colorimetric method. If chloride ion is present, it is recommended that Method 13B be used. Method 13B determines the weight of fluorides by the specific ion electrode method. Section 3.9 and Section 3.10 of this Handbook contain detailed descriptions of Methods 13B and 13A, respectively. The Method can be found in 40 CFR 60, Appendix A.

5.10.2 Audits to Access Accuracy of Sampling and Analytical Procedures -

5.10.2.1 Sampling Accuracy - The audit for the sampling phase is used to determine the accuracy of the flow totalizing system (dry gas meter) of the Method 13 sampling train and the differential pressure gauge used to measure the velocity when the gauge does not meet the specifications in Section 2.2 of Method 2 (40 CFR 60, Appendix A). The flow totalizing system should be audited using the same procedures and with the same frequency as described in detail for Method 5 in Subsection 5.3.2 of this Section. The differential pressure gauge should be audited using the same procedures and with the same frequency as described in detail for Method 2 in Subsection 5.1.2 of this Section.

5.10.2.2 Analytical Accuracy - The analytical procedures for both Methods 13A and 13B should be audited using the same procedure. The auditor should provide two audit samples to be analyzed along with the field samples, one sample at a low concentration (0.2 to 1.0 mg fluoride/dsm^3 of gas sampled or approximately 1 to 5 mg NaF/liter of sample), and one at a high concentration (1 to 5 mg of fluoride/dsm^3 of gas sampled or approximately 5 to 25 mg NaF/liter of sample). The above values are typical for fertilizer plants with emission limits of 0.01 lb/ton and 0.02 lb/ton. Actual values can vary since the allowable concentration is dependent on both process design and operation.

The audit samples should be analyzed at the same time, as the field samples for Method 13A and after preparation of the calibration curve and just prior to analysis for Method 13B. The percent relative error (RE) of the audit sample is determined using the equation below. The calculated RE should be included in the emission test report as an assessment of the accuracy of the analytical phase of the Method 13A or 13B test.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by the lab analyst, mg/ml, and
C_A = Audit or given concentration of the audit sample, mg/ml.

An acceptable relative error has been established as ± 15 percent for this Method. The relative error has been established based on the collaborative test described in Reference 11.

5.10.3 Audit Frequency - When Method 13A or 13B is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters) and all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when (1) a different flow totalizing system is used or (2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when (1) a different differential pressure gauge is used or (2) repairs are made on the differential pressure gauge after auditing.

An audit for accuracy of the analytical procedures should be conducted simultaneously with the analysis of every series of field samples for Method 13A and after the preparation of the calibration curve and prior to field sample analysis for Method 13B. The analytical series may contain field samples from more than one stack or test. A lesser frequency may be acceptable when either Method 13A or 13B is used for other applications, depending on the purpose of the test.

5.10.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain aqueous sodium fluoride (NaF) audit samples and a certified calibrated orifice by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 5 and sent to the USEPA for certification.

If audit samples are to be used for other purposes, aqueous NaF audit samples may be prepared by the procedure described in this Handbook for control sample preparation. This procedure is described in Section 3.10.5, Subsection 5.2.6 for Method 13A and Section 3.9.5, Subsection 5.2.6 for Method 13B.

5.10.5 Cost of Audit - The audit for Method 13A or 13B is an audit for portions of both the sampling and analysis phase. These audits should require less than five technical hours of effort to complete. This effort will generally represent less than 5 percent of the total effort to conduct, calculate and report the Method 13 sampling and analysis.

5.11 Method 15 (Hydrogen Sulfide, Carbonyl Sulfide, and Carbon Disulfide)

5.11.1 Method Description - Method 15 is applicable for determination of hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon disulfide (CS_2) from tail gas control units of sulfur recovery plants. A gas sample is extracted from the emission source through a heated probe and diluted with clean dry air. An aliquot of the diluted sample from the sample line is then analyzed for H_2S, COS, and CS_2 by gas chromatographic (GC) separation and flame photometric detection (FPD). The sampling and analytical procedures are not described in this Handbook. The promulgated Method is in the Federal Register, Vol. 43, page 10866, March 15, 1978 and 40 CFR 60 Appendix A.

5.11.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedure is assessed by conducting a cylinder gas audit. Two audit cylinders [one of hydrogen sulfide (H_2S) and one of carbonyl sulfide (COS)] are needed. The total concentration of the two audit gases should be within about 40 to 200 percent of the applicable standards. For an emissions standard of 0.030 percent by volume reduced sulfur compound and 0.0010 percent by volume hydrogen sulfide, audit gases of 100 to 500 ppm COS and 4 to 20 ppm H_2S would typically be used. The following items are provided as guidance to conduct a proper audit:

1. The standard post-test procedure of determining the sample line loss should be run by the tester.

2. Prior to collection of the field sample, the tester should attach either of the audit cylinders to the opening of the probe. The audit gas should be fed to the probe in sufficient quantity to ensure that the excess sample is vented to the atmosphere. The number of audit sample injections for analysis and the time between sample injections is left to the discretion of the tester.

3. After completion of one audit cylinder, the other audit cylinder should then be attached in the same manner. The tester is responsible for ensuring that the audit gas is introduced into the sample train in an acceptable manner and at an acceptable rate.

4. The results of the audit sample results should be calculated in the same manner used to calculate the field sample results and should be included in the test report.

5. The auditor can then compute the percent relative error (RE) for the audit.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 15, ppm H_2S or ppm COS, and
C_A = Audit or given concentration of the audit sample, ppm H_2S or ppm COS.

6. An acceptable relative error of ±20 percent has been established for this Method. This relative error has been established based on the collaborative test described in Reference 12.

7. The calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phases of the Method 15 test.

5.11.3 Audit Frequency - When Method 15 is used for SPNSS purposes, the following frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted prior to each field test series at the conclusion of the sample line loss determination. A lesser frequency may be acceptable when Method 15 is used for other applications, depending on the purpose of the test.

5.11.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain audit cylinders of H_2S and COS prior to each compliance or enforcement source test. The H_2S and COS audit cylinders may be obtained by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

If the audit cylinders are unavailable, commercial manufacturers should be sought to obtain the desired audit gases.

5.11.5 Cost of Audit - The audit for Method 15 is an audit of both the sampling and analysis phase. This audit should require less than five technical hours of effort to complete. This effort will generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 15 sampling and analysis.

5.12 Method 16 (Sulfur Emissions)

5.12.1 Method Description - Method 16 is applicable for determination of hydrogen sulfide (H_2S), methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills. The four compounds shown above are collectively known as total reduced sulfur (TRS). A gas sample is extracted from the emission source through a heated probe and diluted with clean air. An aliquot of the diluted sample from the sample line is then analyzed for H_2S, MeSH, DMS, and DMDS by gas chromatographic (GC) separation and flame photometric detection (FPD). The sampling and analytical procedures are not described in this Handbook. The promulgated Method can be found in the Federal Register, Vol. 43, page 7568, February 23, 1978 and 40 CFR 60, Appendix A.

5.12.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedure is assessed by conducting a cylinder gas audit. One audit cylinder of hydrogen sulfide is needed. The hydrogen sulfide (H_2S) concentration should be within 40 to 200 percent of the applicable standard. For an emission standard of 5 ppm by volume of total reduced sulfur, an audit concentration of 2 to 10 ppm of H_2S would typically be used. The following items are provided as guidance to conduct a proper audit.

1. The standard post-test procedure of determining the sample line loss should be run by the tester.

2. Prior to collecting the field samples, the tester should attach the audit cylinder to the opening of the probe. The audit gas should be fed to the probe in sufficient quantity to ensure that an excess of sample is vented to the atmosphere. The gas should be vented into a well-ventilated area for safety reasons. The number of audit sample injections for analysis and the time between sample injections is left to the discretion of the tester.

3. The results of the audit gas sampling should be calculated in the same manner used to calculate the field sample results and should be included in the test report.

4. The auditor can then compute the percent relative error (RE) for the audit.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 16, ppm H_2S, and
C_A = Audit or given concentration of the audit sample, ppm H_2S.

5. An acceptable relative error of ±20 percent has been established for this Method. This relative error has been established based on the collaborative test described in Reference 12.

6. The calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phase of the Method 16 test.

5.12.3 Audit Frequency - When Method 16 is used for SPNSS purposes, the following frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted prior to each field test, at the conclusion of the sample line loss determination. A lesser frequency may be acceptable when Method 16 is used for other applications, depending on the purpose of the test.

5.12.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain audit cylinders of H_2S prior to each compliance or enforcement source test. The H_2S audit cylinder may be obtained by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

If the audit cylinders are unavailable, commercial manufacturers should be sought to obtain the desired audit gases.

5.12.5 Cost of Audit - The audit of Method 16 is an audit of both the sampling and analysis phase. This audit should require less than five technical hours of effort to complete. This effort should generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 16 sampling and analysis.

5.13 Method 16A (Total Reduced Sulfur Emissions)

Method 16A should be audited using the quality assurance requirements in Method 16A. (See Reference 13 for details.)

5.13.1 Method Description - Method 16A is an alternative method to Method 16 for determining total reduced sulfur (TRS) compounds from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills. A gas sample is extracted from the sampling point in the stack. SO_2 is selectively removed from the sample using a citrate buffer solution. The reduced sulfur compounds are then oxidized and analyzed as SO_2 using the barium-thorin titration procedure of Method 6. The sampling and analytical procedures are not described in this Handbook. The promulgated Method can be found in the *Federal Register*, Vol. 50, page 9578, March 8, 1985 and 40 CFR 60, Appendix A.

5.13.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedures is assessed by conducting a cylinder gas audit, and the accuracy of the analytical procedures is assessed by analysis of a set of aqueous audit samples.

5.13.2.1 Sampling and Analytical Accuracy - The procedures described in detail in Section 4.2 "System Performance Check" of Method 16A should be used to assess the sampling and analytical accuracy. This audit should be conducted in accordance with the Reference Method and will require a separate sample collection and analysis. The hydrogen sulfide (H_2S) concentration of the audit gas should be between 40 and 200 percent of the applicable standard. For an emission standard of 5 ppm by volume of total reduced sulfur, an audit concentration of 2 to 10 ppm of H_2S would typically be used. The auditor should calculate the percent relative error (RE) for the audit as shown below.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 16A, ppm H_2S, and
C_A = Audit or given concentration of the audit sample, ppm H_2S.

An acceptable relative error of ± 20% has been established for this Method. The calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phase of the Method 16A test.

5.13.2.2 Analytical Accuracy - According to Method 16A, when the Method is used for compliance testing, the analyst must analyze two aqueous audit samples along with the field samples. The percent relative error (RE) for each of the audit samples is determined using the following equation. The calculated RE's must be included in the emission test report as an assessment of the accuracy of the analytical phase of the Method 16A test.

$$RE = \frac{C_d - C_a}{C_a} \times 100$$

where:

C_d = Determined audit sample concentration, mg/m^3, and
C_a = Actual audit concentration, mg/m^3.

Method 16A states that the relative error shall be less than 5 percent for both audit samples. When this specification is not met, the audit samples and field samples must be reanalyzed and the initial and reanalysis results included in the test report. Failure to meet the 5 percent specification on the initial and reanalysis results of the audit samples may void the test.

5.13.3 Audit Frequency - When Method 16A is used for SPNSS purposes, the following frequency is recommended for compliance and enforcement tests. Audits for both sampling and analytical accuracy and analytical accuracy should be conducted once for each field test in accordance with the Method 16A. A lesser frequency may be acceptable when Method 16A is used for other applications, depending on the purpose of the test.

5.13.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain aqueous audit samples prior to each compliance or enforcement source test by contacting the respective EPA Regional Office Quality Assurance Coordinator (shown in Table 5.1). Audit cylinders of H_2S may be obtained by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

If the audit cylinders are unavailable, commercial manufacturers should be sought to obtain the desired audit gases.

5.13.5 Cost of Audit - The audit of Method 16A is an audit of both the sampling and analysis phase. This audit should require less than five technical hours of effort to complete. This effort should generally represent less than 5 percent of the total effort to conduct, calculate and report the Method 16A sampling and analysis.

5.14 Method 17 (Instack Filterable Particulate)

5.14.1 Method Description - This Method applies to the measurement of particulate matter emissions from stationary sources. This Method is not applicable when stack gases are saturated with water vapor or when the projected cross-sectional area of the probe emission-filter holder assembly covers more than 3 percent of the stack cross-sectional area. For SPNSS, the Method should only be used when (1) specified by the applicable subpart of the standards and only within the temperature limits (if specified) or (2) otherwise approved by the Administrator. Particulate matter is withdrawn isokinetically from a gas stream and collected on a glass filter maintained at stack temperature. The particulate matter mass is determined gravimetrically after removal of uncombined water. Subsection 3.11.10 of this Handbook contains a detailed description of Method 17. The Method can also be found in 40 CFR 60, Appendix A.

5.14.2 Audits to Assess Accuracy of Sampling and Analysis

5.14.2.1 Sampling Accuracy - The audit for the sampling phase is used to determine the accuracy of the flow totalizing system (dry gas meter) of the Method 17 sampling train and the differential pressure gauge used to measure the velocity when the gauge does not meet the specifications in Section 2.2 of Method 2 (40 CFR 60, Appendix A). The flow totalizing system should be audited using the same procedures and with the same frequency as described in detail for Method 5 in Subsection 5.3.2 of this Section. The differential pressure gauge should be audited using the same procedures and with the same frequency as described in detail for Method 2 in Subsection 5.1.2 of this Section.

5.14.2.2 Analytical Accuracy - None recommended.

5.14.3 Audit Frequency - When Method 17 is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters) and on all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when (1) a different flow totalizing system is used or (2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when (1) a different differential pressure gauge is used or (2) repairs are made on the differential pressure gauge after auditing. A lesser frequency may be acceptable when Method 17 is used for applications other than compliance and enforcement.

5.14.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain certified calibrated orifices (when available) prior to each compliance or enforcement source test. Orifices may be obtained by contacting:

U. S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 5 and sent to the USEPA for certification.

5.14.5 Cost of Audit - The audit of Method 17 is an audit of the sampling phase. The audit should require less than three technical hours of effort. This effort will generally represent less than 5 percent of the total effort to conduct, calculate and report the Method 17 sampling and analysis.

5.15 Method 18 (Gaseous Organic Compounds)

Method 18 should be audited using the quality assurance requirements in Method 18. (See Reference 2 for details.)

5.15.1 Method Description - Method 18 is applicable to approximately 90 percent of the total gaseous organics emitted from an industrial source. It does not include techniques to identify and measure trace amounts of organic compounds, such as those found in building air and fugitive emission sources. The Method will not determine compounds that (1) are polymeric (high molecular weights), (2) can polymerize before analysis, or (3) have very low vapor pressures at stack or instrument conditions. The Method is based on separating the major components of a gas mixture with a gas chromatograph (GC) and measuring the separated components with a suitable detector. This sampling and analytical technique is not described in this Handbook. The promulgated Method can be found in the Federal Register, Vol. 48, page 48344, November 18, 1983 and 40 CFR 60, Appendix A.

5.15.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedures is assessed by conducting a cylinder gas audit. Two audit cylinders of an appropriate total gaseous organic are needed. The organic compound should be one of the major organic components being tested and the given concentration of the audit gas should be between 25 to 100 percent of the applicable emission limit for the low concentration, and 100 to 250 percent of the applicable emission limit for the high concentration cylinder. The audit cylinder gas will assess both the sampling and analytical procedures. The audit procedures should follow those described in 40 CFR 61, Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis" of the Federal Register, Vol. 47, page 39179, September 7, 1982 (Reference 14). The analysis of the audit samples shall be conducted after the preparation of the calibration curve and prior to the final field sample analysis.

The auditor should compute the percent relative error (RE) for each audit.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 18 in ppm of the stated organic, and
C_A = Audit or given concentration of the audit sample in ppm of the stated organic.

Method 18 requires that the calculated relative error be less than ±10 percent for both audit sample analyses. The calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phase of the Method 18 test.

5.15.3 Audit Frequency - When Method 18 is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted after the preparation of the calibration curve and prior to the field sample final analysis for every field test series. A lesser frequency may be acceptable when Method 18 is used for applications other than compliance and enforcement tests.

5.15.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain EPA Method 18 audit gas cylinders prior to each compliance or enforcement test. The audit gas cylinders may be obtained by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

If an audit gas cylinder is unavailable, commercial manufacturereres should be sought to obtain the desired audit gas.

5.15.5 Cost of Audit - The audit of Method 18 is an audit of both the sampling and analysis phase. This audit should require less than six technical hours of effort to complete. This would generally represent less than 10 percent of the total effort to conduct, calculate, and report the Method 18 sampling and analysis.

A complete list of organic compounds for which audit cylinders are available from the U. S. Environmental Protection Agency is shown in Table 5.3 Audit cylinders are generally available at a low concentration level (5 to 20 ppm) and a high concentration level (50 to 700 ppm) for each organic shown in the table. The table also shows those organic compounds which the U. S. Environmental Protection Agency has found to be unsuitable as audit cylinders because of insufficient stability in compressed gas cylinders.

TABLE 5.3. ORGANIC AUDIT CYLINDERS AVAILABLE FROM U. S. EPA

	Low Concentration Range		High Concentration Range	
Compound****	Concentration Range (ppm)	Cylinder Construction***	Concentration Range (ppm	Cylinder Construction***
Benzene	5-20	S	60-400	Al, S
Ethylene	5-20	Al	300-700	Al
			3000-20,000	Al
Propylene	5-20	Al	300-700	Al
Methane/Ethane	---	--	1000-6000(M)	Al
			200-700(E)	
Propane	5-20	Al	300-20,000	Al
Toluene	5-20	S	100-700	S
Hydrogen Sulfide	5-20	Al	100-700	Al
Meta-Xylene	5-20	S	300-700	LS
Methyl Acetate	5-20	S	300-700	S
Chloroform	5-20	S	300-700	S
Carbonyl Sulfide	5-20	S	100-300	S
Methyl Mercaptan	3-10	Al	--------	--
Hexane	20-80	Al	1000-3000	LS
1,2-Dichloroethane	5-20	Al	100-600	Al
Cyclohexane	----	--	80-200	S
Methyl Ethyl Ketone	30-80	S	--------	--
Methanol	30-80	Al	--------	--
1,2-Dichloropropane	5-20	Al	300-700	Al
Trichloroethylene	5-20	Al	100-600	Al
1,1-Dichloroethylene	5-20	Al	100-600	Al
**1,2-Dibromoethylene	5-20	LS	100-600	LS
Perchloroethylene	5-20	S	300-700	LS
Vinyl Chloride	5-30	S	--------	--
1,3-Butadiene	5-30	S	--------	--
Acrylonitrile	5-20	LS, Al	300-700	LS, Al
**Aniline	5-20	Al	--------	--
Methyl Isobutyl Ketone	5-20	Al	--------	--
**Para-dichlorbenzene	5-20	S	------	--
**Ethylamine	5-20	Al	------	--
**Formaldehyde	5-20	--	------	--
Methylene Chloride	1-20	Al	------	--
Carbon Tetrachloride	5-20	Al	------	--
Freon 113	5-20	Al	------	--
Methyl Chloroform	5-20	Al	------	--
Ethylene Oxide	5-20	Al	------	--
Propylene Oxide	5-20	Al	75-200	Al

(continued)

TABLE 5.3. ORGANIC AUDIT CYLINDERS AVAILABLE FROM U. S. EPA (continued)

	Low Concentration Range		High Concentration Range	
Compound****	Concentration Range (ppm)	Cylinder Construction***	Concentration Range (ppm	Cylinder Construction***
Allyl Chloride	5-20	Al	75-200	S
Acrolein	5-20	Al	------	--
Chlorobenzene	5-20	Al	------	--
Carbon Disulfide	--	--	75-200	Al
**Cyclohexanone	5-20	Al	------	--
*EPA Method 25 Gas	100-200	Al	750-2000	Al
Ethylene Dibromide	5-20	S	100-300	S
Tetrachloroethane	5-20	S	------	--

* The gas mixture contains an aliphatic, an aromatic and carbon dioxide in nitrogen. Concentrations shown are reported in ppmC.

** Cylinders are no longer available in the repository since the compounds are found to be unstable in the cylinders.

*** Cylinder construction: Al = Aluminum, S = Steel, LS = Low Pressure Steel

****All organic compounds in audit cylinders are in a balance of N_2 gas.

5.16 Method 19 (Sulfur Dioxide Removal Efficiency and Particulate, Sulfur Dioxide and Nitrogen Oxides Emissions)

5.16.1 Methods Description - Method 19 is applicable for determining sulfur dioxide removal efficiencies of fuel pretreatment and sulfur dioxide control devices and the overall reduction of potential sulfur dioxide emissions from electric utility steam generators. This Method is also applicable for the determination of particulate, sulfur dioxide and nitrogen oxides emission rates. Fuel samples from before and after fuel pretreatment systems are collected and analyzed for sulfur and heat content. A sulfur dioxide emission reduction efficiency is calculated from the efficiency of the fuel pretreatment system.

Sulfur dioxide and oxygen or carbon dioxide concentration data obtained from sampling emissions upstream and downstream of sulfur dioxide control devices are used to calculate sulfur dioxide removal efficiencies. As an alternative to sulfur dioxide monitoring upstream of sulfur dioxide control devices, fuel samples may be collected in an as-fired condition and analyzed for sulfur and heat content. An overall sulfur dioxide emission reduction efficiency is calculated from the efficiency of fuel pretreatment systems and the sulfur dioxide control devices.

Particulate, sulfur dioxide, nitrogen oxides, and oxygen or carbon dioxide concentration data from downstream of sulfur dioxide control devices are used along with F factors to calculate particulate, sulfur dioxide, and nitrogen oxides emission rates. The sampling and analytical procedures are not described in this Handbook for the sulfur dioxide removal efficiency. The Method for determination of oxygen, particulate, sulfur dioxide and nitrogen oxides is described in Sections 3.2, 3.4, 3.11, 3.5, and 3.6, respectively. The promulgated Method is in the Federal Register, Vol. 44, page 33580, June 11, 1979 and 40 CFR 60, Appendix A.

5.16.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - When Methods 3, 5, 6, 7, and 17 are used in support of Method 19, the same procedures and audit frequency should be used as described in the individual subsections for each of those Methods. When sulfur dioxide continuous emission monitors (CEM's) are used in support of the determination of sulfur dioxide removal efficiency, the audit procedures and frequency described in Appendix F, Procedure 1, 40 CFR Part 60 are to be used.

When fuel sample analysis is used to determine the sulfur dioxide concentration on a ng/Joule or lb/million Btu basis, an audit of the analytical procedures should be performed. A coal audit sample should be analyzed each quarter with the fuel samples. The coal audit sample should be analyzed at the same time, by the same procedure and analysis as the coal samples from the pretreatment process and the furnace. The sample must be analyzed until the repeatability of two consecutive analyses of sulfur agree within 0.05% sulfur for coal containing less than 2% sulfur or 0.10% sulfur for coal containing 2% or more of sulfur as described in Reference 15. The auditor can then compute the percent relative error (RE) from the results on a (lb of SO_2)/ million Btu or (ng of SO_2)/Joule basis only.

$$RE = C_M - C_A$$

where:

C_M = Sulfur concentration or the gross calorific value measured by Method 19, % S or Btu/lb, and
C_A = Audit or known sulfur concentration or the gross calorific value of the audit sample, % S or Btu/lb.

An acceptable relative error for the audit sample, based on reproducibility (between lab) criteria in Reference 15, is 0.10% sulfur for coal containing less than 2% sulfur and 0.20% sulfur for coal containing 2% or more of sulfur. For heating value, an acceptable relative error has been established at 300 Btu/lb based on the EPA coal audit data. The results of the calculated RE from the coal audit plus the audit results from Methods 3, 6, 7 and either 5 or 17, if used in support of Method 19, should be included in the quarterly emissions report as assessments of the accuracy of the sampling and analytical phase during the Method 19 test. The acceptable relative error for Methods 3, 5, 6, 7 and 17 are the same as specified in their respective section.

5.16.3 Audit Frequency - When Method 19 is used for SPNSS purposes, the following audit frequency is recommended for assessing accuracy. Methods 3, 5, 6, 7, and 17 should be audited using the same procedures and frequency as shown in the individual subsection for each Method. The SO_2 CEM should be audited on aquarterly basis using the procedures and frequency described in Appendix F, Procedure 1, 40 CFR Part 60 (see Reference 7 for details). An audit for assessing accuracy of the coal sample analysis should be conducted on a quarterly basis. A lesser frequency may be acceptable when Method 19 is used for applications other than compliance and enforcement.

5.16.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test, may obtain audit materials for Methods 5, 6, 7, and 17 from the locations described in these respective individual subsections. These control agencies may obtain a coal audit sample by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

The coal audit sample may also be used to assess the accuracy of the moisture and/or ash content analysis. Alternatively, coal audit samples may also be obtained from commercial coal testing laboratories.

5.16.5 Cost of Audit - The audit for Method 19 is an audit of the sampling phase for Method 5 and 17 and an audit of the analytical phase for Methods 6, 7, and coal sampling and analysis. The audit of the initial performance test and performance specification procedures for the continuous emission monitors should require less than 16 technical hours of effort to complete. The effort would generally represent less than 10 percent of the total effort to conduct, calculate and report Method 19 sampling and analysis requirements. Since the allowable combinations of testing analysis procedures for a continuous effort are numerous, no estimate of cost is made. It is unlikely, however, that the effort for the audits with the continuous monitoring would be greater than 10 percent of the total effort.

5.17 Method 20 (Nitrogen Oxide, Sulfur Dioxide and Oxygen Emissions from Stationary Gas Turbines)

5.17.1 Method Description - Method 20 is applicable for the determination of nitrogen oxides (NO_x), sulfur dioxide (SO_2), and oxygen (O_2) emissions from stationary gas turbines. For the NO_x and O_2 determinations, this Method includes: (1) measurement system design criteria; (2) analyzer performance specifications and performance test procedures; and (3) procedures for emission testing. A gas sample is continuously extracted from the exhaust stream of a stationary gas turbine; a portion of the sample stream is then conveyed to instrumental analyzers for determination of NO_2 and O_2 content. During each NO_x and O_2 determination, a separate measurement of SO_2 emissions is made by using Method 6, or its equivalent. The O_2 determination is used to adjust the NO_x and SO_2 concentrations to a reference condition. The sampling and analytical procedures are not described in this Handbook. The promulgated Method can be found in the Federal Register, Vol. 44, page 52792, September 10, 1979 and 40 CFR 60, Appendix A.

5.17.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedure is assessed by conducting a cylinder gas audit. One audit cylinder of NO in N_2 and one cylinder of O_2 in N_2 are needed. These audit gases must be certified by comparison to National Bureau of Standards (NBS) gaseous Standard Reference Materials (SRM) or NBS/EPA approved gas manufacturer's Certified Reference Materials (CRM) following EPA Traceability Protocol 1 for audit gases (Section 3.0.4 of this Handbook). CRM's may be used directly as audit gases; procedures for preparation of CRM's are described in Reference 6.

The NO audit sample concentrations should be within the range of 40 to 200 percent of the applicable emissions limit. An audit gas concentration of 60 to 300 ppm of NO would typically be used for an emission standard of 0.015 percent NO at 15 percent oxygen for stationary gas turbines. Note: The audit gas should not be the same gas used for normal calibration.

The O_2 audit gas cylinder concentration should be between 10 and 15 percent O_2 in N_2.

The following items are provided as guidance for conducting a proper audit.

1. The monitors should be operating at normal conditions, and no adjustments are permitted during the audit.

2. After the measurement systems calibration and validation, and just prior to the field sampling, the tester should attach the NO audit cylinder to the opening of the probe. The

163

audit gas should be fed to the probe in sufficient quantity to ensure that an excess of sample is vented to the atmosphere. The tester should record the analyzer readings when a stable value is obtained.

3. The same procedure should be performed with the O_2 audit gas. The tester is responsible for ensuring that the audit gas is introduced into the measurement system in an acceptable manner and at an acceptable rate.

4. The results for the audit gas samples should be calculated in the same manner used to calculate the field test samples.

5. The auditor can then compute the percent relative error (RE) for each audit point.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 20, ppm NO or percent O_2, and

C_A = Audit or given concentration of the audit sample, ppm NO or percent O_2.

6. An acceptable relative error has been established as ± 15 percent for this Method. This relative error is based on the O_2 and NO_x monitors' cylinder gas audits, as described in Reference 7.

7. The calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phase of the Method 20 test.

The Method 6 tests performed in support of Method 20 should be audited using the same procedures as described in the accuracy audit procedures for Method 6 (Section 5.4). The acceptable relative error for Method 6 audits is also shown in Section 5.4.

5.17.3 Audit Frequency - When Method 20 is used for SPNSS purposes, the following audit frequency is recommended for the compliance and enforcement test. An audit for accuracy of the measurement system for NO and O_2 should be conducted before the start of the field testing series. An audit for accuracy of the analytical procedures for Method 6 tests should be conducted simultaneously with the field samples as described in Subsection 5.4.3 of Method 6. A lesser frequency may be acceptable when Method 20 is used for applications other than compliance and enforcement.

5.17.4 Availability of Audit Materials - The given concentrations of O_2 and NO cylinder gases used for audits of Method 20 must be both accurate and stable. Both O_2 and NO are available from several commercial gas manufacturers. These cylinder gases may be obtained by two methods:

1. Require the gas manufacturer to use EPA Traceability Protocol 1 to establish the audit gas concentration. (The gas manufacturer should also be required to guarantee in writing that EPA Traceability Protocol 1 was followed to certify the audit gas concentration.)

2. Obtain a CRM gas from a commercial gas manufacturer. A list of commercial gas manufacturers who have no CRM gases approved for sale by NBS/EPA may be obtained by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77)
Research Triangle Park, North Carolina 27711

Attention: List of CRM Manufacturers

5.17.5 Cost of Audit - The audit for Method 20 is an audit of both the sampling and analysis phase. This audit should require less than five technical hours of effort to complete. This effort should generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 20 sampling and analysis.

5.18 Method 25 (Total Gaseous Nonmethane Organic Emissions as Carbon)

5.18.1 Method Description - This Method applies to the measurement of volatile organic compounds (VOC) as total gaseous nonmethane organics (TGNMO) analyzed in terms of carbon from source emissions. Organic particulate matter will interfere with the analysis and, therefore in some cases, an in-stack particulate filter is required. An emission sample is withdrawn from the stack at a constant rate through a chilled condensate trap by means of an evacuated sample tank. TGNMO are determined by combining the analytical results obtained from independent analyses of the condensate trap and sample tank fractions. After sampling is completed, the organic contents of the condensate trap are oxidized to carbon dioxide (CO_2). The CO_2 is quantitatively collected in an evacuated vessel, then a portion of the CO_2 is reduced to methane (CH_4) and measured by a FID. The organic content of the sample fraction collected in the sampling tank is measured by injecting a portion into a gas chromatographic (GC) column to separate the nonmethane organics from CO, CO_2, and CH_4; the nonmethane organic (NMO) material is oxidized to CO_2, reduced to CH_4 and measured by a flame ionization detector (FID). In this manner, the variable response of the FID associated with different types of organics is eliminated. The sampling and analytical procedures are not described in this Handbook. The promulgated Method can be found in the Federal Register, Vol. 45, page 65956, October 3, 1980 and 40 CFR 60, Appendix A.

5.18.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedures is assessed by conducting a cylinder gas audit. One audit cylinder of EPA Method 25 gas mixture is needed. The audit cylinder will assess both the sampling and analytical procedure. The EPA Method 25 gas mixture includes a combination of aliphatic and aromatic organics plus carbon dioxide in a balance gas of nitrogen. Use of this audit mixture will result in a collection of organics in both the condensate trap and the evacuated sample tank portions of the sampling apparatus. The audit gas should be in the range of about 40 to 200 percent of the concentration of the allowable emission rate.

The following items are provided as guidance to conduct a proper audit.

1. The audit sample analysis should be conducted to coincide with the analysis of source test samples. Normally, it will be conducted after the nonmethane organic analyzer calibration and concurrent with the sample analyses.

2. After a leak check of the sampling apparatus has been completed, attach a manifold to the sample probe. Attach the

audit gas cylinder to the manifold and collect the audit gas with the Method 25 sampling system consistent with normal procedure for the Method.

3. At the end of audit analyses, the auditor requests the calculated concentration from the analyst and then compares the results with the actual audit concentrations. The auditor computes the percent relative error for the audit.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 25, ppm as carbon, and

C_A = Audit or given concentration of the audit sample, ppm as carbon.

4. No acceptable relative error has been established for this Method since major revisions to the Method are currently underway. Due to the cost of the audit only a single audit is recommended. The audit sample and field samples should be prepared and analyzed in the same manner and at the same time.

5. The calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phase of the Method 25 test.

5.18.3 Audit Frequency - When Method 25 is used for SPNSS purposes, the following frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted once for every field test series. A lesser frequency may be acceptable when Method 25 is used for applications other than compliance and enforcement.

5.18.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain an EPA Method 25 audit gas cylinder prior to each compliance or enforcement source test by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

The concentration range of the EPA Method 25 audit gas cylinder available is shown in Table 5.3.

107

If an audit gas cylinder is unavailable, commercial manufacturers should be sought to obtain the desired audit gas.

5.18.5 Cost of Audit - The audit of Method 25 is an audit of both the sampling and analysis phase. This audit should require less than 10 technical hours of effort to complete. This would generally represent less than 10 percent of the total effort to conduct, calculate and report the Method 25 sampling and analysis.

5.19 Method 25A and 25B (Total Gaseous Organic Concentration)

5.19.1 Method Description - Methods 25A and 25B are applicable to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon. Both Methods extract a gas sample from the stack through a heated sample line and, if necessary, a glass fiber filter. Method 25A uses a flame ionization analyzer (FIA) for analysis and Method 25B uses a nondispersive infrared analyzer (NDIR) for analysis. The sampling and analytical procedures are not described in this Handbook. The promulgated Method 25A and 25B can be found in the Federal Register Vol. 48, pages 37595 and 37597, respectively, August 18, 1983 and in 40 CFR 60, Appendix A.

5.19.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedures is assessed by conducting a cylinder gas audit. One audit cylinder of an appropriate alkane or alkene is needed. The organic compound in the audit cylinder should be one of the major organic components being tested and the given concentration of the audit gas should be between 40 and 200 percent of the applicable emission limit. The audit cylinder gas will assess both the sampling and analytical procedures. The audit procedures (with the exception that only a single cylinder is recommended) should follow those described in 40 CFR 61, Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis" or the Federal Register Vol. 47, page 39179, September 7, 1982 (see Reference 14). The analysis of the audit sample should be conducted after the preparation of the calibration curve and prior to the field sample analysis.

The auditor should compute the percent relative error (RE) for the audit:

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 25A or 25B in ppm of the stated organic, and
C_A = Audit or given concentration of the audit sample in ppm of the stated organic.

An acceptable relative error of ±10 percent has been established for this Method. This relative error is based on the audits conducted by EPA in Reference 16.

The calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phase of Method 25A or 25B test.

5.19.3 Audit Frequency - When Method 25A or 25B is used for SPNSS purposes, the following frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted after the preparation of the calibration curve and prior to the field sample analysis for every field test series. A lesser frequency may be acceptable when Method 25A or 25B is used for applications other than compliance and enforcement tests.

5.19.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain an appropriate alkane or alkene audit gas cylinder prior to each compliance or enforcement source test by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

Table 5.3 shows organic compounds available from the U. S. Environmental Protection Agency as audit gas cylinders. An appropriate alkane or alkene audit gas should be selected from this table for a Method 25A or 25B audit.

If an audit gas cylinder is unavailable, commercial manufacturers should be sought to obtain the desired audit gas.

5.19.5 Cost of Audit - The audit of Method 25A or 25B is an audit of both the sampling and analysis phase. This audit should require less than five technical hours of effort to complete. This would generally represent less than 5 percent of the total effort to conduct, calculate and report the Method 25A or 25B sampling and analysis.

5.20 References

1. "Quality Assurance and Quality Control Revisions to Methods 6 and 7," 40 CFR 60, Appendix A or Federal Register Vol. 49, page 26522, June 27, 1984.

2. EPA Method 18 "Measurement of Gaseous Organic Compounds by Gas Chromotography," 40 CFR 60, Appendix A or Federal Register Vol. 48, page 48344, October 18, 1983.

3. "Quality Control Procedures for EPA Method 3," 40 CFR 60, Appendix A or Federal Register Vol. 48, page 49458, October 25, 1983.

4. "Quality Control Procedures for EPA Methods 4 and 5," 40 CFR 60, Appendix A or Federal Register Vol. 48, page 55670, December 14, 1983.

5. Mitchell, W. J., Fuerst, R. G., Margeson, J. H., Streib, E. W., Midgett, M. R., and Hamil, H. F., "New Orifice Opens Way for Fast Calibration," Pollution Engineering, June 1981, pp. 45-57. A correction in this publication was printed in Pollution Engineering, August 1981.

6. "A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials." Joint publication by NBS and EPA. EPA-600/7-81-010. Available from U.S. Environmental Protection Agency, Quality Assurance Division (MD-77A), Research Triangle Park, North Carolina 27711.

7. "Quality Assurance Requirements for Gaseous Continuous Emission Monitoring Systems Used for Compliance Determination," 40 CFR 60, Appendix F, Procedure 1.

8. Constant, P. C., Scheil, G. W., and Sharp, M. C., "Collaborative Study of Method 10 - Reference Method for Determination of Carbon Monoxide Emissions from Stationary Sources - Report of Testing," EPA-650/4-75-001.

9. Scheil, G. W., and Sharp, M. C., "Standardization of Method 11 at a Petroleum Refinery," EPA-600/4-77-008a, January 1977.

10. Mitchell, W. J., and Midgett, M. R., "Evaluation of Stationary Source Particulate Measurement Methods: Volume V, Secondary Lead Smelters," EPA-600/2-79-116, June 1979.

11. Mitchell, W. J., Suggs, J. C., and Bergman, F. J., "Collaborative Study of EPA Method 13A and Method 13B," EPA-600/4-77-050, September 1977.

12. Hamil, H. F., and Swynnerton, N. F., "A Study to Improve EPA Methods 15 and 16 for Reduced Sulfur Compounds," EPA-600/4-80-023, April 1980.

13. Method 16A, Section 4.3 "System Performance Check," and Section 4.4 "Sample Analysis" 40 CFR 60, Appendix A or Federal Register Vol. 50, page 9578, March 8, 1985.

14. "Procedure for Field Auditing GC Analysis," 40 CFR 61, Appendix C, Procedure 2 or Federal Register Vol. 47, page 39179, September 7, 1982.

15. "Total Sulfur in the Analysis of Coal and Coke," ASTM D 3177-84, page 413-417, 1984.

16. Jayanty, R. K. M., Gutknecht, W. F., and Decker, C. E., "Status Report #6 Stability of Organic Audit Materials and Results of Source Test Analysis Audits," report by Research Triangle Institute for U. S. Environmental Protection Agency Environmental Monitoring Systems Laboratory, under Contract No. 68-02-3767, September 1984.

6.0 SPECIFIC PROCEDURES TO ASSESS ACCURACY OF REFERENCE METHODS USED FOR NESHAP

The purpose of this Section is to describe specific procedures to routinely assess and document the accuracy of reference and alternative methods for source test data under NESHAP (National Emission Standards for Hazardous Air Pollutants). Procedures for assessment of precision and completeness are not given, because compliance or enforcement tests are short-term (only a few hours duration), and additional duplicate tests to obtain precision data are costly. Accuracy is determined from results of performance audits (i.e., measurements made by the routine operator or analyst). The routine operator or analyst must not know the concentration or value of the audit standard used, and the results must be submitted to an immediate supervisor or QA coordinator who does know the audit value.

Since a high degree of experience and planning is required for audit sample preparation, and EPA has mandated that quality assurance be an integral part of all agency related measurement programs, the EPA's Environmental Monitoring Systems Laboratory (EMSL) in the Research Triangle Park, North Carolina has been delegated the responsibility for preparation of audit samples and materials for air measurements. Federal, state, and local agency personnel can obtain audit samples and materials for any enforcement and compliance measurement program directly from the Quality Assurance Coordinator at each EPA Regional Office unless otherwise directed in the following Reference Method subsections. The address and telephone number for each EPA Regional Office Quality Assurance Officer is shown in Table 5.1 of Section 3.0.5. When audit materials are unavailable or needed for nonagency use, commercial suppliers should be sought.

Performance audits are recommended here for the assessment of accuracy for the EPA Reference Methods in 40 CFR 61, Appendix B, when used for NESHAP purposes. Several of the methods have no performance audits since there are no reliable and low cost audit procedures available or the time and expense for an audit cannot now be justified. The EPA Reference Methods for which audits are recommended are shown in Table 6.1 with their corresponding subsection number.

The brief description of specific assessment procedures for each promulgated or proposed Reference Method is approximately three pages in length. This brief description includes the following:

1. Method summary (one paragraph).

2. Reference for details on the Method.

TABLE 6.1. EPA REFERENCE METHODS INCLUDED IN SECTION 3.0.6

Method number	Description	Subsection number
101, 101A and 102	Mercury Emissions in Air Streams from Chlor-Alkali Plants, Mercury Emissions from Sewage Sludge Incinerators, and Mercury Emissions in Hydrogen Streams from Chlor-Alkali plants	6.1
104	Beryllium	6.2
105	Mercury in Sewage Sludge	6.3
106	Vinyl Chloride	6.4
108 and 108A	Arsenic	6.5

3. Performance audit program to assess sampling and analytical procedures.

4. Recommended frequency for performance audits of compliance and enforcement tests. A frequency less than that recommended for enforcement could be acceptable when testing for other purposes.

5. Recommended standards and levels for establishing audit values.

6. Procedure to calculate accuracy.

7. Availability of audit materials.

8. Cost of the recommended audits.

The philosophy of these assessments is that relative error calculations will be made of the accuracy (1) to determine errors in the testers'/analysts' techniques and systems; (2) to, where possible, correct errors in these techniques and systems; and (3) for interpretation of the final reported emission test results by the data user. The reported emissions test data are not to be corrected on the basis of these relative error calculations.

The general approach that has been developed for these audits follow those already described in the Reference Method for EPA Methods 6 and 7 (see Reference 1) and/or Method 18 (see Reference 2). These audit procedures require the tester/analyst to provide the auditor with the audit results, either prior to the field sample analysis or prior to including the field sample results in the report. When large relative errors are identified, the tester/analyst is allowed to correct his system. If possible, this is accomplished prior to the taking of the field samples or performing the final analysis on the field samples; this approach works quite well when the auditor is present for an on-site analysis. However, in the absence of the auditor, the tester/analyst must telephone the auditor with results of the audit sample analysis in order to make necessary corrections prior to analyzing the field samples. If the auditor feels that this is unwarranted or the tester/analyst does not wish to take the possible opportunity to correct an error in the system and/or techniques, the audit sample(s) would then be prepared and analyzed in the same manner and at the same time as the field sample. The approach of notifying the auditor prior to the field sample analysis can provide the source and agency with a greater chance of more accurate data, may require the rejection of less test results, and may improve the techniques and system of the tester and/or analyst.

For compliance determination, the audit sample values should be within the range of the allowable emission limit. The audit sample concentration or value should be within 40 to 200 percent of the value of interest for audits containing a single audit sample. For audits containing two audit samples, the low concentration sample should be between 25 and 100 percent of the value of interest and the high concentration between 100 and 250 percent.

6.1 Method 101 (Mercury Emissions in Air Streams from Chlor-Alkali Plants), Method 101A (Mercury Emissions from Sewage Sludge Incinerators) and Method 102 (Mercury Emissions in Hydrogen Streams from Chlor-Alkali Plants)

6.1.1 Methods Description - Method 101 is applicable for the determination of particulate and gaseous mercury emissions when the carrier gas stream is principally air. Method 101A is applicable for determination of particulate and gaseous mercury emissions from sewage sludge incinerators. Method 102 is applicable for determination of particulate and gaseous mercury emissions when the carrier gas stream is principally hydrogen. These Methods are for use in ducts or stacks at stationary sources. Unless otherwise specified, these Methods are not intended to apply to gas streams other than those emitted directly to the atmosphere without further processing.

Particulate and gaseous mercury emissions are isokinetically sampled from the source and collected in acidic iodine monochloride solution. The mercury collected (in mercuric form) is reduced to elemental mercury. Mercury is aerated from the solution and analyzed using spectrophotometry. The promulgated Methods 101 and 102 are found in the *Federal Register*, Vol. 38, page 8826, April 6, 1973. Methods 101 and 102 revisions and Method 101A are found in the *Federal Register*, Vol. 47, page 4703, June 8, 1982. All Methods can also be found in 40 CFR 61, Appendix B.

6.1.2 Audits to Assess Accurcy of Sampling and Analytical Procedures -

6.1.2.1 Sampling Accuracy - The audit for the sampling phase is used to determine the accuracy of the flow totalizing system (dry gas meter) of the Methods 101 and 101A sampling train and the differential pressure gauge used to measure the velocity when the differential pressure gauge does not meet the specifications in Section 2.2 of Method 2 (40 CFR 60, Appendix A). The flow totalizing system should be audited using the same procedures and with the same frequency as described in detail for Method 5 in Subsection 5.3.2 of Section 3.0.5 in this Handbook. The differential pressure gauge should be audited using the same procedures and with the same frequency as described in detail for Method 2 in Subsection 5.1.2 of Section 3.0.5 in this Handbook.

No audit is suggested for Method 102 because of the special equipment or arrangement for sampling a hydrogen stream and the risk of explosion.

6.1.2.2 Analytical Procedures - The analytical procedures should be audited using two audit samples of aqueous mercury chloride. The audit samples should be provided to the tester to be analyzed just prior to the field samples analysis. For Method 101, one sample should be at a low concentration (1.0 to 5.0 μg/ml) and one at a high concentration (5.0 to 10.0 μg/ml). For Method 101A, one sample should be at a low concentration (0.1 to 0.5 μg/ml) and one at a high concentration (0.5 to 1.0 μg/ml). This is based on typical values at sludge dryers for an emission limit of 3200 g/24 hr. This concentration is dependent on both process design and operating conditions. Both concentrations should be obtained by diluting a specified aliquot of the audit sample to exactly 100 ml.

The audit samples should be analyzed after the preparation of the calibration curve and prior to the analysis of the field samples. The percent relative error (RE) of the audit samples is determined using the equation below. The calculated RE should be included with the emission test report as an assessment of the analytical phase of that test.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 101, 101A, or 102, μg/ml Hg, and
C_A = Audit or given concentration of the audit sample, μg/ml Hg.

An acceptable relative error of ±15 percent has been established for this Method. This relative error is based on collaborative test results for Methods 101 and 101A (References 3 and 4).

6.1.3 <u>Audit Frequency</u> - When Methods 101 or 101A are used for NESHAP purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters), and on all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when 1) a different flow totalizing system is used or 2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when 1) a different differential pressure gauge is used or 2) repairs are made on the differential pressure gauge after auditing. An audit for accuracy of the analytical procedures should be conducted after the preparation of the calibration curve and prior to the analyses of the field samples for every field test series. A lesser frequency may be acceptable when Methods 101, 101A, or 102 are used for applications other than compliance and enforcement.

6.1.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain aqueous mercury chloride audit samples and certified calibrated orifices by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 5 and sent to the USEPA for certification.

6.1.5 Cost of Audit - The audit of Methods 101 and 101A is an audit for portions of both the sampling and analysis phase. The audit of Method 102 is an audit of the analysis phase. Each audit should require less than five technical hours of effort to complete. This effort would generally represent less than 5 percent of the total effort to conduct, calculate and report the Method 101, 101A or 102 sampling and analysis.

6.2 Method 104 (Beryllium)

6.2.1 Methods Description - Method 104 is applicable for the determination of beryllium emissions in ducts or stacks at stationary sources. Unless otherwise specified, this Method is not intended to apply to gas streams other than those emitted directly to the atmosphere without further processing.

Beryllium emissions are isokinetically sampled from the source, and the collected sample is digested in an acid solution and analyzed by atomic absorption spectrophotometry. The promulgated Method can be found in the Federal Register, Vol. 48, page 55268, December 9, 1983 and 40 CFR 61 Appendix B.

6.2.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

6.2.2.1 Sampling Accuracy - The audit for the sampling phase is to determine the accuracy of the flow totalizing system (dry gas meter) of the Method 104 sampling train and the differential pressure gauge used to measure the velocity when the differential pressure gauge does not meet the specifications in Section 2.2 of Method 2 (40 CFR 60, Appendix A). The flow totalizing system should be audited using the same procedures and with the same frequency as described in detail for Method 5 in Subsection 5.3.2 of Section 3.0.5 of this Handbook. The differential pressure gauge should be audited using the same procedures and with the same frequency as described in detail for Method 2 in Subsection 5.1.2 of Section 3.0.5 of this Handbook.

6.2.2.2 Analytical Accuracy - The analytical procedures should be audited using two audit samples of aqueous beryllium salts. The analyst should analyze the audit samples along with the field samples. One sample should be a low concentration (5 to 20 μg of beryllium per audit sample) and one sample should be a high concentration (50 to 100 μg of beryllium per audit sample). This is based on typical concentration values at beryllium processing facilities that would be equivalent to an emission limit of 10 g/24 h.

The audit samples must be analyzed after the preparation of the calibration curve and prior to the analysis of the field samples. The auditor should calculate the percent relative error (RE) of the audit samples using the equation below. The calculated RE should be included in the emission test report as an assessment of the analytical phase of that test.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 104, total μg beryllium, and
C_A = Audit or given concentration of the audit sample, total μg beryllium.

An acceptable relative error of ±15 percent has been established for this Method. This relative error is based on the collaborative test results for Method 104 (Reference 6).

6.2.3 Audit Frequency - When Method 104 is used for NESHAP purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters) and on all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when (1) a different flow totalizing system is used or (2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when (1) a different differential pressure gauge is used or (2) repairs are made on the differential pressure gauge after auditing. An audit for accuracy of the analytical procedures should be conducted after the preparation of the calibration curve and prior to the analysis of the field samples for each field test series. A lesser frequency may be acceptable when Method 104 is used for applications other than compliance and enforcement.

6.2.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain aqueous beryllium salt audit samples and certified calibrated orifices by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 5 and sent to the USEPA for certification.

6.2.5 Cost of Audit - The audit of Method 104 is an audit of portions of both the sampling and analysis phase. This audit should require less than six technical hours of effort to complete. This effort should generally represent less than 10 percent of the total effort to conduct, calculate and report Method 104 sampling and analysis.

6.3 Method 105 (Mercury in Sewage Sludge)

6.3.1 Methods Description - Method 105 is applicable for the determination of total organic and inorganic mercury content in sewage sludges, soils, sediments, and bottom-type materials. The normal range of this Method is 0.2 to 5 μg/g. The range may be extended above or below the normal range by increasing or decreasing sample size and through instrument and recorder control.

A weighted portion of the sewage sludge sample is digested in aqua regia for 3 minutes at 95°C, followed by oxidation with potassium permanganate. Mercury in the digested sample is then measured by the conventional spectrophotometer cold vapor technique. An alternative digestion procedure involves the use of an autoclave and is described in this Method. The promulgated Method can be found in the *Federal Register*, Vol. 40, page 48299, October 14, 1975 and 40 CFR 60 Appendix B.

6.3.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

6.3.2.1 Sampling Accuracy - No audit recommended.

6.3.2.2 Analytical Accuracy - The analytical procedures for Method 105 should be audited using the same procedure and frequency as detailed for Methods 101, 101A and 102 in Subsection 6.1.2.2.

6.3.3 Audit Frequency - When Method 105 is used for NESHAP purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the analytical procedures should be conducted after the preparation of the calibration curve and prior to the analysis of the field samples. A lesser frequency may be acceptable when Method 105 is used for applications other than compliance and enforcement.

6.3.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test, may obtain aqueous mercury chloride audit samples by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

6.3.5 Cost of Audit - The audit of Method 105 is an audit of the analysis phase. This audit should require less than four technical hours of effort to complete. This effort generally represents less than 5 percent of the total effort to conduct, calculate and report Method 105 sampling and analysis.

6.4 Method 106 (Vinyl Chloride)

Method 106 should be audited using the quality assurance requirements in Method 106. (See Reference 7 for details.)

6.4.1 Method Description - Method 106 is applicable to the measurement of vinyl chloride in stack gases from ethylene dichloride, and vinyl chloride and polyvinyl chloride manufacturing processes, except where the vinyl chloride is contained in particulate matter. An integrated bag sample of stack gas containing vinyl chloride (chloroethene) is subjected to chromatographic analysis using a flame ionization detector.

Note: Performance of this Method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, as there are many details that are beyond the scope of the Method 106 description. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen. The promulgated Method can be found in the Federal Register, Vol. 47, page 39168, September 7, 1982 and 40 CFR 61, Appendix B.

6.4.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedure is assessed by conducting a cylinder gas audit. Two audit cylinders of vinyl chloride are needed. The audit cylinders are used to assess both the sampling and analytical procedures. The audit cylinders should contain a vinyl chloride concentration between 5 and 20 ppm for the low concentration cylinder and 20 to 50 ppm for the high concentration cylinder. This is based on an emission limit of 10 ppm vinyl chloride. The following recommendations are provided as guidance to conduct a proper audit.

1. The audit should be conducted to coincide with the analysis of source test samples. Normally, it will be conducted immediately after the GC calibration and prior to the sample analyses.

2. After a leak check of the bag has been completed, fill each bag approximately half full with the audit gases. Analyze the bags in the normal manner specified for Method 106.

3. At the end of audit analyses, the auditor requests the calculated concentrations from the analyst and then compares the results with the actual audit concentrations. The auditor computes the percent relative error (RE) for both audit values using the equation below.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 106, ppm, and
C_A = Audit or given concentration of the audit sample, ppm.

4. Method 106 has an established acceptable relative error of less than ±10 percent. If this agreement is not met the tester/analyst should check the system to eliminate problems and repeat the audit prior to field sample collection.

5. The RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phases of the Method 106 test.

6.4.3 Audit Frequency - When Method 106 is used for NESHAP purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted prior to every field test series (but after analyzer calibration). A lesser frequency may be acceptable, when Method 106 is used for applications other than compliance and enforcement.

6.4.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain an audit cylinder of vinyl chloride prior to each compliance or enforcement source test by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

If audit cylinders are unavailable, commercial manufacturers should be sought to obtain the desired audit gases. These commercial gases should meet the specifications described in Section 5.2.3.1 of Method 106.

6.4.5 Cost of Audit - The audit of Method 106 is an audit of both the sampling and analysis phase. This audit should require less than five technical hours of effort to complete. This effort should generally represent less than 5 percent of the total effort to conduct, calculate and report Method 106 sampling and analysis.

123

6.5 Method 108 and 108A (Arsenic)

6.5.1 Method Description - Methods 108 and 108A are applicable to the determination of organic arsenic (As) emissions from nonferrous smelters and other sources, as specified in the regulations. Particulate and gaseous As emissions are withdrawn isokinetically from the source and collected on a glass mat filter and in water. The collected As is then analyzed by means of atomic absorption spectrophotometry. The sampling and analytical procedures are not included in this Handbook. The promulgated Method can be found in 40 CFR 61, Appendix B.

6.5.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

6.5.2.1 Sampling Accuracy - The audit for the sampling phase is used to determine the accuracy of the flow totalizing system (dry gas meter) of the Method 108 and 108A sampling train and the differential pressure gauge used to measure the velocity when the differential pressure gauge does not meet the specifications in Section 2.2 of Method 2 (40 CFR 60, Appendix A). The flow totalizing system should be audited using the same procedures and with the same frequency as described in detail for Method 5 in Subsection 5.3.2 of Section 3.0.5 in this Handbook. The differential pressure gauge should be audited using the same procedures and with the same frequency as described in detail for Method 2 in Subsection 5.1.2 of Section 3.0.5 in this Handbook.

6.5.2.2 Analytical Accuracy - The analytical procedures should be audited using duplicate analysis of a single aqueous audit sample. The audit sample should be at a concentration between 40 and 200 percent of the emission limit. The duplicate analysis of the audit sample should be performed after the preparation of the calibration curve and prior to the analysis of the field samples. The auditor should calculate the percent relative error (RE) of the audit samples:

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 108 or 108A, total μg of As, and
C_A = Audit or given concentration of the audit sample, total μg of As.

An acceptable relative error of $\pm 15\%$ has been established for this Method. The relative error is based on the method evaluation of Method 108 (Reference 8).

The calculated RE should be included in the emission test report as an assessment of the accuracy at the analytical phase of the Method 108 or 108A test.

6.5.3 Audit Frequency - When Method 108 or 108A is used for NESHAP purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters) and on all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when (1) a different flow totalizing system is used or (2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when (1) a different differential pressure gauge is used or (2) repairs are made on the differential pressure gauge after auditing. An audit for accuracy of the analytical procedures should be conducted after the preparation of the calibration curve and prior to the analysis of the field samples for each field test series. A lesser frequency may be acceptable when 108 or 108A is used for applications other than compliance and enforcement.

6.5.4 Availability of Audit Materials - Control agencies responsible for compliance or enforcement test may obtain aqueous audit samples and certified calibrated orifices by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 5 and sent to the USEPA for certification.

6.5.5 Cost of Audit - The audit for Method 108 or 108A is an audit of portions of both the sampling and analysis phase. The audit should require less than eight technical hours of effort to complete. This effort should generally represent less than 10 percent of the total effort to conduct, calculate and report Method 108 or 108A sampling and analysis.

6.6 References

1. "Quality Assurance and Quality Control Revisions to Methods 6 and 7," 40 CFR 60, Appendix A or Federal Register, Vol. 49, page 26522, June 27, 1984.

2. EPA Method 18, "Measurement of Gaseous Organic Compounds by Gas Chromatography," 40 CFR 60, Appendix A or Federal Register, Vol. 48, page 48344, October 18, 1983.

3. Mitchell, W. J. and Midgett, M. R., "Improved Procedure for Determining Mercury Emissions from Mercury Cell Chlor-Alkali Plants." APCA Journal, Vol. 26, No. 7, July 1976.

4. Mitchell, W. J., Midgett, M. R., Suggs, J. C., and Albrinck, D, "Test Methods to Determine the Mercury Emissions from Sludge Incineration Plants." EPA-600/4-79-058, September 1979.

5. Mitchell, W. J., Fuerst, R. G., Margeson, J. H., Streib, E. W., Midgett, M. R., and Hamil, H. F., "New Orifice Opens Way for Fast Calibration." Pollution Engineering, June 1981, pp. 45-57. A correction in this publication was printed in Pollution Engineering, August 1981.

6. Constant, Paul C. and Sharp, Michael C., "Collaborative Study of Method 104 - Reference Method for Determination of Beryllium Emission from Stationary Sources." EPA-650/4-74-023, June 1974.

7. "Preparation of Standard Gas Mixtures, Calibration, and Quality Assurance," EPA Method 106, 40 CFR 61, Appendix B, or Federal Register, Vol. 47, page 39168, September 7, 1982.

8. Ward, T. E., Logan, T. J., Midgett, M. R., Jayanty, R. K. M., and Gutknecht, W. F., "Field Validation of EPA Proposed Method 108 for Measurement of Inorganic Arsenic Emissions from Stationary Sources." APCA Journal, Vol. 35, No. 8, August 1985, pp. 822-827.

7.0 CALCULATION AND INTERPRETATION OF ACCURACY FOR CONTINUOUS EMISSION MONITORING SYSTEM (CEMS)

This section contains a discussion on the accuracy calculations required in Appendix F[1] and their interpretation. The goals of Appendix F, Procedure 1, are to (1) assess CEMS accuracy, (2) indicate when a CEMS is out-of-control and correction is required, and (3) specify criteria for unacceptable CEMS data. The quarterly accuracy assessments required in Appendix F provide a mechanism for identifying and correcting CEMS's that are out-of-control. This results in an increase in acceptable CEMS data. Increasing acceptable CEMS data strengthens decisions made with regard to compliance.

The following subsections discuss the meaning, interpretation, calculation, and reporting of accuracy data.

7.1 Meaning of Accuracy

Accuracy is the measure of the closeness of a measurement to its "true value." Although the true value is not known, it can be approximated by the use of an appropriate standard of reference, for example, an NBS-SRM (National Bureau of Standards - Standard Reference Materials), a primary standard. Secondary standards are also used as an approximation to "truth," although errors may be introduced in this process.

The preferred measure of accuracy depends on the situation. If the magnitude of the difference tends to be dependent on the true value, T, then the percentage difference is preferable. If it is desired to follow or observe the pattern of the differences over time, then the signed difference or signed percentage difference is preferable.

In the context of accuracy data based on Appendix F, three types of audits for CEMS accuracy assessment are specified: Relative Accuracy Test Audits (RATA), Relative Accuracy Audits (RAA), and Cylinder Gas Audits (CGA). The procedure for the RATA and the RAA are the same as for the Relative Accuracy Test described in the applicable EPA performance specification (e.g., Performance Specification 2 for SO_2 and NO_x, and Performance Specification 3 for O_2 and CO_2), with the exception that the RAA requires three rather than nine sets of measurements, and the accuracy is based on the average of the three sets of data. In addition, EPA performance audit samples must be analyzed concurrently with the RATA samples to demonstrate and document the proficiency and accuracy of the analytical system. The <u>same</u> person must conduct the RATA and the EPA audit sample analysis. Thus, the RATA approximates "truth" by the reference method test results, which are in turn checked for analytical accuracy by EPA audit sample analyses. The EPA audit sample analysis must agree within 5 percent of the audit concentration on each of two SO_2 audit samples or within 10 percent of the audit concentration on each of two NO_x audit samples.

In Appendix F, each CEMS must be audited at least once each calendar quarter. Successive audits shall occur no closer than two months apart. The audits must be conducted as follows:

1. The RATA must be conducted at least once every four calendar quarters. The RATA is conducted as described in the Performance Specifications in Appendix B (e.g., Performance Specification 2 for SO_2 and NO_x). In addition, the appropriate performance audit samples received from EPA are analyzed as described in the applicable Reference Methods (e.g., Methods 6 for SO_2 and 7 for NO_x).

2. If applicable, a CGA may be conducted in three of the four calendar quarters. A CGA is conducted by challenging the CEMS's (both pollutant and diluent monitors, if applicable) with an audit gas of known concentration at two points within the following ranges:

Audit point	Audit range		
	Pollutant monitors	Diluent monitors for-- CO_2	Diluent monitors for-- O_2
1	20 to 30% of span value	5 to 8% by volume	4 to 6% by volume
2	50 to 60% of span value	10 to 14% by volume	8 to 12% by volume

A separate audit gas cylinder must be used for audit points 1 and 2. No dilution of the gas from the audit cylinder is allowed when challenging the CEMS. Challenge the CEMS three times at each point, and use the average of the three responses in determining accuracy. The monitor should be challenged at each point for a sufficient period of time to assure absorption-desorption of the CEMS sample transport surfaces has stabilized. Each monitor is audited in its normal sampling mode, i.e., pass the audit gas through all filters, scrubbers, conditioners, and other monitor components used during normal sampling and as much of the sampling probe as is practical. At a minimum, the audit gas should be introduced at the connection between the probe and the sample line. Audit gases must be certified by comparison with gaseous NBS-SRM or NBS/EPA approved CRM (Certified Reference Material) following EPA Traceability Protocol No. 1. Procedures for preparation of CRM's are described in Reference 2. Procedures for preparation of EPA Traceability Protocol No. 1 gases are described in Reference 3. The difference between the actual concentration of the audit gas and the concentration indicated by the monitor is used to assess the accuracy of the CEMS.

3. The RAA may be conducted three of the four calendar quarters. To conduct a RAA, follow the procedures described in the applicable Performance Specification in Appendix B for the Relative Accuracy Test, except that only three sets of measurement data are required. Analysis of EPA performance audit samples is required for the RAA. The relative difference between the mean of the reference method values and the mean of the CEMS values (in terms of the standard) are used to assess the accuracy of the CEMS.

The performance of RATA's, RAA's, and CGA's provides an independent check of the CEMS accuracy. These independent audits serve to document that the CEMS is providing quality data. Examples of audit calculations are given in the subsection that follows.

In summary, an accuracy assessment is a measure of the deviation of a measurement obtained under standard operational procedures from a known reference measurement. There is no reason to expect that accuracy will remain constant over each quarter because of changes in calibration gases, analysts, and environment.

7.2 Example Calculations and Interpretation for Accuracy

7.2.1 Relative Accuracy Test Audit Calculations - Example data from a RATA on a SO_2/O_2 CEMS are shown in Table 7.1.

The SO_2 and O_2 CEMS data shown in Table 7.1 were corrected to a dry basis using Equation 7-1:

$$\text{CEMS}_{\text{ppm, dry}} = \frac{\text{CEMS}_{\text{ppm, wet}}}{1 - B_{ws}} \qquad \text{Equation 7-1}$$

where

B_{ws} = moisture fraction of the CEMS gas sampled.

TABLE 7.1 RELATIVE ACCURACY TEST AUDIT DATA FOR SO_2 AND O_2 CEMS

	SO_2	SO_2	O_2	O_2	SO_2	SO_2	SO_2
Run number	RM_d, ppm	$CEMS_d$, ppm	RM_d, %	$CEMS_d$, %	RM_d, ng/J	$CEMS_d$, ng/J	Diff, ng/J
1	500	475	3.0	3.1	422.4	403.5	18.9
2	505	480	3.0	3.1	426.6	407.7	18.9
3	510	480	3.0	3.0	430.8	405.4	25.4
4	510	480	2.9	2.9	428.4	403.2	25.2
5	500	480	2.9	3.0	420.0	405.4	14.6
6	500	500	3.0	3.1	422.4	424.7	-2.3
7	510	510	3.0	3.1	430.8	433.3	-2.5
8	505	505	2.9	3.0	424.2	426.6	-2.4
9	510	520	2.9	3.0	428.4	439.3	-10.9
Avg	---	---	---	---	426.0	413.1	9.43

RM_d = reference method data, dry basis.

$CEMS_d$ = monitor data, dry basis.

The SO_2 and O_2 CEMS and RATA data in Table 7.1 were converted to the units of the applicable standard using Equation 7-2:

$$E = CF \frac{20.9}{20.9 - \text{percent } O_2} \qquad \text{Equation 7-2}$$

where

E = pollutant emission, ng/J (lb/million Btu),

C = pollutant concentration, ng/dsm^3 (lb/dscf),

F = factor representing a ratio of the volume of dry flue gas generated to the calorific value of the fuel, dsm^3/J (dscf/million Btu), and

Percent O_2 = oxygen content by volume (expressed as percent), dry basis.

Note: For the calculations shown in Table 7.1, ppm of SO_2 was converted to ng/J using a conversion factor of 2.66×10^6 ng/scm/ppm and an F factor of 2.72×10^{-7} dsm^3/J.

For complete explanation of the equations and calculations, see 40 CFR; Part 60; Appendix A; Method 19; 5. Calculation of Particulate, Sulfur Dioxide, and Nitrogen Oxides Emission Rates.

After the data are converted to the units of the standard, the Relative Accuracy (RA) is calculated by using the equations in Section 8 of Performance Specification 2. For convenience in illustrating the calculation, these equations (7-3 through 7-8) are also shown here.

The average difference, $\bar{d}$, is calculated for the SO_2 monitor using Equation 7-3:

$$\bar{d} = \frac{1}{n} \sum_{i=1}^{n} (X_i - Y_i) = \frac{1}{n} \sum_{i=1}^{n} d_i \qquad \text{Equation 7-3}$$

$$= \frac{1}{9} (84.9) = 9.43 \text{ ng/J}$$

where

n = number of data points,

X_i = concentration from reference method (RM_d in Table 7.1), ng/J,

Y_i = concentration from the CEMS ($CEMS_d$ in Table 7.1), ng/J,

d_i = signed difference between individual pairs, X_i and Y_i, ng/J, and

Σd_i = algebraic sum of the individual differences, d_i, ng/J.

The standard deviation S_d is calculated using Equation 7-4:

$$S_d = \sqrt{\frac{1}{n-1}\left[\sum_{i=1}^{n} d_i^2 - \frac{1}{n} \left(\sum_{i=1}^{n} d_i\right)^2\right]} \qquad \text{Equation 7-4}$$

$$= \sqrt{\left[\frac{1}{8} \quad 2344 - \frac{1}{9} \quad (84.9)^2\right]} = 13.9 \text{ ng/J.}$$

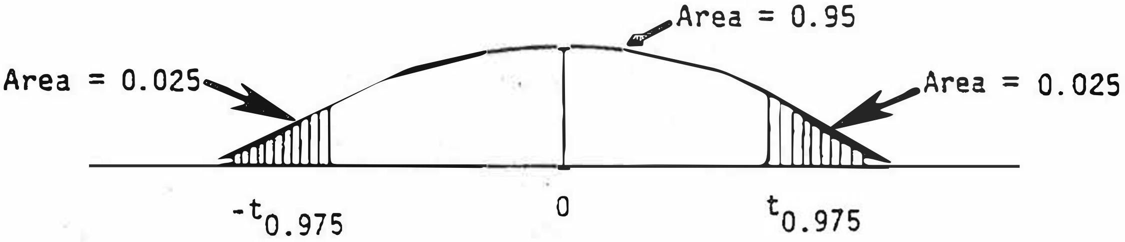
The 2.5 percent error confidence coefficient, CC, is calculated using Equation 7-5:

$$CC = t_{0.975} \frac{s_d}{\sqrt{n}} \qquad \text{Equation 7-5}$$

$$= 2.306 \quad \frac{13.9}{\sqrt{9}} = 10.68 \text{ ng/J.}$$

where $t_{0.975}$ = t-values in Table 7.2 for n = 9.

TABLE 7.2. VALUES OF t FOR 95 PERCENT PROBABILITY[a]



n[a]	$t_{0.975}$	n[a]	$t_{0.975}$	n[a]	$t_{0.975}$
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.262	15	2.145
6	2.571	11	2.228	16	2.131

[a] The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of individual values.

The RA for the RATA is calculated using Equation 7-6:

$$RA = \frac{|\bar{d}| \quad + \quad |CC|}{\overline{RM}} \times 100 \qquad \text{Equation 7-6}$$

$$= \frac{|9.43| \; + |10.68|}{426} \times 100 = 4.72\%$$

where

RA = relative accuracy, %,

$|\bar{d}|$ = absolute value of the mean differences from Equation 7-3, ng/J,

$|CC|$ = absolute value of the confidence coefficient from Equation 7-5, ng/J, and

$\overline{RM}$ = average reference method value or applicable standard, ng/J.

7.2.2 Relative Accuracy Audit Calculations - Example data from an RAA on an SO_2/O_2 CEMS are shown in Table 7.3.

TABLE 7.3 RELATIVE ACCURACY AUDIT DATA FOR SO_2 AND O_2 CEMS

	SO_2	SO_2	O_2	O_2	SO_2	SO_2
Run number	RM_d, ppm	$CEMS_d$, ppm	RM_d, %	$CEMS_d$, %	RM_d, ng/J	$CEMS_d$, ng/J
1	500	475	3.0	3.1	422.4	403.5
2	505	480	3.0	3.1	426.6	407.7
3	510	480	3.0	3.0	430.8	405.4
Avg	---	---	---	---	426.6	405.5

RM_d = reference method data, dry basis.

$CEMS_d$ = monitor data, dry basis.

The SO_2 and O_2 CEMS data shown in Table 7.3 were corrected to a dry basis using Equation 7-1. The SO_2 and O_2 CEMS and RAA data were converted to the units of the applicable standard using Equation 7-2.

The accuracy (A) for the RAA is calculated using Equation 7-7.

$$A = \frac{C_m - C_a}{C_a} \times 100 \qquad \text{Equation 7-7}$$

$$= \frac{405.5 - 426.6}{426.6} \times 100 = -4.95\%$$

where

A = accuracy of the CEMS, %,

C_m = average CEMS response during audit in units of applicable standard, and

C_a = average audit value of the three reference method runs in units of the applicable standard.

7.2.3 <u>Cylinder Gas Audit Calculations</u> - Example data from a CGA on an SO_2/O_2 CEMS are shown in Table 7.4.

TABLE 7.4 CYLINDER GAS AUDIT DATA FOR SO_2 AND O_2 CEMS

		SO_2	SO_2	A	O_2	O_2	A
Audit number	Reading No.	CGA_d, ppm	$CEMS_d$, ppm	Diff, %	CGA_d, %	$CEMS_d$, %	Diff, %
1	1	212	218		5.0	5.2	
	2	212	219		5.0	5.3	
	3	208	225		5.1	5.2	
	Avg	210.7	220.7	4.75	5.03	5.23	3.98
2	1	398	409		9.1	8.9	
	2	399	416		9.1	8.9	
	3	403	414		8.9	8.9	
	Avg	400.0	413	3.25	9.03	8.90	-1.44

CGA_d = cylinder gas audit value, dry basis.

$CEMS_d$ = average of the three monitor values, dry basis.

The SO_2 and O_2 CEMS data shown in Table 7.4 were corrected to a dry basis using Equation 7-1. The accuracy (A) for the GCA is calculated using Equation 7-8.

$$A = \frac{C_m - C_a}{C_a} \times 100 \qquad \text{Equation 7-8}$$

$$= \frac{220.7 - 210.7}{210.7} \times 100 = 4.75\%$$

where

A = accuracy of the CEMS component, %,

C_m = CEMS component mean response for three values during audit with CGA in units of the appropriate concentration, and

C_a = audit value of the cylinder gas in units of appropriate concentration.

7.3 Reporting Requirements

At the reporting interval specified in the applicable regulation, a report of each CEMS accuracy audit must be submitted in the form of a Data Accuracy Report (DAR). One copy of the DAR must be included for each quarterly audit along with the report of emissions required under the applicable regulation. As a minimum, the DAR must contain the following information:

1. Source owner or operator name and address.

2. Identification and location of monitors in the CEMS.

3. Manufacturer and model number of each monitor in the CEMS.

4. Assessment of CEMS data accuracy and date of assessment as determined by a RATA, RAA, or CGA, including the RA for the RATA, the A for the RAA or CGA, the reference method results, certified values for the cylinder gases, the CEMS responses, and the CEMS accuracy calculation results. If the accuracy audit results show the CEMS to be out-of-control, the CEMS operator shall report both the audit results showing the CEMS to be out-of-control and the results of the audit following corrective action showing the CEMS to be operating within specifications.

5. Results from the EPA performance audit samples.

6. Summary of all corrective actions taken when the monitor was determined out-of-control.

An example of a DAR form is shown in Figure 7.1.

Period ending date ________________ Year ________________

Company name ________________________________

Plant name ________________ Source unit no. ________

CEMS manufacturer ________________ Model no. ____________

CEMS serial no. ____________ CEMS type (e.g., in situ) ________

CEMS sampling location (e.g., control device outlet) ____________

CEMS span values as per the applicable regulation, SO_2 ppm ________

O_2 __________ percent, NO_x __________ ppm, CO_2 __________ percent

I. Accuracy assessment results (Complete A, B, or C below for each CEMS or for each pollutant and diluent analyzer, as applicable.) If the quarterly audit results show the CEMS to be out-of-control, report the results of both the quarterly audit and the audit following the corrective action showing the CEMS to be operating properly.

A. Relative accuracy test audit (RATA) for ________________ (e.g., SO_2 in ng/J).

1. Date of Audit __________

2. Reference methods (RM's) used ______ (e.g., Methods 3 and 6).

3. Average RM value ________ (e.g., ng/J, mg/dsm^3, or percent volume).

4. Average CEMS value ____________.

5. Absolute value of the mean difference $|\bar{d}|$ __________.

6. Confidence coefficient |CC| __________.

7. Percent relative accuracy (RA) ______________ percent.

8. EPA performance audit results:

a. Audit lot number (1)________ (2)________
b. Audit sample number (1)________ (2)________
c. Results (mg/dsm^3) (1)________ (2)________
d. Actual value (mg/dsm^3)* (1)________ (2)________
e. Relative error* (1)________ (2)________

---

*To be completed by the Agency.

Figure 7.1 Example format for data assessment report (DAR).

B. Cylinder gas audit (CGA) for ______________ (e.g., SO_2 in ppm).

1. Date of audit ________________.

	Audit point 1	Audit point 2	
2. Cylinder ID number	______	______	
3. Date of certification	______	______	
4. Type of certification	______	______	(e.g., EPA Protocol 1 or CRM).
5. Certified audit value	______	______	(e.g., ppm).
6. CEMS response value	______	______	(e.g., ppm).
7. Accuracy	______	______	percent.

C. Relative accuracy audit (RAA) for __________ (e.g., SO_2 in ng/J).

1. Date of audit ___________________________.

2. Reference methods (RM's) used _____________ (e.g., Methods 3 and 6).

3. Average RM value __________________ (e.g., ng/J).

4. Average CEMS value ________________.

5. Accuracy ________________ percent.

6. EPA performance audit results:

a. Audit lot number (1)__________ (2)__________
b. Audit sample number (1)__________ (2)__________
c. Results (mg/dsm^3)* (1)__________ (2)__________
d. Actual value (mg/dsm^3)* (1)__________ (2)__________
e. Relative error* (1)__________ (2)__________

---

*To be completed by the Agency.

Figure 7.1 (continued)

D. Corrective action for excessive inaccuracy.

1. Out-of-control periods.

a. Date(s) ________________________.

b. Number of days ____________________.

2. Corrective action taken ________________________________

____

____

____.

3. Results of audit following corrective action. (Use format of A, B, or C above, as applicable.

II. Calibration drift assessment.

A. Out-of-control periods.

1. Date(s) ________________________.

2. Number of days ____________________.

B. Corrective action taken ________________________________

____

____

____.

Figure 7.1 (continued)

7.4 References

1. Standards of Performance for New Stationary Sources: 40 CFR 60, Appendix F - Quality Assurance Procedures, Procedure 1 - Quality Assurance Requirements for Gaseous Continuous Emission Monitoring Systems Used for Compliance Determination.

2. A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials. Joint publication by NBS and EPA, EPA-600/7-81-010. Available from the U. S. Environmental Protection Agency, Quality Assurance Division (MD-77), Research Triangle Park, North Carolina 27711.

3. Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol Number 1). June 1978, Section 3.0.4 of the Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods. EPA-600/4-77-027b. August 1977. U. S. Environmental Protection Agency, Office of Research and Development Publications, 26 West St. Clair Street, Cincinnati, Ohio 45268.

Out of Date

8.0 AUDIT MATERIALS AVAILABLE FROM U. S. EPA

In a memo dated May 30, 1979, Douglas M. Costle, the EPA Administrator, presented the Environmental Protection Agency Quality Assurance Policy Statement. He made participation in the quality assurance efforts mandatory for all EPA-supported or required monitoring activities. Furthermore, in a June 14, 1979 memo, Mr. Costle made "quality assurance requirements" mandatory for all environmental measurements conducted under extramural funding. Continued support for the mandatory quality assurance requirements was extended in a memo issued November 2, 1981 by Anne M. Gorsuch, the EPA Administrator. Initially in response to the policy statement and currently in response to the reference method requirements, the Quality Assurance Division of the Environmental Monitoring Systems Laboratory of the U. S. Environmental Protection Agency (EPA) has developed reference materials for performance audits of environmental measurements.

The purpose of the audit materials are two fold: (1) to provide agencies with a means of assessing the relative error of environmental measurements, and (2) to provide EPA with a continuing index of the quality of data reported.

The preparation and distribution of all audit materials are coordinated by the Quality Assurance Division of the Environmental Monitoring System Laboratory, Research Triangle Park, NC. The audit materials are available to all federal, state, and local agencies in support of performance audits for all enforcement testing. The audit materials are generally not available for internal audits by the private sector, except when requested by a federal, state, or local agency. However, the audit materials are available to contractors of government agencies. To request futher information about the source audit materials, write to:

Source Test Audit Coordinator
Quality Assurance Division, MD-77A
Environmental Monitoring Systems Laboratory
Research Triangle Park, NC 27709
Commercial: (919) 541-7834
FTS: 629-7834

The available audit materials are shown in the following three tables. Table 8.1 lists available organic gas audit cylinders in the parts per million range. Table 8.2 lists available organic gas audit cylinders in the parts per billion range. Table 8.3 describes the solid samples, aqueous samples, and other audit materials. The audit materials should be requested at least thirty (30) days prior to their actual need.

TABLE 8.1. PARTS PER MILLION LEVEL ORGANIC AUDIT CYLINDERS AVAILABLE FROM U. S. EPA

Compound***	Low Concentration Range (ppm)	High Concentration Range (ppm)
Benzene	5-20	60-400
Ethylene	5-20	300-700 3000-20,000
Propylene	5-20	300-700
Methane/Ethane	---	1000-6000(M) 200-700(E)
Propane	5-20	300-700
Toluene	5-20	300-700
Hydrogen Sulfide	5-40	100-700
Meta-Xylene	5-20	300-700
Methyl Acetate	5-20	300-700
Chloroform	5-20	300-700
Carbonyl Sulfide	5-20	100-400
Methyl Mercaptan	3-10	-------
Hexane	20-80	1000-3000
1,2-Dichloroethane	5-20	100-600
Cyclohexane	----	80-200
Methyl Ethyl Ketone	30-80	--------
Methanol	30-80	--------
1,2-Dichloropropane	5-20	300-700
Trichloroethylene	5-20	100-600
1,1-Dichloroethylene	5-20	100-600
**1,2-Dibromoethylene	5-20	100-600
Perchloroethylene	5-20	300-700
Vinyl Chloride	5-30	--------

(continued)

TABLE 8.1 (continued)

Compound***	Low Concentration Range (ppm)	High Concentration Range (ppm)
1,3-Butadiene	5-50	--------
Acrylonitrile	5-20	300-700
**Aniline	5-20	--------
Methyl Isobutyl Ketone	5-20	75
**Para-dichlorbenzene	5-40	------
Ethylamine	5-20	------
**Formaldehyde	--	------
Methylene Chloride	1-20	------
Carbon Tetrachloride	5-20	------
****F-113	5-20	------
Methyl Chloroform	5-20	------
Ethylene Oxide	5-20	------
Propylene Oxide	5-20	75-200
Allyl Chloride	5-20	75-200
Acrolein	5-20	75-200
Chlorobenzene	5-20	------
Carbon Disulfide	--	75-200
**Cyclohexanone	5-20	------
*EPA Method 25 Gas	100-200	750-2000
Ethylene Dibromide	5-20	75-400
1,1,2,2-Tetrachloroethane	5-20	------

* The gas mixture contains an aliphatic, an aromatic and carbon dioxide in nitrogen. Concentrations shown are reported in ppmC.

** Cylinders are no longer available in the repository since the compounds are found to be unstable in the cylinders.

*** All organic compounds in audit cylinders are in a balance of N_2 gas.

****F-113 is the compound 1,1,2-trichloro 1,2,2-trifluoroethane.

TABLE 8.2 PARTS PER BILLION LEVEL ORGANIC AUDIT CYLINDERS AVAILABLE FROM U. S. EPA

Group	Concentration Range of Each Compound (ppb)
Group I*	7-90 90-430 430-10,000
Group II**	7-90 90-430
Group III***	7-90 90-430
Group IV****	7-90 430-10,000

* Group I Compounds are carbon tetrachloride, chloroform, perchloroethylene, vinyl chloride, and benzene in a balance of N_2 gas.

** Group II Compounds are trichloroethylene, 1,2-dichloroethane, 1,2-dibromoethane, acetonitrile, trichlorofluoromethane (F-11), dichlorodifluoromethane (F-12), bromomethane, methyl ethyl ketone, and 1,1,1-trichloroethane in a balance of N_2 gas.

*** Group III Compounds are vinylidene chloride, 1,1,2-trichloro 1,2,2-trifluorethane (F-113), 1,2-dichloro 1,1,2,2-tetrafluorethane (F-114), acetone, 1-4 dioxane, toluene, and chlorobenzene in a balance of N_2 gas.

**** Group IV audit cylinders are under development, and will be available about December 1986. Group IV compounds are acrylonitrile, 1,3-butadiene, ethylene oxide, methylene chloride, propylene oxide and ortho-xylene.

TABLE 8.3. SOLID, LIQUID, AND OTHER AUDIT MATERIALS, AVAILABLE FROM THE U. S. EPA

Material	Description
SO_2 and CO_2 Gas Samples	SO_2 and CO_2 in a balance of N_2 are contained in gas cylinders in a range of 200 to 400 ppm SO_2 and 12 to 16% CO_2 for auditing EPA Method 6B
CO_2, O_2, and CO Gas Samples	CO_2, O_2, and CO are contained in a pressurized canister; one canister per set with range of 5 to 8% for CO_2, 10 to 15% for O_2, and 0.5 to 4% for CO
Calibrated Orifices	Calibrated critical orifices in either of two standard quick connects to check both rate and volume meters at 0.5 to 1.0 cfm for auditing EPA Methods 5, 5A, and 5D
SO_2 Samples*	Aqueous sulfuric acid solution in glass ampoules; two per set in three ranges with normal values of 750, 1500, and 2500 mg of SO_2 per dscm for auditing EPA Methods 6, 6A, and 6B
NO_x Samples*	Aqueous potassium nitrate solution in glass ampoules; two per set in three ranges with nominal values of 450, 900, and 1750 mg of NO_2 per dscm for auditing EPA Methods 7, 7A, 7C, and 7D
Sulfuric Acid Samples*	Same as the SO_2 samples; use for auditing EPA Method 8
Inorganic Lead Samples	Lead salts impregnated on a glass fiber filter in the range of 100 to 600 µg and 900 to 2000 µg of lead per audit sample for auditing EPA Method 12

(continued)

TABLE 8.3 (continued)

Material	Description
Total Fluoride Samples*	Aqueous sodium fluoride in Nalgene^R bottle; two per set in the ranges of 0.2 to 1.0 mg of fluoride per dscm and 1 to 5 mg of fluoride per dscm for auditing EPA Methods 13A and 13B
Coal Samples	Coal samples with known quantities of Btu's per pound, %S content, and moisture content; two per set in the range of 11,000 to 14,500 Btu's per pound for heating value, 0.5% to 4% for sulfur content, and 2% to 12% moisture content for auditing EPA Method 19
Mercury Samples*	Aqueous mercury chloride in glass ampoules; two per set in the ranges of 5 to 20 µg of mercury per ml and 50 to 100 µg of mercury per ml of sample for auditing EPA Methods 101, 101A, 102, and 105
Arsenic Samples*	Aqueous arsenic salts in glass ampoules; one per set in the range of 10 to 50 µg/ml or 100 to 500 µg/ml of arsenic for auditing EPA Methods 108 and 108A
Beryllium Samples*	Aqueous beryllium salts in glass ampoules; two per set in the ranges of 5 to 20 µg of beryllium per audit sample and 50 to 100 µg of beryllium per audit sample for auditing EPA Method 104

*Aqueous audit samples can be reduced to known concentration less than the stated range by taking smaller aliquots and/or dilution.

Audit gas cylinder samples can be obtained by contacting:

Audit Cylinder Gas Coordinator
Quality Assurance Division, MD-77B
Environmental Monitoring Systems Laboratory
Research Triangle Park, NC 27711
Commercial: (919) 541-4531
FTS: 629-4531

All other source audit materials can be obtained by contacting the "Source Test Audit Coordinator" listed on Page 1 of this section.

9.0 CONTINUOUS EMISSION MONITORING (CEM) SYSTEMS GOOD OPERATING PRACTICES

Continuous emission monitoring (CEM) systems are required to be installed in facilities specified by the EPA Standards of Performance for New Stationary Sources (SPNSS) and by other Federal and state regulations. The systems are used to continuously monitor the effectiveness of air pollution control techniques and to determine if source compliance standards are being met.

This section of Volume III is intended to provide guidance for technical personnel in air pollution control agencies and in industry who are responsible for CEM programs. Guidelines are given to aid agency personnel in evaluating operation and quality assurance practices associated with permanently installed CEM systems. The guidelines may also be useful to operators of CEM systems in developing quality assurance and quality control procedures that meet agency minimum requirements. Section 3.0.9 does not address the use of continuous monitors in mobile testing vans or as <u>portable compliance</u> monitors. However, much of the information presented here is relevant to these applications.

CEM systems have been developed to monitor pollutant gases, such as SO_2 and NO, and the so-called diluent gases, CO_2 and O_2, present in the exhaust gas streams of combustion sources. Systems have also been developed to monitor flue-gas opacity. A <u>system</u> is defined as the total equipment required for the determination of flue-gas opacity, a gas concentration, or the emission rate. A system is normally composed of a sample interface, the pollutant and diluent analyzers, and the data recording subsystem. The <u>system</u> is used to generate emission data that are representative of the total emissions from the facility.

The <u>sample interface</u> is the portion of the monitoring system that protects the analyzer from the effects of the effluent. In extractive systems, the interface consists of the probe assembly, sampling lines, and conditioning subsystems. The sample is normally taken from a single point in the stack or duct and then transported to the analyzer. A conditioning system is often used to remove particulate matter from the sample and to dry the sample before it enters the analyzer.

In-situ monitors have been developed to measure the stack gas concentrations, without transporting the gas itself. Gas measurements are made either at a point or along a path of known length within the flue. For in-situ path monitoring, the interface may consist of optical windows and blower assemblies used to keep the windows clean. For point in-situ designs, it may consist of ceramic thimbles and support housings. These different approaches taken toward the measurement of effluent gases will be discussed later in this section.

The SPNSS require data obtained from a CEM system to be representative, accurate, and precise. In contrast to EPA certification procedures for ambient air monitors, source emission monitors are not categorically approved by model or manufacturer. Instead, installed systems are approved on a case-by-case basis through the procedures established in the Performance Specifications for Continuous Emission Monitoring Systems in Stationary Sources (40CFR60 Appendix B).[1] After an installed monitoring system is found to meet these specifications, it is expected that it will be properly maintained at the same or better level of performance.

The proper operation and maintenance of a CEM system is imperative if the data are to be used for regulatory purposes. The responsibility for the system lies with the owner, and in general, ownership lies with the plant or industrial facility. The generation of valid data from a CEM system through proper operation and maintenance procedures must therefore come from plant personnel or through services contracted by the plant. It is, however, the plant personnel or their contractors who will actually operate and maintain these systems.

9.1 CEM Operation/Maintenance Programs - Levels of Quality Control

A maintenance program for a CEM system should be part of a larger, plant instrumentation quality assurance (QA) program. Quality control practices within the QA program are those activities performed to assure that accurate and precise data are generated from the monitoring system. Daily operation checks, preventive maintenance routines, and audits are quality control activities that can be used for this purpose.

There are four levels of quality control that should be established for a CEM system:

Level 1. Operation Checks (daily checks, observations, and adjustments)
Level 2. Routine Maintenance (periodic preventive maintenance)
Level 3. Performance Audits
Level 4. Corrective Maintenance

Operation checks are performed on a routine basis, generally daily, to see that the equipment is operating properly. Thes procedures will include daily zero and calibration checks, checks of reference signals from control panels, and checks of flow rates, pressures, vacuum levels.

Routine maintenance is performed at regular intervals. Activities include the replacement of filters, lamps, motor bearings, or other parts. Detailed service checks of electronic and optical systems may also take place at this time to uncover incipient problems in the instrumentation. Depending on the system, the replacement and check intervals may vary from 30 days to a year or more.

Performance audits, which provide a check of the system's operation, identify problems, identify the need to improve preventive maintenance procedures, or alert the operator to the need for corrective maintenance.

Corrective maintenance is performed to bring the monitoring system into operation after a breakdown in the system occurs. It is also termed nonroutine maintenance, the unscheduled need to repair a faulty system.

9.2 Gas CEM Systems - Operation Practices

The day-to-day operation of a CEM system is not difficult once the instruments are turned on and operating properly; generally all that needs to be done is to periodically check the zero and the span of the instruments in the system. This check may be conducted either manually or automatically by using calibration gases or optical filters. However, routine and corrective maintenance practices vary, depending upon the methods of analysis and the overall design of the system. For this reason, it is important to understand the special demands of different monitoring systems. Extractive systems have different maintenance requirements than in-situ systems. Within the categories of extractive systems, or in-situ systems, the different types of analyzers will require servicing dependent on the principle by which they analyze the pollutant.

To help understand maintenance requirements, this section will present an overview of the various analysis principles used in the commercial systems.[2] Table 9.1 summarizes these principles.

9.2.1 Extractive Monitoring Systems - This section will first discuss the design of extractive systems and then the various analytical techniques used to measure the gas concentration.

9.2.1.1 **Extractive System Design.** A complete extractive system consists of a sample probe and conditioning system, analyzer, and

TABLE 9.1. PRINCIPLES OF DETECTION USED IN CONTINUOUS EMISSION MONITORS

Extractive System	In-Situ Systems	
Gaseous Emission Monitors	Gaseous Emission Monitors	Opacity Monitors
Absorption Spectroscopy Nondispersive Infrared Differential Absorption	Absorption Spectroscopy Nondispersive Infrared (Gas filter-correlation) Differential Absorption Second Derivative Spectroscopy	Visible Light Scattering and Absorption
Luminescence Methods Fluorescence Chemiluminescence Flame Photometry	Electroanalytical Methods Electrocatalysis	
Electroanalytical Methods Polarography Electrocatalysis		
Paramagnetic Methods		

data recording system. Sampling probes and conditioning systems are today commonly purchased from the analyzer vendor rather than assembled from miscellaneous parts by plant technicians. Also, a number of companies specialize in marketing hybrid systems (complete extractive systems composed of components supplied by different vendors).

There are two approaches taken in extractive system design. One is to condition the gas near the analyzer; the other, to condition the gas as close as possible to the stack or duct. In the first approach, a probe is inserted into the flue gas and the gas is drawn through a coarse particulate filter into a heated sampling line. The sample line may extend to over 60 m to a control room or environmental enclosure, where the gas is conditioned. The conditioning system cools the gas and removes water vapor by some type of refrigeration, dilution, or permeation device. Usually a fine filter is placed just before the analyzer to prevent small particles from entering the analyzer. Diaphragm pumps, rotary vane pumps, or air aspirators are used to transport the sample from the probe to the analyzer.

In the second approach of sample extraction, gas is conditioned at the stack or duct. Filters, chillers, or dilution systems are located at the sampling site, and in the case of some dilution designs, the probe itself does the conditioning. This approach allows a low moisture sample to be transported to the analyzer. Long sections of heat-traced or insulated lines may therefore be avoided.

Calibration gases are used in both approaches to check the performance of the system. The gases are injected as close to the probe as is technically feasible. Also, blow-back devices are often installed to clean the coarse particulate filters. As the system operates, these filters may eventually plug up. A burst of high pressure air "blown back" through the filter reduces plugging and provides for continued operation.

Extractive systems are normally constructed from components that are familiar to plant mechanics. Valves, filters, tubing, tube fittings, solenoids, etc., are commonly encountered. These components must be maintained if the system is to provide continuous data.

9.2.1.2 Extractive Analyzers - Spectroscopic Absorption Techniques. Two basic absorption spectroscopic techniques are utilized in commercially available extractive analyzers: (1) <u>non-dispersive infrared spectroscopy</u> and (2) <u>differential absorption spectroscopy.</u>

<u>Nondispersive infrared spectroscopy</u> utilizes infrared light in a limited range of the electromagnetic spectrum. The light is not scanned or "dispersed" as with scanning laboratory spectrometers. In general, the light is filtered to select light wavelengths that will be absorbed by the molecules that are to be measured. The light passes through a gas cell that contains the flue gas extracted from the stack. A portion of the light from the lamp passes through a cell containing a reference gas that does not absorb the filtered light. A detector senses the amount of light absorption in the sample cell relative to the signal from the reference cell. Through proper calibration, the detector responses are electronically converted to pollutant concentration readings. A variant of this technique, called gas filter correlation spectroscopy, uses a reference cell that absorbs 100% of the light in the molecular absorption region of the pollutant.

Infrared analyzers have been developed to measure gases such as SO_2, NO, NO_2, HCl, CO_2, and CO. The commercially available monitors differ primarily in the design of the detector and the level of rejection of interfering gases.

Differential absorption spectroscopy also takes advantage of the characteristics of molecules to absorb light of certain wavelengths. Instead of using a sample cell and reference cell as do the common infrared systems, differential absorption spectrometers use a measuring "wavelength" corresponding to a region of the spectrum where the molecule absorbs light energy. The reference wavelength corresponds to a region where there is little or no absorption.

Most extractive differential absorption systems operate in the ultraviolet (UV) region of the spectrum, although it is possible to use the technique in the infrared region. The gases may be measured hot in the UV without removing water vapor, although it is generally advisable to dry the sample.

SO_2 is commonly measured using this technique. A technique has also been devised to measure flue gas NO by injecting oxygen into the sample chamber, sealing it, and monitoring the production of NO_2 from NO at an NO_2 absorption wavelength.

9.2.1.3 Extractive Analyzers - Luminescence Techniques. Luminescence is the emission of light from a molecule or atom that has been excited in some manner. Three luminescence techniques are used in the field of source monitoring: (1) fluorescence, (2) chemiluminescence, and (3) flame photometry.

Ultraviolet fluorescence is used to measure SO_2. Ultraviolet light in the region of 210 nm is used to excite an SO_2 molecule. The molecular excited state persists for a few nanoseconds, during which time some of the energy is lost in vibrational transitions. The molecule eventually returns to its unexcited state with the release of light at a longer wavelength (near 350 µm). This light is then detected by a photomultiplier tube, resulting in a measurement of the SO_2 concentration in the sample gas.

Fluorescence monitors can be affected by changes in the flue-gas composition (%O_2, %CO_2). This is caused by the de-excitation of excited SO_2 molecules through the process of quenching. For this reason, fluorescence analyzers are most successful in flue-gas analysis when they are coupled with a dilution system, thereby providing a relatively constant background composition.

Chemiluminescence is used in flue-gas analysis to measure NO and NO_2 concentrations. In this application of chemiluminescence, excited NO_2 molecules are produced by reacting ozone with the flue gas NO. The excited NO_2 product (NO_2*) de-excites to its ground state with the release of light energy. The light is measured with a photomultiplier tube. Quenching effects also occur in this method, but dilution of the sample through the introduction of the reactant ozone gas stream minimizes the effect.

Since the light is produced only through the reaction of ozone with NO, NO_2 must first be reduced to NO before it can be measured. A catalytic reaction chamber is used when a measurement of both NO and NO_2 (NO_x) must be obtained.

Flame photometry can be used to measure compounds that contain sulfur. In this technique, the compounds are "burned" in a hydrogen flame, leading to the formation of excited diatomic sulfur molecules, S_2^*. The conversion of the high energy S_2^* molecules to the lower energy ground state, S_2, occurs with the emission of light. The intensity of this light is measured and related to the concentration of sulfur species in the sample. The flame photometric method does not discriminate between different sulfur-containing compounds, so scrubbers or gas chromatographic columns may be required if more than one species is present in the sample.

9.2.1.4 Extractive Analyzers - Electroanalytical Techniques. Two principal electroanalytical techniques have been developed for the measurement of flue gases. These are polarography and electrocatalysis. A clean, dry sample must be supplied to an analyzer operating by the polarographic method. The electrocatalytic technique can, however, be applied to both extractive and in-situ measurement methods.

Polarographic analyzers are, basically, diffusion-controlled electrochemical cells. The cells are constructed much like batteries, with a sensing electrode, electrolyte, and counter-electrode. The main difference is the addition of a thin-film membrane, through which the pollutant must diffuse to initiate the electrochemical reactions and current flow. The current across the cell is proportional to the rate of diffusion of the pollutant into the cell and is also proportional to the pollutant concentration.

Polarographic analyzers have been developed to measure gases such as SO_2, NO, O_2, and CO_2. Different choices of electrodes and electrolytes are made for each gas. As with batteries, the electrolyte will eventually be consumed, and the cell will need to be replaced or recharged.

Electrocatalytic analyzers have been developed for the measurement of O_2 and SO_2. This technique uses a solid electrolyte instead of liquid electrolytes generally associated with electrochemical cells. A platinum film, coated on the solid surface, catalyzes a reaction that allows molecules to migrate through the solid and generate a measurable flow of electrons.

In oxygen electrocatalytic analyzers, a zirconium oxide disc, coated with a thin film of platinum, is heated to 850°C. A reference gas of about 21% oxygen is maintained on one side of the solid, and the sample gas is on the other side. Oxygen ions are generated at the platinum surface and then migrate through vacancies in the heated, solid electrolyte. Electrons are released in the process as the system attempts to equalize the oxygen concentration.

An electrocatalytic analyzer has also been developed for the measurement of SO_2. This system uses a potassium sulfate crystal and requires the simultaneous measurement of the sample oxygen concentration.

9.2.1.5 Extractive Analyzers - Paramagnetic Techniques. Oxygen exhibits paramagnetic behavior by being attracted to a magnetic field. This behavior has been utilized in the design of several different types of extractive flue-gas analyzers. For example, in <u>thermomagnetic</u> oxygen analyzers, a magnet causes O_2 to flow through a tube and cool a resistor. The resistance is then related to O_2 concentration. In <u>magnetodynamic</u> systems, O_2 disturbs a magnetic field around a torsion pendulum, and in <u>paramagnetic pressure analyzers</u>, a magnetic field causes a pressure imbalance that can be measured.

9.2.2 Recommended Maintenance - Extractive Monitoring Systems

9.2.2.1 Operation Checks (Daily Checks). Operation checks of an extractive monitoring system should be performed each day by a qualified and trained instrument operator. The operator should be familiar with the system and be able to recognize a problem from discrepancies found during the operation check procedure. Many extractive monitoring systems are designed to automatically perform daily zero and calibration checks and internal self checks without operator intervention. Unfortunately, this can reduce the level of operator attention to the system. Small problems, as a result, may go undetected and very quickly lead to large problems. On the other hand, "intelligent" systems, which monitor key system parameters and report out-of-control conditions at remote panels, have helped to alleviate such situations.

A daily operation check of an extractive monitoring system should start with a check of the strip chart record and/or other data recording devices. The operator should mark the exact time on the chart for calibration purposes, and write down the date, his or her name, and the chart recorder settings. This should all be written directly on the chart. The paper in the recorder and printer (if applicable) should be checked to see if the supply is sufficient for the next 24-h run.

Indicator lights on the system or monitor control panel should be checked next. It is advised that a record of the system status be recorded in ink in a hardbound logbook. All maintenance, unscheduled repairs, or system modifications should be described in the logbook. This book will serve as an invaluable tool in tracking the long-term performance of the system and will enable other technicians or servicemen to become familiar with the system.

The system indicator lights will notify the operator of out-of-range conditions occurring in the system or of other problems felt to be important by the system designer. If a problem occurs, it should be attended to immediately since subsequent data will be otherwise suspect. Some systems contain reset buttons, installed to override the indicator lights. These should not be used until after the problem is resolved. The values of other systems indicators, such as vacuum or pressure gauges, sample flow rates, and lamp and detector reference levels (if applicable), should also be recorded at this time.

A calibration check should be performed next.[3] This involves injecting a zero (or low-level) gas and a high-level gas (calibration gas) into the sample line. It is recommended that the gas be injected at a point where as many of the conditioning system components as possible can be checked. In some systems, this can be done at the probe itself, providing the advantage of checking the system for sample line losses.

Gas injected from gas cylinders may pressurize the system. Consequently, the flow rate of the cylinder gas into the analyzer sample cell may differ from the flow rate of the extracted stack gas. Also, cylinder gas is <u>dry</u> gas; it does not contain moisture. These two factors may adversely affect the calibration process if flow rates and moisture content of gases entering the analyzer sample cell are not similar. It is also important to note that if the system is pressurized, leaks in the system may not be detected. Ambient air will not enter the system as it otherwise might if a vacuum is used to draw a sample into the analyzer when leaks are present.

Gases used for the daily checks should first be validated against certified calibration gases or be certified themselves. Certified gases should have their concentration established through EPA

Traceability Protocol No. 1.[3] Using gases of uncertain concentration can result in gross miscalibration of the system.

The monitor should first be checked with the zero (or low-level) gas, and the instrument reading should be noted in the logbook. The high-level gas should next be injected into the system and the reading likewise noted. The readings should also be recorded appropriately on the strip chart record. The differences noted between the cylinder gas value and the monitor readings are used to assess the low-level and high-level calibration drift.

The instrument operator may not have to "rezero" and "recalibrate" the system every 24 h when the values are checked. Small values for drift may be due merely to system noise. It is recommended as a minimum that the system be adjusted when the drift exceeds twice the limits of the drift performance specification.[4] For example, if the performance specification is 2.5% for an instrument span value of 1000 ppm, adjustments should be made when drift exceeds 50 ppm. For systems with lower span values, the drift tolerance will be accordingly less. (The span value is given in the Code of Federal Regulations for source categories affected by continuous monitoring regulations. The span value is defined as "The upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable subpart of the regulation." [1])

The operator should record values from the instrument meter, the strip chart, and digital printer. If a microprocessor controller is used to check and/or adjust monitor data automatically to the appropriate values, it must be programmed to record the unadjusted values first. If a strip chart recorder is used in conjunction with the microprocessor, the system should be programmed so that the adjusted values will appear on both the strip chart and the printer output. This may be difficult since the microprocessor adjustment is often only done numerically by the program, i.e., the analyzer itself is not physically adjusted. In such a case, the meter readings and strip chart readings may differ significantly from the microprocessor output. Data interpretation in such cases may become difficult.

To assist in performing the daily operation checks, a data sheet has been provided in Figure 9.1. The figure is meant to serve as a guide for the inspector or operator in developing a data sheet applicable to a specific system.

9.2.2.2 Routine Maintenance (30-day Checks). Routine maintenance should be initially performed on an extractive system at least every 30 days. With experience, this time period can be either increased

158

Example Format for Extractive Gas Monitoring System
Daily QC Check Sheet

Plant Calvander/Acme Power
Unit Boiler #2 Outlet
Gas Monitored SO_2
Analyzer I.D. Measuretech #476
Span Value 1000 ppm
Calibration Gas Value 948
Zero Gas Value (air, N_2, other) air, 0
Hours Operating in Period 24/24

Date 8/20/85 Time 9:30 am
Name Joe Jones
Phone 919-549-863
Zero Offset Value 50 ppm
Date Certified 9/14/83
Paper Status: Strip Chart OK
Printer 24 hrs - refill needed

Part 1 Indicators

Indicator Lights/Gauges	Status	Problem/Action taken
Sample pressure/vacuum	10 psi	Low/ Boost to 12 psi
Sample flow	0.35 l/min	-
Lamp	OK	-
Detector	OK	-

Part 2 Calibration Check

Unadjusted Readings	Time	Meter	Strip Chart	Digital Printer
Zero (low-level) gas	9:50 am	16	16	26
Calibration (high-level) gas	10:00	895	895	905
Stack Concentration	10:10	248	248	258

Part 3 Zero and Span Adjustment (if outside of control limits)

Control limit ± 50 ppm

Adjusted Readings	Time	Meter	Strip Chart	Digital Printer
Zero (low-level) gas	10:20 am	16	16	16
Calibration (high-level) gas	10:30	948	948	948
Stack Concentration	10:40	264	264	264

Joe Jones 8/20/85
Operator Signature Date

Sam Smith 8/21/85
Supervisor Signature Date

Figure 9.1. Example format for extractive gas monitoring system daily QC check sheet.

or decreased, and depending on the system, maintenance intervals of varying frequency may be established for subsystems or for individual components.

In extractive monitoring systems, most maintenance lies with the sample conditioning systems rather than with the analyzers. Particulate matter and water vapor are usually removed from the gas stream before the gas reaches the analyzer. The filters that remove the particulate matter must be periodically cleaned or replaced. Condensed water in condensing-type moisture removal systems must be drained.

The plumbing associated with extractive systems is prone to corrosion and leaks; therefore, the system should be periodically checked for leaks. Fittings, valves, and gas regulators should also be checked. Solenoid valves have been commonly used to automate extractive systems. These valves are prone to failure and should be checked frequently to ensure they move freely and on command. The use of motorized or air-activated rotary valves instead of solenoid valves may also help to reduce the frequency of valve failures. Care should be taken to avoid over-design or over-automation of a system. The more valves there are, the more valves there are to check. Spare valves should be kept in the parts inventory.

Electrical cables and heat-traced lines should also be checked frequently. In a plant environment, damage can occur from construction projects or through normal plant operations. The ambient atmosphere, particularly near flue-gas leakage or stack downwash areas, may cause electrical insulation to deteriorate rapidly. Acid gases circulating near the stack may corrode both electrical fittings and the plumbing of the extractive system.

The pumps and chillers used in extractive systems work 24 h/day. At some time, the motor brushes will wear out, a pump diaphragm will break, or a part will require oiling. Rather than treating such events as problems, they should be anticipated by establishing a regular schedule of overhaul and maintenance.

The overall cleanliness of an extractive system is also important. The particulate matter in the flue-gas can migrate into unexpected places. If a system is located outside, near the stack, sensitive components should be installed in dust-free cabinets. The system should be cleaned if fly ash settles on it, and in no case should cabinets be opened when fly ash is circulating in the ambient air.

The extractive analyzers contain components which have limited lifetimes. Lamps and bulbs generally have given performance periods. They should be replaced before this period is up, since a weakened bulb can often produce spurious results. Analyzers are often designed to operate best over a given range of lamp intensity. When the intensity drops too low, the detector will not be able to respond as accurately as it should to the incoming signal. Detectors may also have to be replaced, but this is not common.

Many instruments have test points on the back panel or on circuit boards. These test points are checked with a voltmeter or an oscilloscope to indicate certain limiting values. The instrument operator should perform these electronic tests routinely to check for electronic integrity.

Figure 9.2 gives an example of a checklist designed for a routine maintenance procedure. Again, this list is suggested to help the inspector or operator design his or her own list. It is not uncommon for instrument operators to spend a year or more in designing a system maintenance schedule. Vendor instruction manuals are often lacking in this regard, so points of maintenance may have to be determined through experience. The system logbook is an invaluable tool in developing such a schedule.

9.2.2.3 Performance Audits. Performance audits should be conducted on extractive monitoring systems at appropriate intervals. EPA 40CFR60 Appendix F - Quality Assurance Procedure 1[5] requires that an audit be performed at least once every quarter for monitoring systems used for determining compliance with emission standards. This frequency is recommended to identify CEM systems that may be generating biased results.

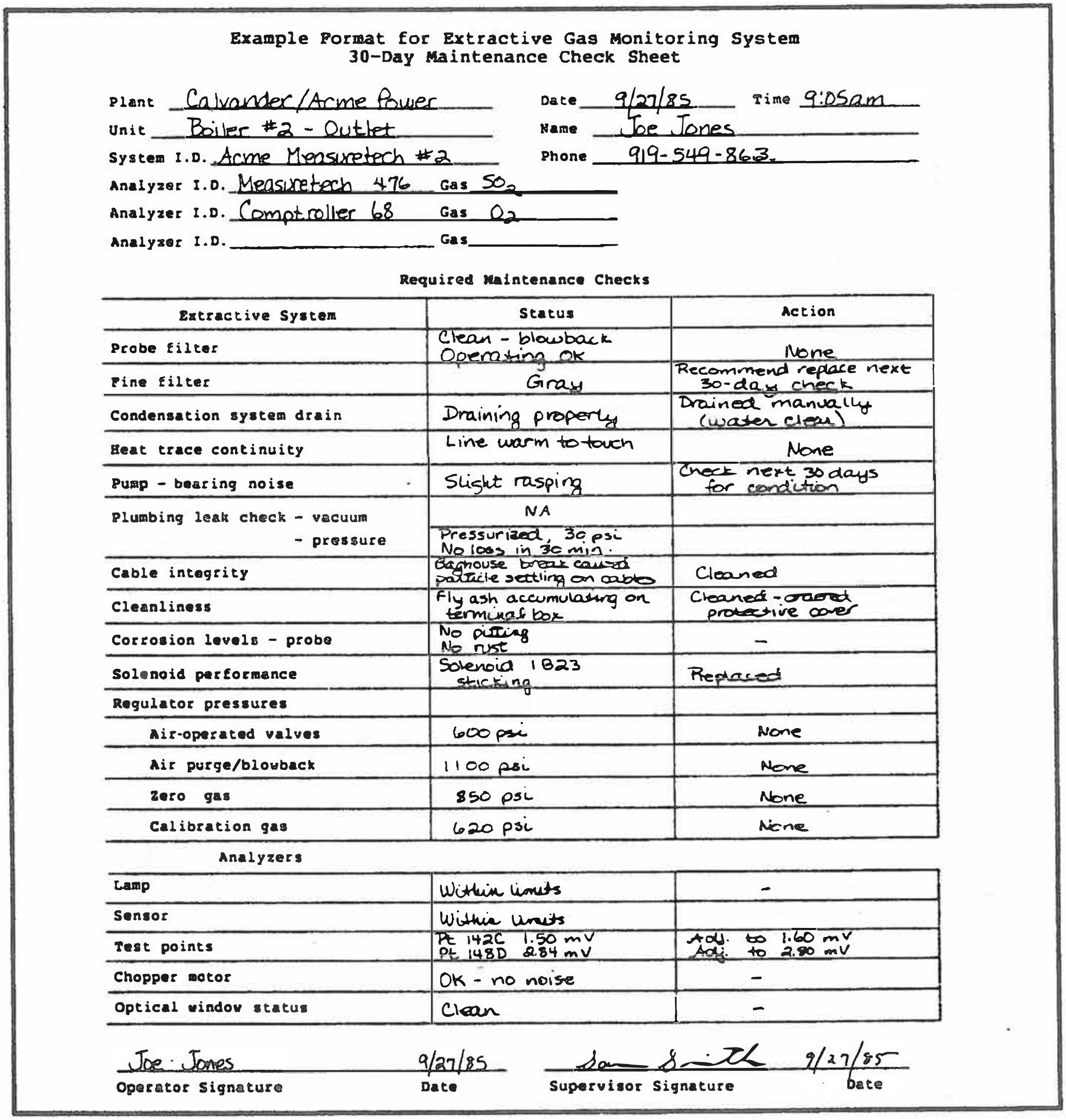
The performance audit is essentially an independent check of the system, and can vary, depending upon the resources of the owner of the system. For CEM systems installed to demonstrate compliance with emissions standards, EPA requires an audit at least once each quarter, using one of the following[5]:

- Relative Accuracy Test Audit (RATA)

  A repeat of the relative accuracy test procedures as defined in Appendix B Performance Specifications.[1]

- Cylinder Gas Audit (CGA)

  Challenging the monitoring system with cylinder gas of known concentration (certified gases).



Example Format for Extractive Gas Monitoring System
30-Day Maintenance Check Sheet

Plant Calvander/Acme Power
Date 9/27/85 Time 9:05am
Unit Boiler #2 - Outlet
Name Joe Jones
System I.D. Acme Measuretech #2
Phone 919-549-863.
Analyzer I.D. Measuretech 476 Gas SO_2
Analyzer I.D. Comptroller 68 Gas O_2
Analyzer I.D. ____ Gas ____

Required Maintenance Checks

Extractive System	Status	Action
Probe filter	Clean - blowback Operating OK	None
Fine filter	Gray	Recommend replace next 30-day check
Condensation system drain	Draining properly	Drained manually (water clear)
Heat trace continuity	Line warm to touch	None
Pump - bearing noise	Slight rasping	Check next 30 days for condition
Plumbing leak check - vacuum	NA	
- pressure	Pressurized, 30 psi No loss in 30 min.	
Cable integrity	Baghouse break caused particle settling on cables	Cleaned
Cleanliness	Fly ash accumulating on terminal box	Cleaned - ordered protective cover
Corrosion levels - probe	No pitting No rust	–
Solenoid performance	Solenoid 1B23 sticking	Replaced
Regulator pressures		
Air-operated valves	600 psi	None
Air purge/blowback	1100 psi	None
Zero gas	850 psi	None
Calibration gas	620 psi	None

Analyzers

Lamp	Within limits	–
Sensor	Within limits	
Test points	Pt 142C 1.50 mV Pt 148D 2.84 mV	Adj. to 1.60 mV Adj. to 2.90 mV
Chopper motor	OK - no noise	–
Optical window status	Clean	–

Joe Jones 9/27/85 Sam Smith 9/27/85
Operator Signature Date Supervisor Signature Date

Figure 9.2. Example format for extractive gas monitoring system 30-day maintenance check sheet.

- Relative Accuracy Audit (RAA)

  An audit similar to the RATA except that only three sets of measurement data (instead of nine) are taken.

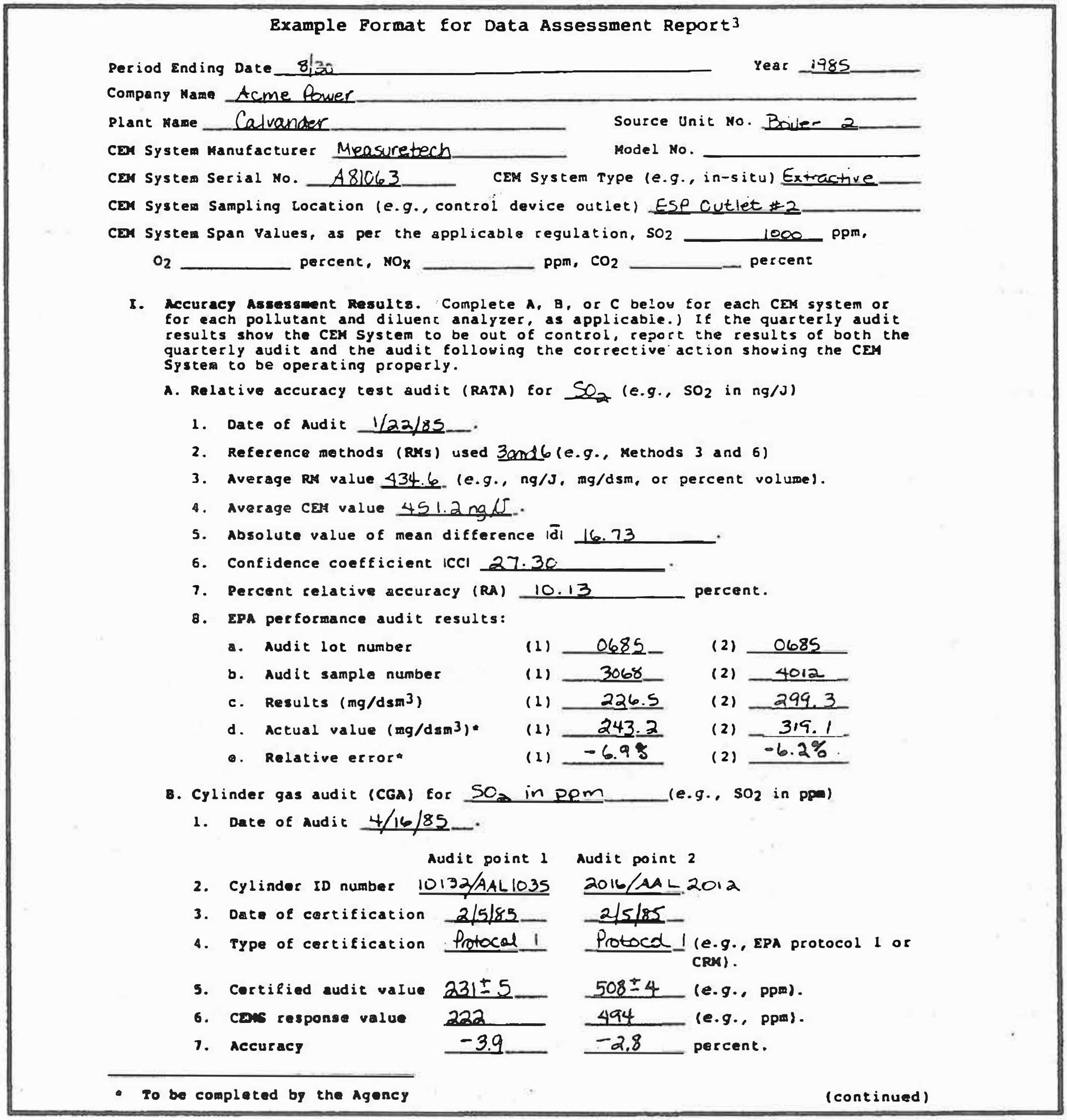
Appendix F requires that at least one of the quarterly audits be a RATA, and either the CGA or RAA can be used for the other three quarters. If the relative accuracy between the audit and analyzer values exceeds 20% for the RATA, the instrument is viewed as being out of control. If the relative accuracy between the audit and analyzer values exceeds 15% for the CGA or RAA, the instrument is viewed as being out of control. A RATA, CGA, or RAA must be conducted after repairs are made to out-of-control systems.

Additional techniques can also be used during an audit. For example, portable gas monitoring instruments can be used to check the stack gas concentrations rapidly. Although the portable monitor itself may not meet the performance specifications that the CEM system meets, it can give valuable information during an audit.

The main idea behind the performance audit is to provide an independent assessment of the monitoring system accuracy. Daily calibration drift determinations and routine maintenance do not necessarily guarantee that data will be accurate. An independent assessment using an appropriate auditing technique can, however, provide an indication of data validity. Figure 9.3 gives the Appendix F example format for an audit "Data Assessment Report."

9.2.2.4 Corrective Maintenance (Problems and Troubleshooting). Maintenance problems with extractive monitoring systems usually occur in the gas transport and gas conditioning components. Valves, fittings, tubing, and filters in the presence of acid gases, submicron particulate matter, and continuous vibration are likely to have limited life unless they are routinely maintained. Lack of routine maintenance or lack of foresight will result in the need for corrective maintenance. The need for corrective maintenance can be avoided by establishing good quality assurance and quality control programs.

The extractive system gas analyzers normally will have few problems unless they are located in a severe environment or if the gas conditioning system fails. If the conditioning system fails, acid gases can condense in the sample cell and particulate matter can settle in the system to plug the probe or sample lines, or the analyzer itself.



Example Format for Data Assessment Report[3]

Period Ending Date 8/30 Year 1985
Company Name Acme Power
Plant Name Calvander Source Unit No. Boiler 2
CEM System Manufacturer Measuretech Model No. ______
CEM System Serial No. A81063 CEM System Type (e.g., in-situ) Extractive
CEM System Sampling Location (e.g., control device outlet) ESP Outlet #2
CEM System Span Values, as per the applicable regulation, SO_2 1000 ppm,
O_2 ______ percent, NO_x ______ ppm, CO_2 ______ percent

I. **Accuracy Assessment Results.** Complete A, B, or C below for each CEM system or for each pollutant and diluent analyzer, as applicable.) If the quarterly audit results show the CEM System to be out of control, report the results of both the quarterly audit and the audit following the corrective action showing the CEM System to be operating properly.

A. Relative accuracy test audit (RATA) for SO_2 (e.g., SO_2 in ng/J)

1. Date of Audit 1/22/85.
2. Reference methods (RMs) used 3 and 6 (e.g., Methods 3 and 6)
3. Average RM value 434.6 (e.g., ng/J, mg/dsm, or percent volume).
4. Average CEM value 451.2 ng/J.
5. Absolute value of mean difference |d| 16.73.
6. Confidence coefficient |CC| 27.30.
7. Percent relative accuracy (RA) 10.13 percent.
8. EPA performance audit results:

a. Audit lot number	(1)	0685	(2)	0685
b. Audit sample number	(1)	3068	(2)	4012
c. Results (mg/dsm^3)	(1)	226.5	(2)	299.3
d. Actual value (mg/dsm^3)*	(1)	243.2	(2)	319.1
e. Relative error*	(1)	-6.9%	(2)	-6.2%

B. Cylinder gas audit (CGA) for SO_2 in ppm (e.g., SO_2 in ppm)

1. Date of Audit 4/16/85.

	Audit point 1	Audit point 2	
2. Cylinder ID number	10132/AAL1035	2016/AAL2012	
3. Date of certification	2/5/85	2/5/85	
4. Type of certification	Protocol 1	Protocol 1	(e.g., EPA protocol 1 or CRM).
5. Certified audit value	231 ± 5	508 ± 4	(e.g., ppm).
6. CEMS response value	222	494	(e.g., ppm).
7. Accuracy	-3.9	-2.8	percent.

---

* To be completed by the Agency

(continued)

Figure 9.3. Example format for data assessment report.

C. Relative accuracy audit (RAA) for SO2 in ng/J (e.g., SO_2 in ng/J)

1. Date of audit 7/23/85.
2. Reference methods (RMs) used 3 and 6 (e.g., Methods 3 and 6)
3. Average RM value 328.4 (e.g., ng/J).
4. Average CEM value 243.8.
5. Accuracy 25.8 percent.
6. EPA performance audit results:

a. Audit lot number	(1)	0685	(2)	0685
b. Audit sample number	(1)	3088	(2)	404C
c. Results (mg/dsm^3)	(1)	240.6	(2)	180.5
d. Actual value (mg/dsm^3)*	(1)	225.2	(2)	170.3
e. Relative error*	(1)	+6.9%	(2)	+6.0%

D. Corrective action for excessive inaccuracy.

1. Out-of-control periods.
   - a. Date(s) 7/23/85-7/31/85.
   - b. Number of days 8.
2. Corrective action taken Replaced lamp 7/31/85
   Adjusted resistors R13 and R18 on 7/31/85
   Re-zeroed and recalibrated system 7/24/85
3. Results of audit following corrective action. (Use format of A, B, or C, above, as applicable.)

II. Calibration Drift Assessment.

A. Out-of-control periods.

- a. Date(s) 7/19/85-7/22/85, 7/24 - 7/31/85
- b. Number of days 4.

B. Corrective action taken Re-zeroed and recalibrated on 7/23/85. System still drifting because of lamp problems. Replaced lamp on 7/31/85.

Joe Jones 8/30/85
Operator Signature Date

Sam Smith 9/3/85
Supervisor Signature Date

---

* To be completed by the Agency

Figure 9.3. (continued).

Most problems inherent to extractive analyzers will be electronic in nature. Procedures recommended in the maintenance manuals can be used to troubleshoot circuit boards and components. Extractive analyzers are often compact enough so that in the case of severe electronic problems, they can be returned to the instrument vendor for repair.

The system operator will often be warned of problems by a loss of signal, inconsistent readings, or poor calibration response. Approaches to resolving problems largely depend on the skill of the operator; however, some general guidelines can be given:

- Loss of signal or abnormally low values - check conditioning system for plugging, leaks, pump failure.

- Noisy, erratic signals - check for electronic problems, electrical supply problems, weak lamps, moisture condensation, particulate matter in analyzer.

- Loss of linearity - check for sample cell contamination, leaking calibration manifold, incorrect gas cylinder values.

- Slow response - check for leaks, water in lines, measuring cell failures.

Failure of the conditioning system and consequent drawing of unconditioned sample gas into the analyzer is one of the worst situations that can occur with an extractive monitoring system. Once unconditioned gas enters the system, it may take months before the system will again operate properly. Therefore, redundancy and fail-safe devices should be built into the system from the start.

Table 9.2 lists some common problems that occur with extractive monitoring systems. Those listed range from the physical problems often associated with the conditioning system to those associated with the analyzers. Many of these problems are due to poor system design resulting from a failure on the part of the system manufacturer to understand the constraints imposed by the plant environment and stack gas conditions. These problems also may be the result of inadequate specifications provided by the user at the time of purchase. It is difficult to foresee problems and it may often require a redesign of the system before the frequency of corrective maintenance is minimized.

TABLE 9.2. EXTRACTIVE SYSTEM PROBLEMS

Common Physical Problems	Possible Corrective Actions
A. Conditioning Systems	
Probe plugging	Install blowback system, increase blowback frequency probe shield. Relocate. Change probe design. Change system design. Enter probe at downward angle.
Probe/filter corrosion	Relocate probe. Obtain corrosion-resistant alloy for probe construction.
Probe breakage (due to vibration or embrittlement from chloride)	Support probe. Shorten. Select resistant alloy.
Condensation in sample lines	Resize heaters. Don't let heat go off on heat trace. Use backup power. Avoid shorts - don't loop lines. Install thermal conductivity sensor if continuing problem. Remove water at stack probe. Filter at lower temperature (acid may be condensing) - increase temperature or heat.
Inadequate water removal	Improve chiller design. Connect two chillers in series. Back up chiller with Permapure dryer (but heat front end of Permapure). Dilute the gas stream to lower moisture content.
Dirt in sample lines, plugged valves, plugged sample lines	Decrease pore size of probe filter. Increase sample flow rate to fine filter. Increase diameter of line. Use clear Teflon tubing to detect areas of accumulation. Redesign to reduce number of valves. Use redundant filters.
Leaks in sample lines/fittings	Reduce number of fittings as much as possible. Detect leaks by pressurizing system and using soap bubble indicator. Check for leaks in gas regulators. Don't wrench down on compression fittings too severely. Don't use glue, paint, glyptal, etc., to cover leaks - rebuild system if necessary.
Pump failure	Perform routine maintenance - check brushes periodically. Check diaphragms of diaphragm pumps.

(continued)

TABLE 9.2. (continued)

Common Physical Problems	Possible Corrective Actions
B. Analyzers	
Internal corrosion/damage	Check moisture removal system for failure. Build redundancy in system. Add extra chiller. Put thermal conductivity sensor in line to stop pump when moisture breaks through. When moisture breaks through, dismantle sample cell, clean, and dry. May have to replace entire cell in some models. Clean and dry <u>all</u> sample lines.
Poor response time (False positive zero values or poor calibration check values)	Check sample line length. Shorten line or increase flow rate. Some analyzers have slow response times. Increase time for calibration gas flow during daily checks.
Excessive drift	Check fouling of sample cell for dirt or water. Electrical problems. Passivation of cell surfaces. Lamp weakening - light levels too low. Detector problems. Electronic problems. Erratic power supply.
Component failures Lamps, fan, chopper motors	Check component wear. Check and replace on regular schedule.
Electronic problems	
Loose circuit boards, poor contacts	Check for vibration problems. Install circuit board clamps. Check for SO_2 corrosion in exposed units
Ground loops and noise	Trace and rewire.
Large voltage drops when plant equipment is started. Spikes in strip chart record.	Install transient suppressor, dedicated power transformer or constant voltage/isolation transformer for monitoring system.
Static electrical charges	Connect probe case to dedicated earth ground.
Burned out electronic circuits from lightning strikes	Add phenolic gaskets between metal stack and probe. Add surge arrestors at junction box.

(continued)

TABLE 9.2. (continued)

Common Physical Problems	Possible Corrective Actions
B. Analyzers	
Electronic problems (cont'd)	
No output from instrument, no calibration cycle, etc.	Check fuses.
Improper instrument response - faulty calibration, improper or no output	Check electronics. Check to see that cards and components are secure. Use trouble-shooting guide supplied by vendor to check electronic test points. Replace appropriate components or replace cards. Check software for errors in programming - particularly in calibration adjustment routines.

9.2.3 In-situ Gas Monitoring Systems

9.2.3.1 In-situ System Design. In-situ gas analyzers measure pollutant and diluent gases as they exist in the stack or the flue. There are two basic types of in-situ monitoring systems: path and point.

Path monitors generally consist of two units, placed opposite each other across a duct or stack. The systems use electro-optical techniques in which either infrared or ultraviolet light is beamed through the flue gas. Absorption of light energy at specific wavelengths provides a quantitative measurement of different molecular species. Such instruments can be designed to pass the light either once or twice through the gas. The once-through systems are known as single-pass monitors and the twice-through systems as double-pass monitors.

In single-pass monitors, the stack units consist of a transmitter and a receiver. The transmitter contains an infrared or UV lamp that beams light to the receiver unit directly across from it on the other side of the stack. The receiver unit senses the transmitted light energy and analyzes it to provide an indication of the gas concentration. The transmitter and receiver units are protected from the flue gases by windows, over which a curtain of air is blown. The air prevents particulate matter from soiling the windows, cools the parts of the unit mounted on the stack, and prevents the condensation of corrosive materials on the cooler instrument windows. The purge air is generally provided by blowers that draw in filtered ambient air. The use of plant air for this purpose is not advised.

Double-pass in-situ path monitors consist of a transceiver unit and a retroreflector unit. Light is transmitted and received by the transceiver. The transmitted light is bounced off the retroreflector located on the opposite side of the flue and returns to be analyzed. The light passes over a path twice the length of that of a single-pass unit, and in so doing, may be considerably weakened upon returning to the transceiver unit. For this reason, most commercial path in-situ gas monitors are single-pass designs rather than double-pass. Double-pass in-situ monitors also use purge air systems to protect window interfaces.

Path in-situ monitor systems come with a number of accessories that are needed to protect them from the often hostile environment encountered at the installation site. For stack-mounted systems, protective hoods and covers are necessary to protect the transmitter/ transceiver, receiver/reflector units from rain, wind, and temperature fluctuations. Lightning protection is frequently necessary. Also, anti-vibration systems are often required to prevent the optical and electrical components from shaking loose. A constant voltage transformer dedicated to the monitor is also frequently necessary to avoid large plant voltage transients from affecting the sensitive electronics of the transceiver units.

Frequently, pipes are used to maintain the alignment between the two cross-stack instrument units. A modification of the support pipe provides a system in which an added outer pipe can rotate to shut out flue gas from entering the light path. Ambient air can be used to purge out any remaining flue gas in the closed tubes so that a zero reference reading can be obtained by the monitor. Calibration gas cells are generally slipped in the light path at this time to obtain an upscale calibration reading.

Point monitors measure the flue gas over a small distance relative to the larger duct or stack diameter. This distance may be less than 5 cm or, in some cases, on the order of 1/3 to 1 m in length. The length of the probes available for these systems are generally fixed, projecting the measurement section of the probe from 1 m to 2 or 3 m into the stack.

If the pollutant gases are greatly stratified, the fixed, one-point measurement may not adequately represent pollutant emissions. The same problem, of course, exists for the single-point probes of extractive systems.

In-situ point monitors normally use a ceramic thimble to protect the measuring cavity from particulate matter. Pollutant or diluent gases diffuse through the thimble, which excludes the particles. Because thimbles may become plugged or glazed over in wet scrubber applications, they must periodically be checked or replaced. Point monitors that use ceramic thimbles do not require blowers as do the path monitors, but still may require protective hoods, lightning protection, and constant voltage transformers.

Another type of in-situ point monitor utilizes an open probe to support a retroreflector. Much like a double-pass path monitor, light from a transceiver hits the retroreflector and returns to be measured. The measurement path, however, will be on the order of only a meter or less, classifying the instrument as an in-situ point monitor, since it measures only a relatively small distance in the flue gas. In this case, purge air blowers are required to keep the retroreflector and transceiver windows clean.

In-situ monitors provide an alternative to extractive systems since they can avoid the requirements for gas conditioning systems. There are trade-offs, however, since the in-situ analyzers installed directly on the stack may experience severe environmental conditions. Table 9.3 summarizes some of the advantages and disadvantages of in-situ and extractive systems.

9.2.3.2 In-situ Analyzers - Absorption Spectrometers and Electrocatalytic Systems. The basic principles of operation of in-situ systems are similar to those of the extractive analyzers. Absorption spectroscopy and electrocatalytic methods are the two most common techniques employed.

The absorption spectroscopic techniques used in in-situ monitors are

- differential absorption
- gas filter correlation
- second derivative spectroscopy.

The most common differential absorption systems are single-pass path monitors that use a diffraction grating to distinguish between measuring and reference wavelengths in the UV region of the spectrum. SO_2 and NO are measured by this technique, although by changing the optical system, it is possible to measure other gases. Filters can also be used to distinguish between measuring and reference wavelengths in in-situ analyzers. CO_2 is measured by infrared light with this method.

TABLE 9.3. COMPARISON OF EXTRACTIVE AND IN-SITU SYSTEMS

Extractive Systems	In-Situ Systems	
	Path	Point
Advantages		
	Linearly averages stack concentrations to possibly reduce stratification effects	
	Does not alter sample	Does not alter sample
May be zeroed and calibrated with cylinder gases		May be zeroed and calibrated with cylinder gases
Analyzers can easily be located in controlled environments	Has fewer separate components than extractive systems	Has fewer separate components than extractive systems
	Rapid response	
Can time share analyzer		
Maintenance may not require special training		
Disadvantages		
	Can monitor at only one location	Can monitor at only one location
System (other than analyzer) may require frequent maintenance	Difficult to repair on site	Difficult to repair on site
Probe plugging possible in dirty gas streams	May lose light levels in dirty gas streams or in wet scrubber applications	May clog in dirty gas streams or in wet scrubber applications
May alter sample	Requires temperature compensation	Requires temperature compensation
Long sample lines reduce response time		
Zero and calibration gases expensive	Generally cannot be calibrated with cylinder gases. Audits are expensive: must perform reference method testing	
	Special training or vendor service often needed	Special training or vendor service often needed

Gas filter correlation spectroscopy is a nondispersive spectroscopic technique that has been used in single-pass in-situ analyzers as well as in ambient air analyzers. The method requires a gas cell to be filled with the pollutant or diluent gas that is to be measured. Light, usually in the infrared, is transmitted through the flue gas into the receiver unit, where it passes through the gas filter cell and then through a neutral density filter (or no filter at all). The gas filter essentially "filters out" the spectroscopic regions in which the pollutant molecule absorbs light energy. This 100% filter thus gives a reference signal to which the light passing through the neutral filter can be compared. The advantage of this method, as well as with the differential absorption technique, is that low levels of particulate matter will not affect the measurement. Gas filter correlation instruments have been designed to measure SO_2, NO, CO_2, and CO.

Second derivative spectroscopy is employed in a point in-situ monitor that has been quite widely marketed. Using an oscillating lens, UV absorption peaks of SO_2 and NO are scanned 45 times per second. This scanning creates a signal that is related to the second derivative of the absorption peak, taken with respect to wavelength. Using the Beer-Lambert Law, it can be shown that this signal is proportional to the concentration of the pollutant in the flue gas. The instrument has a measurement cavity, generally 5 cm in length, that is protected by a ceramic thimble. The system can be calibrated by using either gas cells or cylinder gases.

Electrocatalytic analyzers used for in-situ measurements are exclusively point monitors. Currently, this technique has been applied for the measurement of O_2 and SO_2. As discussed in Section 9.2.1.4 for extractive analyzers, solid electrolytes can be used to generate a measurable flow of electrons. Here, a ceramic thimble keeps the measurement side of the solid electrolyte free of particulate matter. Calibration gases can be injected into the measurement cavity to check the instrument operation.

9.2.4 Recommended Maintenance - In-situ Monitoring Systems

9.2.4.1 Operation Checks (Daily Checks). The daily operation checks associated with in-situ gas monitors are similar to those for extractive gas monitoring systems. The operation checks should be performed by a trained and qualified operator who has been given responsibility for the system. The monitoring system will have a better record of performance if the operator checks the system daily - automatic zero and calibration procedures can create a sense of false confidence that can lead to system failures.

The daily operation checks should start with a review of the previous 24 hours of strip chart recordings and computer printouts. Discrepancies should be noted on the check sheet and instrument logbook. Again, any system faults identified by the indicator lights should be resolved immediately.

Many in-situ systems use a gas cell containing pollutant gas at a known concentration for calibration. In the optical in-situ analyzers, the cell is put into the path of the light beam, and the signal is attenuated by a specific amount. This method may not, however, always check the complete optical system over which the flue gas is measured, although the use of pipes that close out the stack gas from the light path have, in some cases, alleviated the problem. Also, the gas cell pollutant concentrations are not normally certified by independent laboratories (their concentrations may, however, be independently verified). Degradation of cell concentrations by leakage, adsorption, or internal reactions can cause discrepancies in the calibration data.

It is possible to calibrate some in-situ monitors with certified cylinder gas. This can be done with in-situ point monitors by flooding the volume within the ceramic thimble with calibration gas or with zero gas. A "flow-through" gas cell can be used in either single-pass or double-pass monitors. By flowing gas of a certified concentration through a fixed cell in the instrument, a calibration "traceable" to NBS or other certified gases can be obtained. However, problems associated with the optical path used in the calibration sequence may still be present. It should also be noted if the temperature compensation circuit is disconnected in any of these calibration sequences. Problems in these circuits may be overlooked in such cases.

The optical alignment of the components of in-situ systems is very important for proper operation. Alignments should be checked at appropriate intervals. Many of the systems do not, however, incorporate alignment sights in their design. In such cases, detailed electronic or optical checks may need to be performed to optimize the system alignment.

Note again that actual calibration adjustments should not be performed arbitrarily. Control limits should be set to avoid calibrating against normal system fluctuations. The Federal monitoring requirements specify that that the calibration be adjusted whenever the zero (or low-level) or the high-level calibration value exceeds two times the limit of the applicable performance specifications.[4] Performance specifications are given in Appendix B of Part 60 of the U.S. Code of Federal Regulations - Title 40. If either calibration value exceeds four times the applicable performance specification during any calibration drift check, all of the data collected since the last check are considered to be data collected during a CEM system out-of-control period and are rejected. Similarly, if the system exhibits drift (either low-level or high-level) greater than the performance specification for five consecutive 24-h periods, the system is again viewed as being out of control, and subsequent data are rejected until the system problems are corrected.[5]

Figure 9.4 gives a format for developing a daily QA check sheet for in-situ systems.

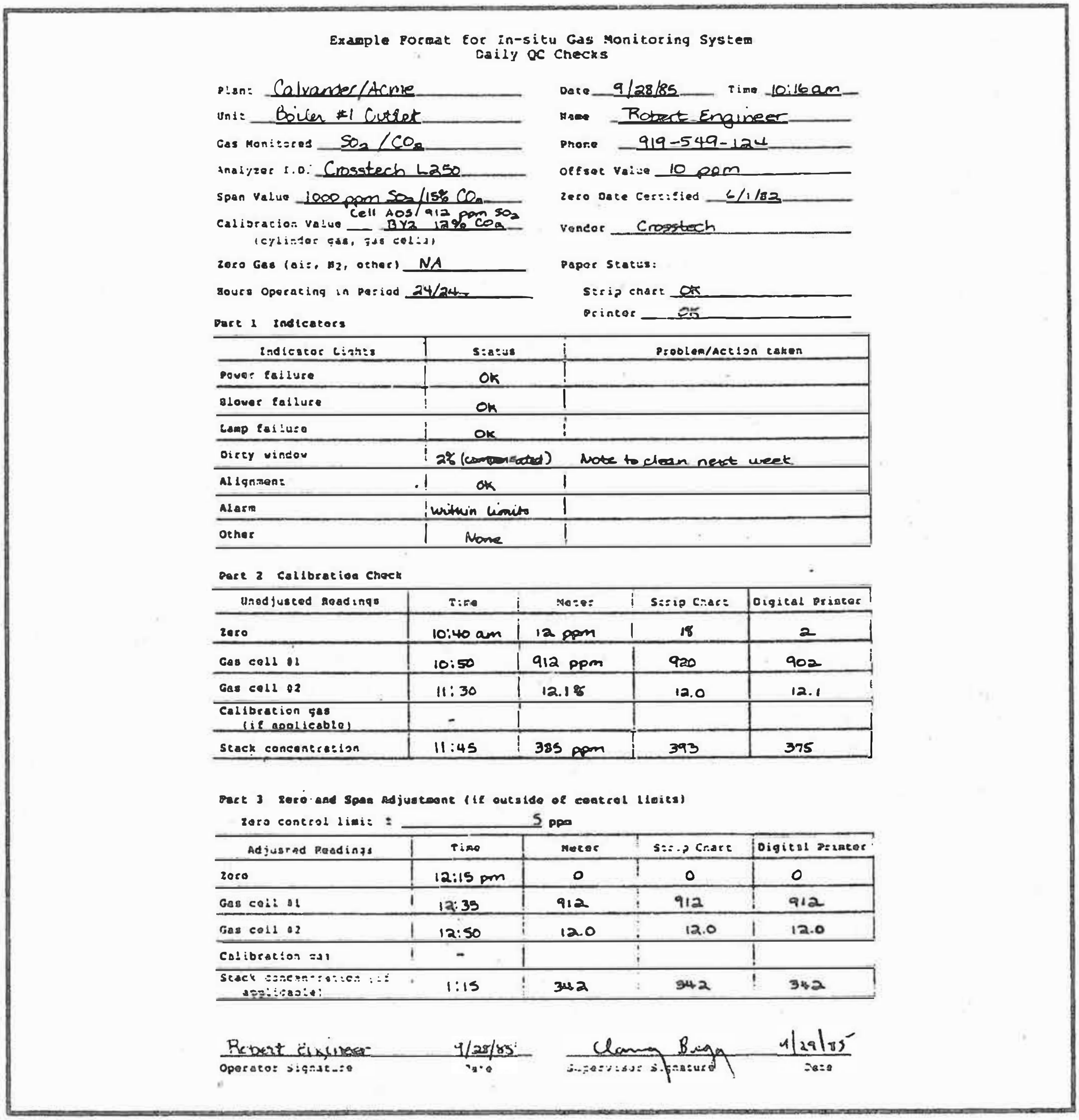
9.2.4.2 Routine Maintenance (30-day Checks). Routine maintenance should be initially performed on in-situ monitors, at a minimum, every 30 days. Although many equipment vendors recommend routine maintenance at periods of two or three months, it is advisable to gain experience with the system before waiting these longer periods.

Routine maintenance for in-situ systems should consist of ensuring that key components of the system are clean and operational. In general, windows, filters, and desiccants should be cleaned and/or replaced.

In the cleaning procedures for windows or optics, great care should be taken. Lens tissue or clean, soft rags should be used with a solution of alcohol and water. In severe cases, mild detergent may be necessary to clean windows exposed to the flue gas. Sensitive optical components such as diffraction gratings should never be touched or cleaned in the field. Fingerprints or traces of cleaning materials can severely affect their performance, so special techniques must be used.

A systematic procedure should be instituted for checking the electrical performance to compare it with the original factory or start-up performance. This normally involves using a digital voltmeter and oscilloscope to check the analyzer at various test points. These test points should include a check of lamp voltages, power supply voltages, and detector outputs. The procedures involved in these checks will generally require a well-trained serviceman or electronic technician.

Many in-situ analyzers use chopper motors in the transceiver assembly to modulate the light beam or switch instrument functions. These motors should be checked for bearing noise or for excessive vibration. For motors that automatically move mirrors or gas cells



Example Format for In-situ Gas Monitoring System
Daily QC Checks

Plant: Calvander/Acme
Date 9/28/85 Time 10:16 am
Unit Boiler #1 Outlet
Name Robert Engineer
Gas Monitored SO_2 / CO_2
Phone 919-549-124
Analyzer I.D. Crosstech L250
Offset Value 10 ppm
Span Value 1000 ppm SO_2/15% CO_2
Zero Date Certified 6/1/82
Calibration Value Cell A05/ 912 ppm SO_2 B72 12% CO_2
(cylinder gas, gas cell)
Vendor Crosstech
Zero Gas (air, N_2, other) NA
Paper Status:
Hours Operating in Period 24/24
Strip chart OK
Printer OK

Part 1 Indicators

Indicator Lights	Status	Problem/Action taken
Power failure	OK	
Blower failure	OK	
Lamp failure	OK	
Dirty window	2% (compensated)	Note to clean next week
Alignment	OK	
Alarm	within limits	
Other	None	

Part 2 Calibration Check

Unadjusted Readings	Time	Meter	Strip Chart	Digital Printer
Zero	10:40 am	12 ppm	18	2
Gas cell #1	10:50	912 ppm	920	902
Gas cell #2	11:30	12.18	12.0	12.1
Calibration gas (if applicable)	-			
Stack concentration	11:45	385 ppm	393	375

Part 3 Zero and Span Adjustment (if outside of control limits)

Zero control limit ± 5 ppm

Adjusted Readings	Time	Meter	Strip Chart	Digital Printer
Zero	12:15 pm	0	0	0
Gas cell #1	12:35	912	912	912
Gas cell #2	12:50	12.0	12.0	12.0
Calibration gas	-			
Stack concentration (if applicable)	1:15	342	342	342

Robert Engineer 9/28/85
Operator Signature Date

9/29/85
Supervisor Signature Date

Figure 9.4. Example format for in-situ gas monitoring system daily QC checks.

into position, the operations should be manually checked to see that the movements are smooth and complete.

Observations made during the routine maintenance period should be noted in the system logbook to provide the base data necessary to optimize the maintenance procedures. After six months to one year of operation, trends in performance should become apparent. These trends may indicate that some maintenance procedures may need to be improved or that others may need to be performed more frequently or less frequently.

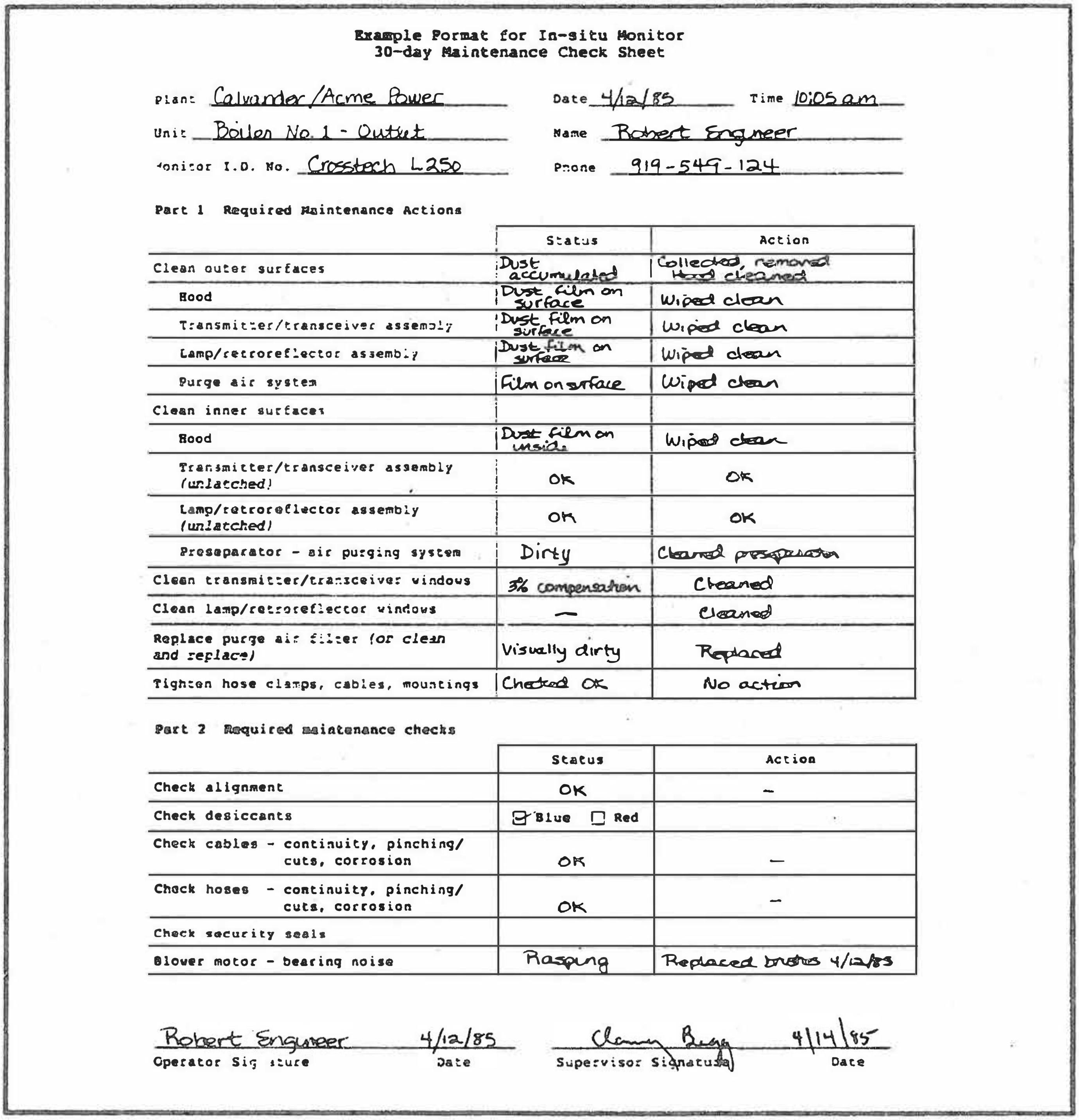
Figure 9.5 gives a suggested format for the development of an in-situ system maintenance check sheet.

9.2.4.3 Performance Audits. The discussion in Section 9.2.2.3 for performance audits on extractive systems is also applicable to in-situ systems. However, in the case of path in-situ monitors that come under the requirements of Appendix F, it is not possible to conduct a cylinder gas audit (CGA) unless a flow-through cell is incorporated in the system. RATA and RAA audits can, however, still be conducted on these systems. Path monitors should be checked quite frequently to see if they are giving representative data, since, as mentioned previously, the methods used for internal zero and calibration may not check the complete optical system. The in-situ point monitors can, in most cases, be checked with cylinder gas, but audits independent of the monitoring system should also be performed at regular intervals.

9.2.4.4 Corrective Maintenance (Problems and Troubleshooting). In-situ monitors avoid many of the problems associated with extractive systems; however, in-situ systems are not devoid of problems. In-situ systems installed directly on a stack or duct are subjected to severe environments. Temperature cycling, acid gases, and vibration can damage the sensitive optical components and alter the optical alignment that is important to these systems. The electrical components located in the mounted system assemblies are subjected to the same type of abuse and can fail if not adequately protected.

The often complex nature of in-situ systems requires a higher level of troubleshooting skill. It is advisable that the operator responsible for a CEM system first be trained by the instrument vendor, preferably in a formal training session at the vendor's facility.

The basic problems that occur are often a result of the environment, such as vibration and ambient temperature variation. The solutions to these problems are very specific to a given installation



Example Format for In-situ Monitor
30-day Maintenance Check Sheet

Plant Calvander/Acme Power
Date 4/12/85
Time 10:05 am
Unit Boiler No. 1 - Outlet
Name Robert Engineer
Monitor I.D. No. Crosstech L250
Phone 919-549-124

Part 1 Required Maintenance Actions

	Status	Action
Clean outer surfaces	Dust accumulated	Collected, removed Hood cleaned
Hood	Dust film on surface	Wiped clean
Transmitter/transceiver assembly	Dust film on surface	Wiped clean
Lamp/retroreflector assembly	Dust film on surface	Wiped clean
Purge air system	Film on surface	Wiped clean
Clean inner surfaces		
Hood	Dust film on inside	Wiped clean
Transmitter/transceiver assembly *(unlatched)*	OK	OK
Lamp/retroreflector assembly *(unlatched)*	OK	OK
Preseparator - air purging system	Dirty	Cleaned preseparator
Clean transmitter/transceiver windows	3% compensation	Cleaned
Clean lamp/retroreflector windows	—	Cleaned
Replace purge air filter *(or clean and replace)*	Visually dirty	Replaced
Tighten hose clamps, cables, mountings	Checked OK	No action

Part 2 Required maintenance checks

	Status	Action
Check alignment	OK	—
Check desiccants	☑ Blue ☐ Red	
Check cables - continuity, pinching/ cuts, corrosion	OK	—
Check hoses - continuity, pinching/ cuts, corrosion	OK	—
Check security seals		
Blower motor - bearing noise	Rasping	Replaced brushes 4/12/85

Robert Engineer 4/12/85
Operator Signature Date

4/14/85
Supervisor Signature Date

Figure 9.5. Example format for in-situ monitor 30-day maintenance check sheet.

and may require re-installation or the construction of environmentally controlled enclosures around the analyzers.

Table 9.4 lists some of the problems associated with in-situ systems and recommendations for corrective action.

9.3 Opacity CEM System Operation Practices

9.3.1 System Design - Many types of instruments have been developed that can measure the opacity of a gas in a stack or duct. These instruments are called opacity monitors, or alternatively, transmissometers. They are in-situ monitors and can be designed either as single-pass or as double-pass units.

9.3.1.1 Single-pass Systems. Single-pass opacity monitors are quite simple in design. Light emitted from a lamp passes through the stack and is sensed by a detector on the other side of the stack. Blowers located on each side help keep the windows of the apparatus clean.

One problem associated with the design is that of calibration. The electronic and optical components of the system cannot be checked unless the stack or duct is free of particulate matter. This can be achieved if the industrial process is shut down and provisions are made so that residual dust does not recirculate in the stack. Since most industrial processes cannot shut down just to zero and calibrate an opacity monitor, instrument designers have used optical light fibers or zero-pipes to provide this capability. The light fibers pass from the lamp to the detector around the outside of the stack. The zero-pipes pass through the stack and can be purged with air to provide a zero reading for the instrument.

9.3.1.2 Double-pass Systems. In double-pass opacity monitors, light crosses the stack and is returned by using a retroreflector. The retroreflector returns it to the main analyzer housing, where a detector then senses the light. This instrument can be zeroed and calibrated by flipping a mirror up into the light path to approximate a clean-stack condition. The mirror close to the transceiver prevents the beam from crossing the stack and merely sends the light through the clean interior to give a "pseudo-zero" reading. A calibration filter can then be flipped into the path of light to give an upscale calibration reading. Rotating choppers have also been used for zero and calibration procedures.

Blowers again are used to keep clean the optical surfaces exposed to the stack gas. Filters are needed before the blower so that clean air will pass through the analyzer.

TABLE 9.4. IN-SITU GAS ANALYZER PROBLEMS

Problem	Possible Corrective Action
Excessive dirt buildup on windows or thimbles	Clean blower filters on path systems. Increase blower capacity. Rotate ceramic thimbles on point systems or replace.
Cyclic drift in signal unrelated to plant performance - due to ambient temperature changes. Signal becomes erratic from high temperatures	Insulate protective hood or install temperature conditioning system about monitor.
Optics misalignment/electrical noise due to stack or duct	Mount assemblies independently from duct. Use flexible bellows for duct connection. Dampen mountings. Relocate monitor.
Signal becomes erratic at high opacities	Relocate monitor after control device. Water droplets from scrubber may also cause this problem. In such cases, analyzer may have to be located before the scrubber.
Misaligned system	Realign, check, and tighten system.
Probe/seal leaks (in-stack monitors)	Return to vendor for repair.
Lightning strikes	Add phenolic gaskets. Add surge arrestors. Relocate monitor.
Static charge buildup burning out circuit boards	Run copper cables to earth ground.
Lamp burnout/degradation	Replace on regular schedule. Check lamp power supply for high incidence of lamp failure.
Gas cells unreliable	Cell leakage, losses to walls - recalibrate cells or replace.
Spurious readings during plant start-up, shutdown, etc.	Install transient suppressor, dedicated transformer for monitoring system.
Improper temperature compensation	Adjust circuits, recalibrate, or repair or replace boards.
Increased response time	For in-stack in-situ monitors, check ceramic thimble for plugging. Replace if necessary.

Any transmissometer, be it single-pass or double-pass, will have similar components, including a light source, a detector, and various optical components. The light source may be specifically selected for the system or may merely be a lamp normally used in an automobile headlight assembly. Detectors are chosen so that they will sense the light emitted by the source. This light is normally in the visible and infrared regions of the spectrum. Optical components include focusing lenses, mirrors, and optical filters. Filters are used to help the instrument respond only to light in the visible region of the spectrum - the so-called photopic region, to which the human eye is sensitive. Filters normally prevent infrared light from being sensed by the detector.

Mirrors, of course, direct the light from point to point inside the instrument, so that the operations of measurement, zeroing, and calibrating can take place. Lenses focus the light so that a well-collimated beam is sent across the stack and through the instrument. In addition to these components, chopper wheels and light modulating wheels are often used to direct or modify the light beam.

Various accessories can be purchased for the opacity monitor. These include integrators, beam combiners, "reasons" panels, and so on. The main instrument panel for the monitor is normally installed in the control room of the plant. Here, the instrument outputs are observed and recorded.

Transmissometers are generally installed to meet requirements of pollution control agencies. The Federal EPA has developed specifications for these instruments.[1] There are basically two types of specifications: design specifications and performance specifications. The design specifications detail how the instrument is to be constructed.

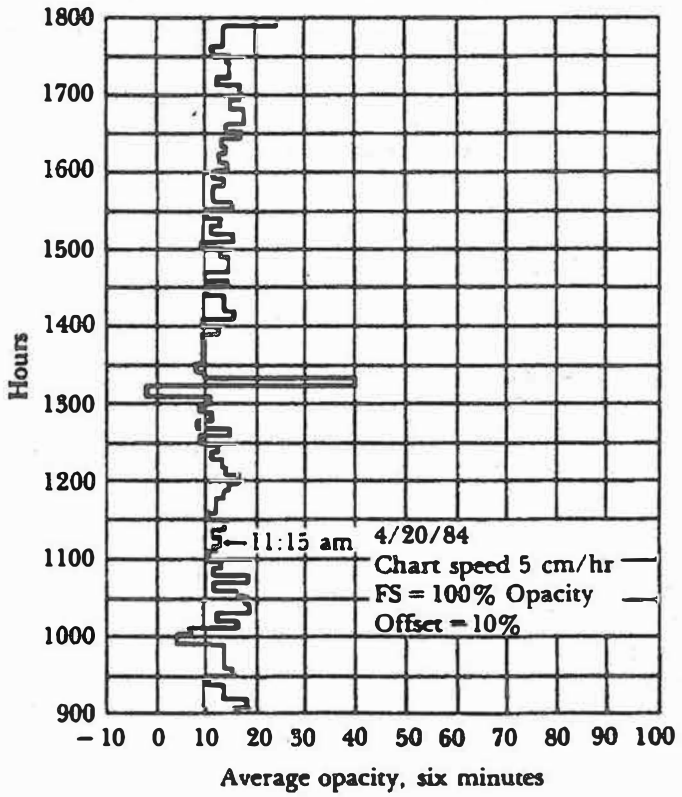
Monitors that satisfy the design specifications are purchased and installed in a location according to EPA guidelines.[1] The installed monitor undergoes the performance specification test procedures. These procedures check the system for zero and calibration drift over a one-week period. Passing this test indicates that the monitor is acceptable for the opacity monitoring.

However, testing should not stop at this point. As with all instruments, problems can occur over long periods of operation. Blower filters must be checked and regularly cleaned, burned-out lamps replaced, and the integrity of the data must be consistently audited. The continued success of a monitoring program depends heavily on how well the instruments are maintained.

9.3.2 Recommended Maintenance - Opacity Monitoring Systems

9.3.2.1 Operation Checks (Daily Checks). Operation checks should be conducted daily. These checks can generally be performed at the remote control unit located in the station control room. It is not necessary to go into the plant to check the transmissometer itself, unless a fault lamp indicates a problem has developed.

At this level, the activities include noting the status of the system indicator (fault) lights and recording the daily zero and span values on an appropriate form. The day's strip chart record should be examined to check for trends or problems that might not be identified by the system fault lights. At this time, the strip chart should be annotated. Figure 9.6 gives examples of the type of information that should be noted.



5←11:15 am

4/20/84
Chart speed 5 cm/hr
FS = 100% Opacity
Offset = 10%

Figure 9.6. Strip chart annotations.

The first level of quality control serves to alert the operator to problems or necessary adjustments. If the window indicator or zero compensation light (where applicable) warns that the windows are dirty, someone will have to go to the duct or stack and clean the windows of the transceiver and retroreflector assemblies. If the span reading or zero reading has drifted to an unacceptable degree, the span or zero potentiometers may have to be adjusted to bring the readings back to the proper values, or other corrective action may be necessary. Care should be taken in such adjustments, however. If there is only a small difference from the proper values, the difference may be due just to random noise in the system. Also, if the drift is large, problems may be developing that cannot be solved by merely adjusting zero and span potentiometers. For these reasons, "control limits" are commonly established to aid in deciding whether to adjust the system. The specific limits should be established at a level that (1) ensures the monitoring data will be sufficiently precise for its intended use and (2) is achievable.

To make the daily check thorough and complete, log sheets are often developed by the operator. Figure 9.7 should be regarded as a starting point for developing such a form.

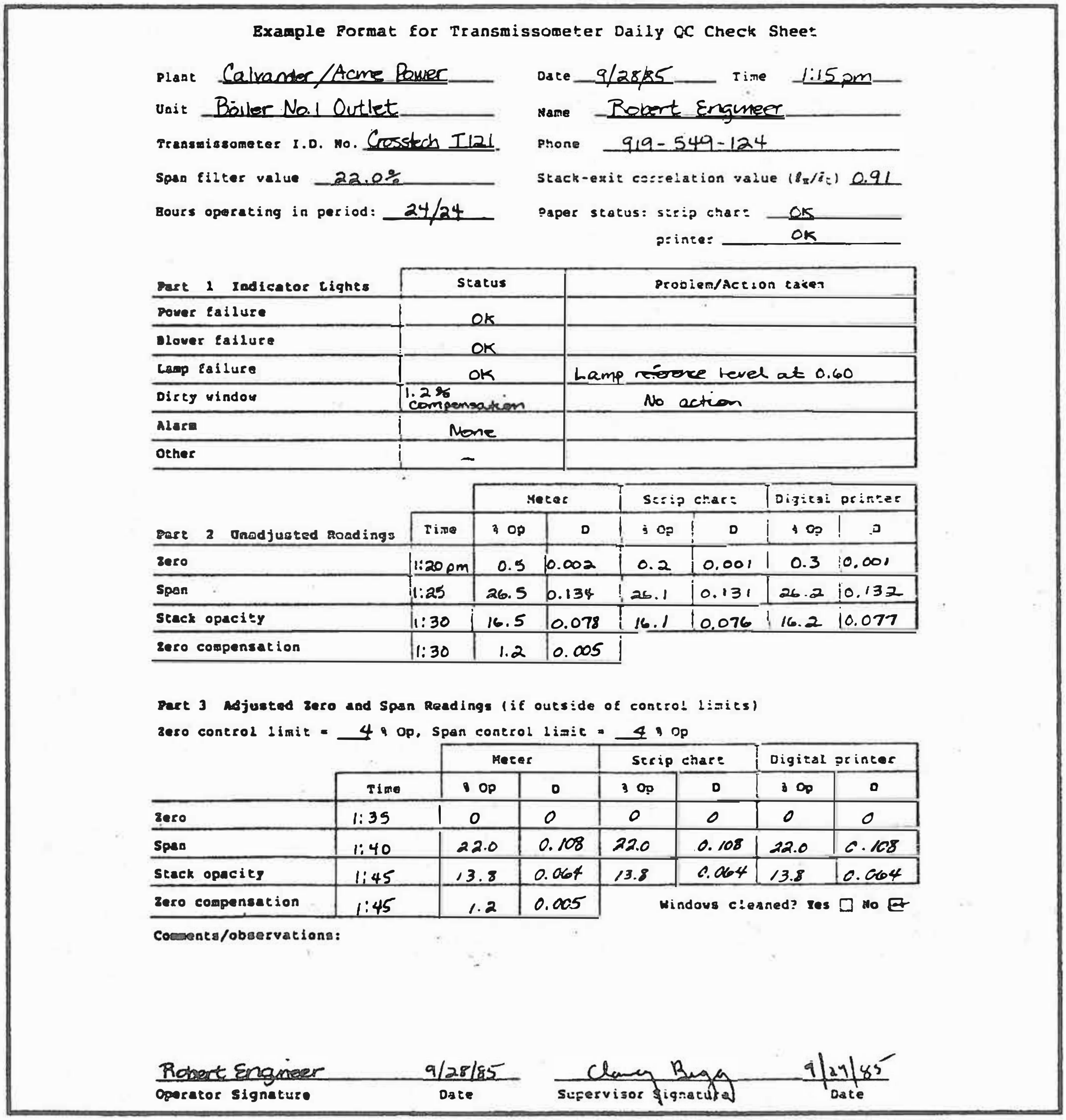
Part 1 of Figure 9.7 provides a checklist for the indicator lights on the remote control panel. Items incorporated in Part 1 will depend on the specific instrument system. Depending on the status of the lights, the daily operation check may develop into more than just a check. A blower failure or dirty window alarm will require a visit to the transmissometer for corrective action.

Note also that Parts 2 and 3 of Figure 9.7 require data from the meter, the strip chart, and the digital printer. If the monitoring system presents data in all three of these formats, the data obtained from each should be identical. If they are not, the correct one must be determined. In poorly maintained systems, improperly zeroed meters or recorders can create discrepancies. Also, meter readings often differ from the computer printout because the transmissometer and computer are improperly connected.

Zero compensation values should also be recorded so that they can be evaluated at a later time. After several weeks, these data can be drawn from the daily logs to evaluate the rate of window soiling.

As a part of the quality assurance program, the form should be signed by the person performing the checks. At appropriate intervals, the operator's supervisor should review and initial the logs to see that assigned responsibilities are being carried out.

9.3.2.2 Routine Maintenance (30-day Checks). The second level of quality control for transmissometer systems involves establishing a



Example Format for Transmissometer Daily QC Check Sheet

Plant Calvander/Acme Power
Date 9/28/85 Time 1:15 pm
Unit Boiler No.1 Outlet
Name Robert Engineer
Transmissometer I.D. No. Crosstech T121
Phone 919-549-124
Span filter value 22.0%
Stack-exit correlation value (ℓ_x/ℓ_t) 0.91
Hours operating in period: 24/24
Paper status: strip chart OK
printer OK

Part 1 Indicator Lights	Status	Problem/Action taken
Power failure	OK	
Blower failure	OK	
Lamp failure	OK	Lamp ~~[illegible]~~ level at 0.60
Dirty window	1.2% compensation	No action
Alarm	None	
Other	–	

Part 2 Unadjusted Readings		Meter		Strip chart		Digital printer	
	Time	% Op	D	% Op	D	% Op	D
Zero	1:20 pm	0.5	0.002	0.2	0.001	0.3	0.001
Span	1:25	26.5	0.134	26.1	0.131	26.2	0.132
Stack opacity	1:30	16.5	0.078	16.1	0.076	16.2	0.077
Zero compensation	1:30	1.2	0.005				

Part 3 Adjusted Zero and Span Readings (if outside of control limits)

Zero control limit = 4 % Op, Span control limit = 4 % Op

		Meter		Strip chart		Digital printer	
	Time	% Op	D	% Op	D	% Op	D
Zero	1:35	0	0	0	0	0	0
Span	1:40	22.0	0.108	22.0	0.108	22.0	0.108
Stack opacity	1:45	13.8	0.064	13.8	0.064	13.8	0.064
Zero compensation	1:45	1.2	0.005				

Windows cleaned? Yes ☐ No ☒

Comments/observations:

Robert Engineer 9/28/85
Operator Signature Date

9/29/85
Supervisor Signature Date

Figure 9.7. Example format for transmissometer daily QC check sheet.

schedule for routine maintenance. A basic schedule may be provided in the instruction manual, but such schedules do not address problems specific to an installation. Over a period of time, after the operator is comfortable and experienced with the system, a maintenance routine can be developed. It may take a year or two to perfect the schedule, but once developed, it should be adhered to.

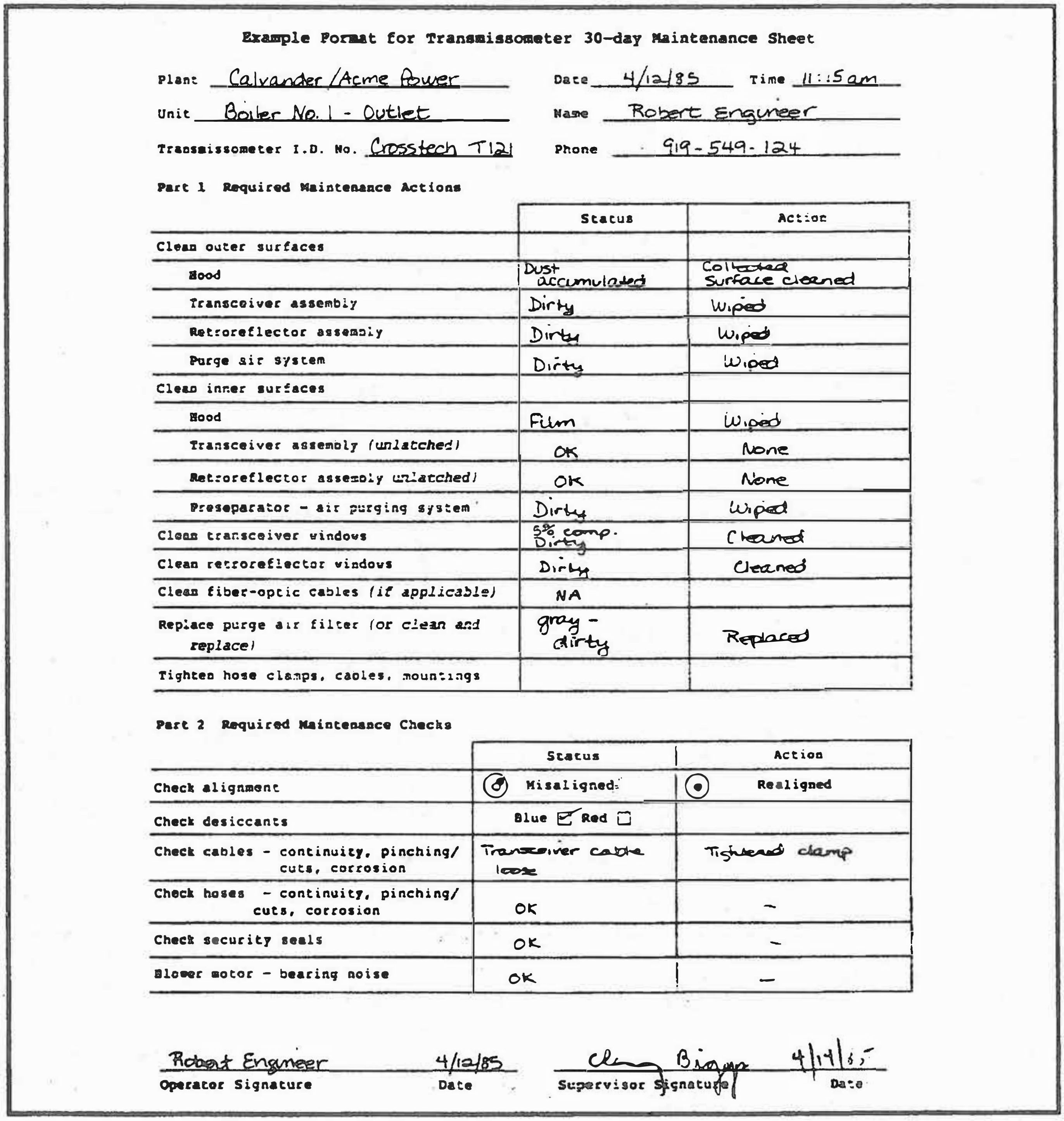
It is recommended that, at least initially, a 30-day maintenance routine be established. Housekeeping of the transmissometer equipment located on the stack is the predominant form of maintenance performed at this interval. Cleaning of outer surfaces, windows, parts, and filters is the major activity. Once the operator or serviceman is at the instrument site, the alignment, desiccants, and blower motors can also be checked.

After a few system failures have been experienced, a replacement schedule can be developed for parts having a lifetime of a year or more. For example, transmissometer lamps will generally have a lifetime of over two years (20,000 h). Rather than allowing the lamp to burn out and cause a system failure, it can be replaced routinely at the end of every two-year period. Blower motors also require maintenance. Since the motors are "on" continuously, at some point the bearings are going to wear out. The period of time it takes for this to happen will depend on several things - such as the amount of particulate matter and acid in the ambient air and the amount of stack vibration. These factors will aggravate wear to cause a problem eventually. When breakdown does occur, the period for motor maintenance can then be established.

In the transmissometer check sheet given in Figure 9.8, there are two parts, one for required maintenance actions, the other for required maintenance checks. The serviceman or operator should perform the basic housekeeping chores of cleaning and then check for other problems. If a problem is observed or if one appears to be developing, corrective action should then be taken.

The form should be modified to fit both the plant maintenance routines and the characteristics of the actual system. Within a year after the system has passed Performance Specification 1, the operator should use the logbook and daily logs to devise a schedule of periodic preventive maintenance that best fits the installation.

9.3.2.3 Performance Audits. The third level of activity that a company should institute for its opacity monitoring system involves conducting performance audits.



Example Format for Transmissometer 30-day Maintenance Sheet

Plant Calvander/Acme Power
Date 4/12/85 Time 11:15am
Unit Boiler No. 1 - Outlet
Name Robert Engineer
Transmissometer I.D. No. Crosstech T121
Phone 919-549-124

Part 1 Required Maintenance Actions

	Status	Action
Clean outer surfaces		
Hood	Dust accumulated	Col~~lected~~ Surface cleaned
Transceiver assembly	Dirty	Wiped
Retroreflector assembly	Dirty	Wiped
Purge air system	Dirty	Wiped
Clean inner surfaces		
Hood	Film	Wiped
Transceiver assembly *(unlatched)*	OK	None
Retroreflector assembly *unlatched)*	OK	None
Preseparator - air purging system	Dirty	Wiped
Clean transceiver windows	5% comp. Dirty	Cleaned
Clean retroreflector windows	Dirty	Cleaned
Clean fiber-optic cables *(if applicable)*	NA	
Replace purge air filter *(or clean and replace)*	gray - dirty	Replaced
Tighten hose clamps, cables, mountings		

Part 2 Required Maintenance Checks

	Status	Action
Check alignment	● Misaligned	● Realigned
Check desiccants	Blue ☑ Red ☐	
Check cables - continuity, pinching/ cuts, corrosion	Transceiver cable loose	Tightened clamp
Check hoses - continuity, pinching/ cuts, corrosion	OK	–
Check security seals	OK	–
Blower motor - bearing noise	OK	–

Robert Engineer 4/12/85
Operator Signature Date

Clay Biggs 4/14/85
Supervisor Signature Date

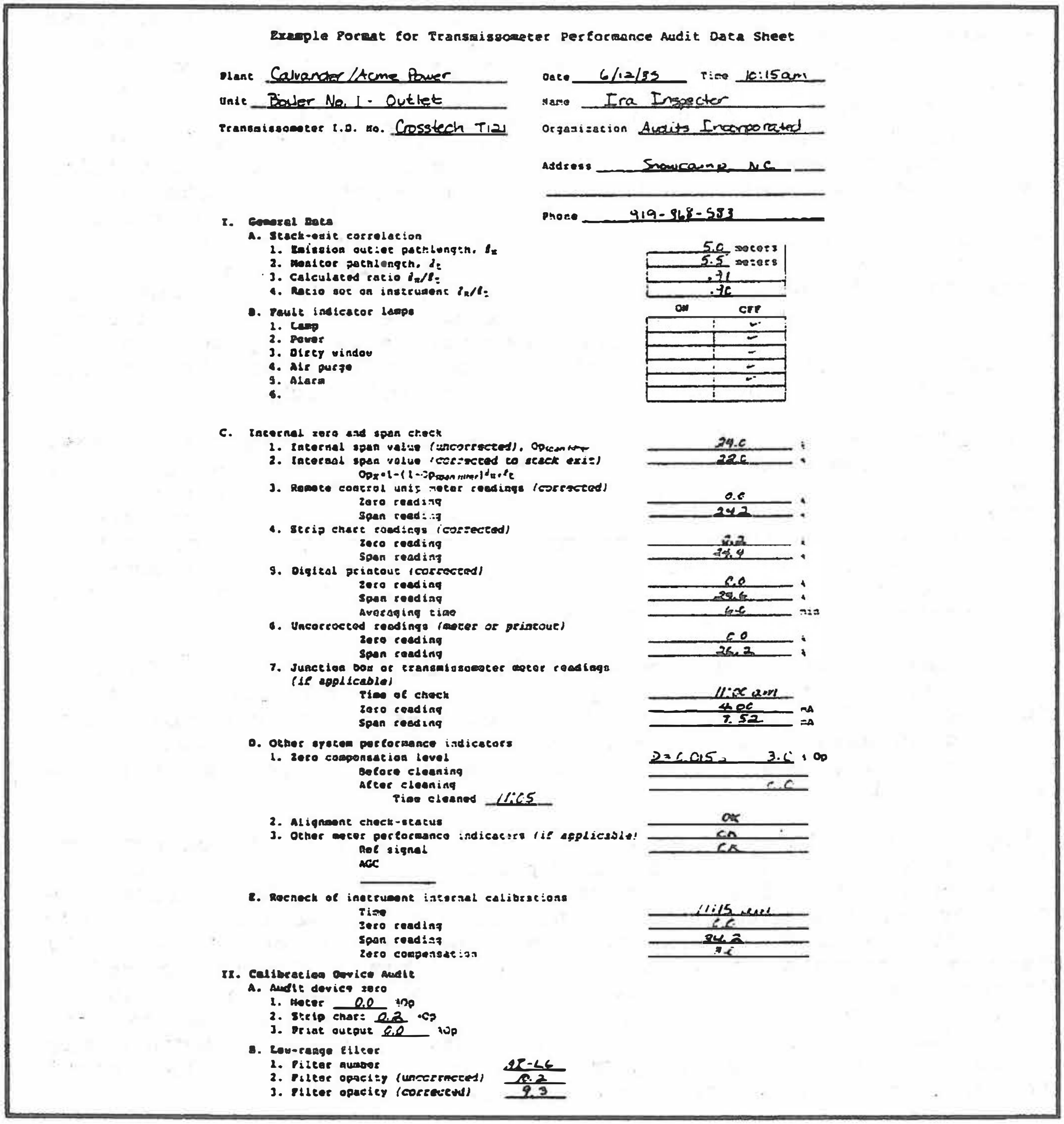
Figure 9.8. Example format for transmissometer 30-day maintenance check sheet.

Audit devices have been developed for most of the double-pass transmissometer systems and for some of the single-pass systems. Basically, the devices designed for double-pass systems consist of holders that can be attached onto the transceiver. The holder consists of a slot for holding calibration filters and a short-range retroreflector. The device and the transceiver basically constitute a "mini-transmissometer" that can accommodate audit calibration filters. The device also contains an iris, which allows the reflectance of the mirror to be adjusted so that it will correspond to a simulated, stack zero. It is best to make this adjustment initially when the system is set up for the performance specification calibration and response time test. After the instrument is installed, it provides a method of checking the simulated, instrument zero. This "audit zero," of course, may not necessarily be identical to a clean-stack zero, but comparing it to the instrument's internal "simulated zero" provides a good quality control check.

An audit does not just involve obtaining data from audit devices. An audit is a check of the performance of the entire transmissometer system. Indicator lamp status, stack-exit correlation corrections, alignment, and other functions of the system should all be checked at this time by the auditor. The most common problems uncovered in audits are errors associated with the calculation of stack-exit corrected opacity values. An auditor can easily uncover such a problem through a well-designed program.

A system of auditing procedures has been developed for double-pass transmissometers.[6] This system, designed for use by control agency personnel, gives detailed step-by-step instructions for conducting an audit using the calibration filter audit devices. A generalized form, based on the work detailed in reference 6, is presented in Figure 9.9.

Figure 9.9 indicates the type of information that can be obtained during an audit. Using a calibration audit device, both the transceiver optics and electronics are evaluated. Using a reference signal source, the data handling system can be evaluated. In the case of a double-pass system, these procedures check only the transceiver assembly and data handling system. Since the retroreflector assembly is not involved in the checks, the audit evaluates only part of the system. It is possible that a system can pass an audit without problems, but the cross-stack opacity readings may still be inaccurate if misalignment or window fouling problems occur at the retroreflector side of the instrument.



Example Format for Transmissometer Performance Audit Data Sheet

Plant Calvander/Acme Power
Unit Boiler No. 1 - Outlet
Transmissometer I.D. No. Crosstech T121
Date 6/12/85 Time 10:15am
Name Ira Inspecter
Organization Audits Incorporated
Address Snowcamp, N.C.
Phone 919-968-583

I. General Data

A. Stack-exit correlation

1. Emission outlet pathlength, ℓ_x 5.0 meters
2. Monitor pathlength, ℓ_t 5.5 meters
3. Calculated ratio ℓ_x/ℓ_t .91
4. Ratio set on instrument ℓ_x/ℓ_t .90

B. Fault indicator lamps

	ON	OFF
1. Lamp		✓
2. Power		✓
3. Dirty window		✓
4. Air purge		✓
5. Alarm		✓
6.		

C. Internal zero and span check

1. Internal span value *(uncorrected)*, $Op_{span\ value}$ 24.0 %
2. Internal span value *(corrected to stack exit)* 22.0 %
   $Op_x = 1-(1-Op_{span\ value})^{\ell_x/\ell_t}$
3. Remote control unit meter readings *(corrected)*
   Zero reading 0.0 %
   Span reading 24.2 %
4. Strip chart readings *(corrected)*
   Zero reading 0.2 %
   Span reading 24.4 %
5. Digital printout *(corrected)*
   Zero reading 0.0 %
   Span reading 23.6 %
   Averaging time 6.0 min
6. Uncorrected readings *(meter or printout)*
   Zero reading 0.0 %
   Span reading 26.2 %
7. Junction box or transmissometer meter readings *(if applicable)*
   Time of check 11:00 am
   Zero reading 4.00 mA
   Span reading 7.52 mA

D. Other system performance indicators

1. Zero compensation level D=0.015 = 3.0 % Op
   Before cleaning
   After cleaning 0.0
   Time cleaned 11:05
2. Alignment check-status OK
3. Other meter performance indicators *(if applicable)* OK
   Ref signal OK
   AGC

E. Recheck of instrument internal calibrations
   Time 11:15 am
   Zero reading 0.0
   Span reading 24.2
   Zero compensation 3.0

II. Calibration Device Audit

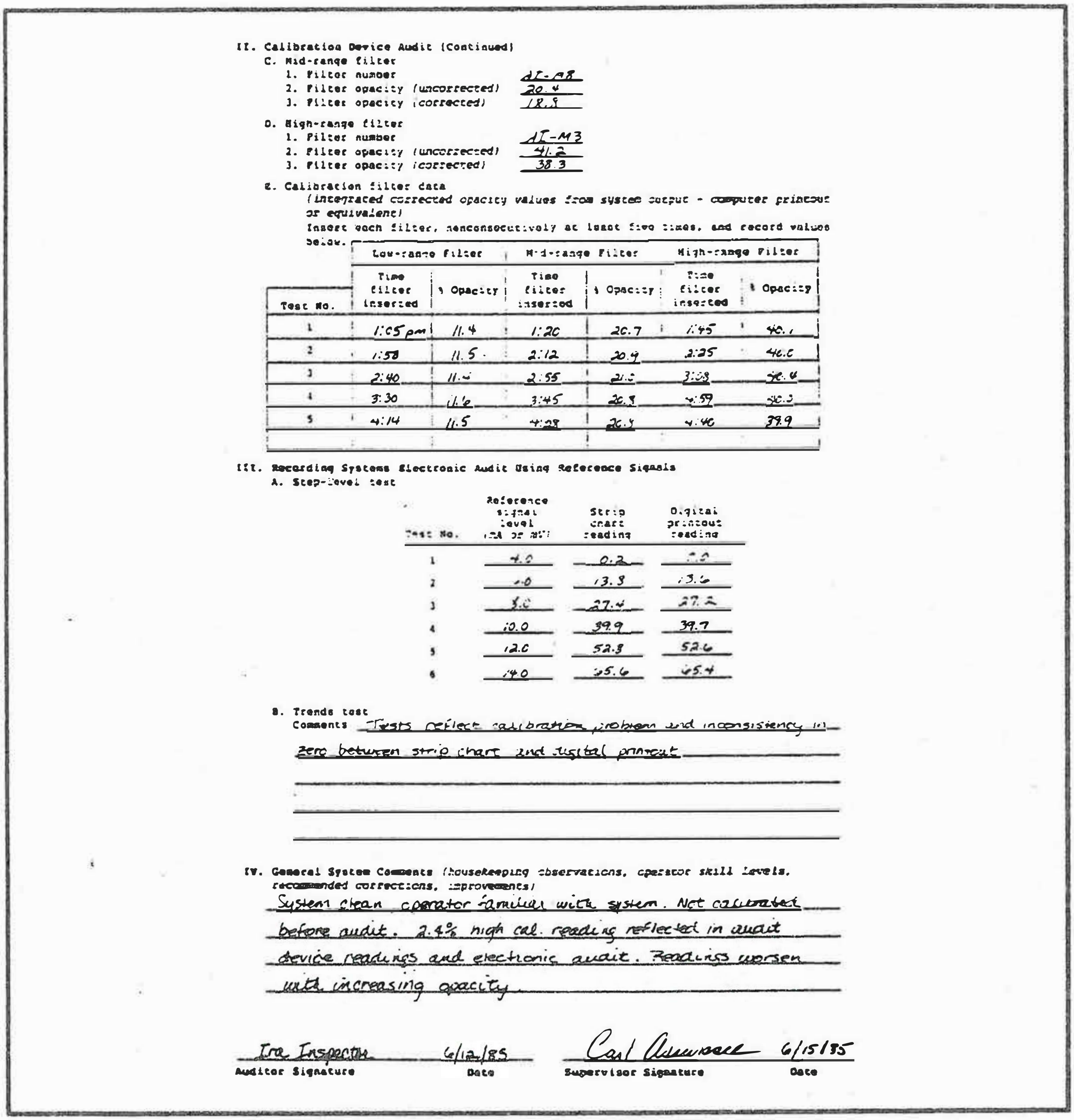
A. Audit device zero

1. Meter 0.0 %Op
2. Strip chart 0.2 %Op
3. Print output 0.0 %Op

B. Low-range filter

1. Filter number 9T-L6
2. Filter opacity *(uncorrected)* 10.2
3. Filter opacity *(corrected)* 9.3

Figure 9.9. Example format for transmissometer performance audit data sheet.



II. Calibration Device Audit (Continued)

C. Mid-range filter

1. Filter number AI-M8
2. Filter opacity (uncorrected) 20.4
3. Filter opacity (corrected) 18.9

D. High-range filter

1. Filter number AI-M3
2. Filter opacity (uncorrected) 41.2
3. Filter opacity (corrected) 38.3

E. Calibration filter data
(Integrated corrected opacity values from system output - computer printout or equivalent)
Insert each filter, nonconsecutively at least five times, and record values below.

Test No.	Low-range Filter		Mid-range Filter		High-range Filter	
	Time filter inserted	% Opacity	Time filter inserted	% Opacity	Time filter inserted	% Opacity
1	1:05 pm	11.4	1:20	20.7	1:45	40.1
2	1:58	11.5	2:12	20.9	2:25	40.0
3	2:40	11.4	2:55	21.0	3:08	40.4
4	3:30	11.6	3:45	20.8	4:59	40.3
5	4:14	11.5	4:28	20.9	4:40	39.9

III. Recording Systems Electronic Audit Using Reference Signals

A. Step-level test

Test No.	Reference signal level (mA or mV)	Strip chart reading	Digital printout reading
1	4.0	0.2	0.0
2	6.0	13.8	13.6
3	8.0	27.4	27.2
4	10.0	39.9	39.7
5	12.0	52.8	52.6
6	14.0	65.6	65.4

B. Trends test

Comments Tests reflect calibration problem and inconsistency in zero between strip chart and digital printout

IV. General System Comments (housekeeping observations, operator skill levels, recommended corrections, improvements)

System clean operator familiar with system. Not calibrated before audit. 2.4% high cal. reading reflected in audit device readings and electronic audit. Readings worsen with increasing opacity.

Ira Inspector 6/12/85
Auditor Signature Date

Carl Assurance 6/15/85
Supervisor Signature Date

Figure 9.9. (continued).

Sufficient data should be taken to calculate mean errors, confidence intervals, and the like. Detailed methods for these calculations have been documented.[2]

9.3.2.4 Corrective Maintenance (Problems and Troubleshooting). Even in the best of systems, problems will eventually develop. Quality control technique and quality assurance programs can help to minimize problems, but they cannot eliminate them. Table 9.5 lists some common and uncommon problems associated with transmissometer systems. Faults and component failures are generally immediately obvious. Some problems can be so subtle that they will be detected only during a period of corrective maintenance or during a performance audit. But then again, some otherwise obvious problems are not recognized for long periods of time and are discovered only during the independent performance audit.

Problems that are site-specific or instrument-specific may develop at an installation. The problem and the corrective action taken should be described in the logbook. If a recurring problem is preventable, the method used to prevent it or the means of corrective action should be incorporated into the preventive maintenance schedule.

Troubleshooting is an acquired skill. A good instrument technician can piece together a number of clues and rapidly identify a problem. If the monitoring system is new and unfamiliar, it may take longer, but the time required should decrease as experience is gained.

One of the most useful troubleshooting tools for transmissometers is the strip chart recorder. A common tendency is to eliminate the strip chart recorder with the rationalization that a computer can be programmed to identify system faults. This can be done, but computers and programming have their own faults. In any case, a recorder provides a good backup to any data handling system, since it is easier to detect trends from the analog output. At a glance, noise levels and system performance can generally be evaluated. The strip chart record can indicate a number of the problems that have been identified in Table 9.5. Figure 9.10 illustrates the type of strip chart traces that might be observed.[7]

The problems that can be detected vary from environmental ones, such as temperature effects and vibration, to instrumentation problems, such as sticking zero mirrors.

Figure 9.10 presents only a few examples of clues that can help the instrument serviceman. Microprocessors incorporated in modern

TABLE 9.5. Opacity Monitoring System Problems

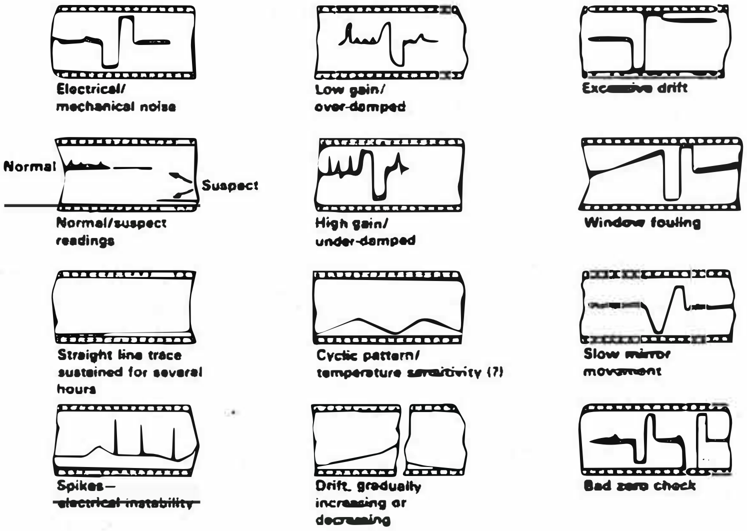
Problem	Corrective Action
Part 1. Common Operator Problems	
Rezeroing and calibrating without cleaning windows.	Clean windows first.
Excessive zeroing and calibrating (attempts to adjust random noise).	Set statistical criteria for making adjustments.
Wrong stack-exit correlation value set in instrument.	Correct calculation. Flange-to-flange distance often mistakenly used rather than inside stack diameter.
Alarm goes off when system goes through span check.	Reprogram system. A common programming error - although this is sometimes done intentionally to check the alarm system.
Lack of correspondence between (1) meter opacity and optical density readings; (2) meter scales; or (3) meter, strip chart, and digital printout values.	Recalibrate system. Most systems can be adjusted to produce consistent readings. It may take some work, but a good operator will see that it is done.
Failure to clean windows when fault light indicates cleaning required. Failure to clean retroreflector window.	Clean windows.
Improper use or no use of combiner equations for multiple monitor system.	Correct calculations.
Part 2. Physical Problems	
Blower motor bearings freeze-bearing noise.	Replace bearings - develop better preventive maintenance program.
Excessive dirt buildup on windows.	Clean filters.
Cyclic drift in signal unrelated to plant performance - due to ambient temperature changes.	Insulate protective hood or install temperature conditioning system about monitor.
Monitor reads 100% opacity for long period of time; protective shutter in place.	Reset shutter or troubleshoot purge air supply (once activated and in place, some shutters have to be manually reset).

(continued)

TABLE 9.5. (Continued)

Problem	Corrective Action
Part 2. Physical Problems (Continued)	
Excessive duct or stack vibration causing misalignment and electrical noise.	A definite problem. One solution is to mount transceiver and retroreflector assemblies independently from this stack or duct. Make connections between duct and monitor using a flexible bellows. Another is to move the monitor to a less vibration-prone location.
Improper alignment.	Realign, check, and tighten system.
Part 3. Electrical Problems	
Ground loops and noise.	Trace and rewire.
Large voltage drops when plant equipment is started; spikes in strip chart record.	Install transient suppressor, dedicated power transformer for monitoring system.
Static electrical charges.	Connect transmissometer case to dedicated earth ground.
Lightning strikes burning electronic circuits.	Add phenolic gaskets between metal stack and transmissometer. Add surge arrestors to junction at junction box.
System stuck in simulated zero or span calibration mode.	Check solenoids and motors in transceiver clean or replace.
Lamp out, erratic lamp output (a fault light should indicate this problem).	Check modulator and motor; adjust or replace motor if necessary. Check lamp and replace; when replacing, keep glass surfaces of lamp clean; avoid fingerprints and clean with lens solution before turning on.
No output from instrument, no calibration cycle, etc.	Check fuses (hope that it is this simple).
Improper instrument responses - faulty calibrations, improper or no outputs.	Check electronics. Check to see that cards and components are secure. Use troubleshooting guide supplied by vendor to check electronic test points. Replace appropriate components or replace cards.

instrument systems are today being programmed to directly alert the operator about such problems. However, a computerized system can be programmed to identify only a set number of malfunctions. If problems occur that are not identified by such a system, a strip chart recorder can be a valuable tool in uncovering them.



Source: Larkin, R., 1977, Ref. 7.

Figure 9.10. Possible strip chart traces indicating problems.

9.4 References

1. Code of Federal Regulations. Title 40 Protection of the Environment. Part 60 Appendix B. 40 CFR 60 App. B, 1985.

2. Jahnke, J.A. and Aldina, G.J. Continuous Air Pollution Source Monitoring Systems. EPA 625/6-79-005, June 1979.

3. Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol Number 1). June 1978, Section 3.0.4 of the Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods. EPA-600/4-77-027b. August 1977. U.S. Environmental Protection Agency, Office of Research and Development Publications, 26 West St. Clair Street, Cincinnati, OH 45268.

4. Code of Federal Regulations. Title 40 Protection of the Environment. Part 60.13, Monitoring Requirements. 40 CFR 60.13, 1985.

5. Standards of Performance for New Stationary Sources: 40 CFR 60, Appendix F - Quality Assurance Procedures, Procedure 1 - Quality Assurance Requirements for Gaseous Continuous Emission Monitoring Systems Used for Compliance Determination.

6. Purcell, R.Y. and Rosenquest, J.M. Field Performance Audit Procedures for Opacity Monitors. EPA CEM report series No. 5-271-7/82 (see also, Performance Audit Procedures for Opacity Monitors. EPA 340/1-83-010), 1982.

7. Larkin, R., Jaye, F., and Steiner, J. Resource Manual for Implementing the NSPS Continuous Monitoring Regulations. Manual 4 - Source Operating and Maintenance Procedures for Continuous Monitoring Systems. EPA 340/1-78-005d, 1978.

Additional References

1. Entropy Environmentalists, Inc. Assessment of the Adequacy of the Appendix F Quality Assurance Procedures for Maintaining CEMs Data Accuracy: Status Report #1. EPA 600/4-83-047, 1983.

2. Entropy Environmentalists, Inc. Guidelines for the Observations of Performance Specification Tests of Continuous Emission Monitors. EPA 340/1-83-009, 1983.

3. Jahnke, J.A. APTI Course SI: 476A Transmissometer Systems - Operation and Maintenance. An Advanced Course. EPA 450/2-84-004, September 1984.

4. Logan, J.T. and Rollins, R. Quality Assurance for Compliance Continuous Emission Monitoring Systems: Evaluation of Span Drift for Gas CEMs, Proceedings - APCA/ASQC Specialty Conference: Quality Assurance in Air Pollution Measurements. October 10-14, 1984, Boulder, CO.

5. Osborne, M.C. and Midgett, M.R. Survey of Continuous Source Emission Monitors: Survey No. 1 NO_x and SO_2. EPA 600/4-77-022, 1977.

6. Peeler, J.W. A Compilation of SO_2 and NO_x Continuous Emission Monitor Reliability Information. EPA 340/1-83-012, 1983.

7. Peeler, J.W. Performance Audit Procedures for SO_2, NO_x, CO_2, and O_2 Continuous Emission Monitoring Systems. EPA 340/1-85-015, 1983.

8. Reynolds, W.E. Development and Evaluation of SO_2 CEM QA Procedures. Proceedings - APCA/ASQC Specialty Conference: Quality Assurance in Air Pollution Measurements. October 10-14, 1984, Boulder, CO.

9. Wayne, A. Opacity Monitoring Quality Assurance Programs in U.S. EPA Region VIII. Proceedings-APCA/ASQC Specialty Conference: Quality Assurance in Air Pollution Measurement. October 10-14, 1984, Boulder, CO.

10.0 GUIDELINE FOR DEVELOPING QUALITY CONTROL PROCEDURES FOR GASEOUS CONTINUOUS EMISSION MONITORING SYSTEMS

10.1 Introduction

This guideline describes the minimum content for a quality control plan to satisfy the requirements of Section 3 of Appendix F, Procedure 1 to 40 CFR Part 60. Source owners or operators may wish to add other items to assure the generation and reporting of valid data from their continuous emission monitoring systems (CEMS's).

Appendix F, Procedure 1 requires written procedures for each of the following activities:

1. Calibration of the CEMS.
2. Calibration drift determination and adjustment of the CEMS.
3. Preventive maintenance of the CEMS (including maintaining a spare parts inventory).
4. Data recording, calculations, and reporting for emissions and QA data.
5. Accuracy audit procedures including sampling and analysis methods.
6. Program of corrective action for the malfunctioning CEMS.

Figure 1 is a flow chart showing the requirements in Appendix F, Procedure 1 for quality assurance and in Part 60.13 for monitoring requirements. This flow chart is included to show how these requirements for CEMS's interact.

10.2 Calibration of the CEMS

Calibration refers to the adjustment of the CEMS response relative to specified standards such as gas cells or calibration gases, or relative to independent effluent measurements. Appendix F, Procedure 1 requires that sources have written procedures for CEMS calibration. Sources may develop their own written procedures; alternatively, they may specify applicable sections of the instrument manual as their written procedures.

There are no currently promulgated regulations that require either specific calibration frequencies or specific criteria for initiating calibration procedures. Sources may therefore choose their own frequency or criteria for calibration based on operating experience or manufacturer's recommendations.

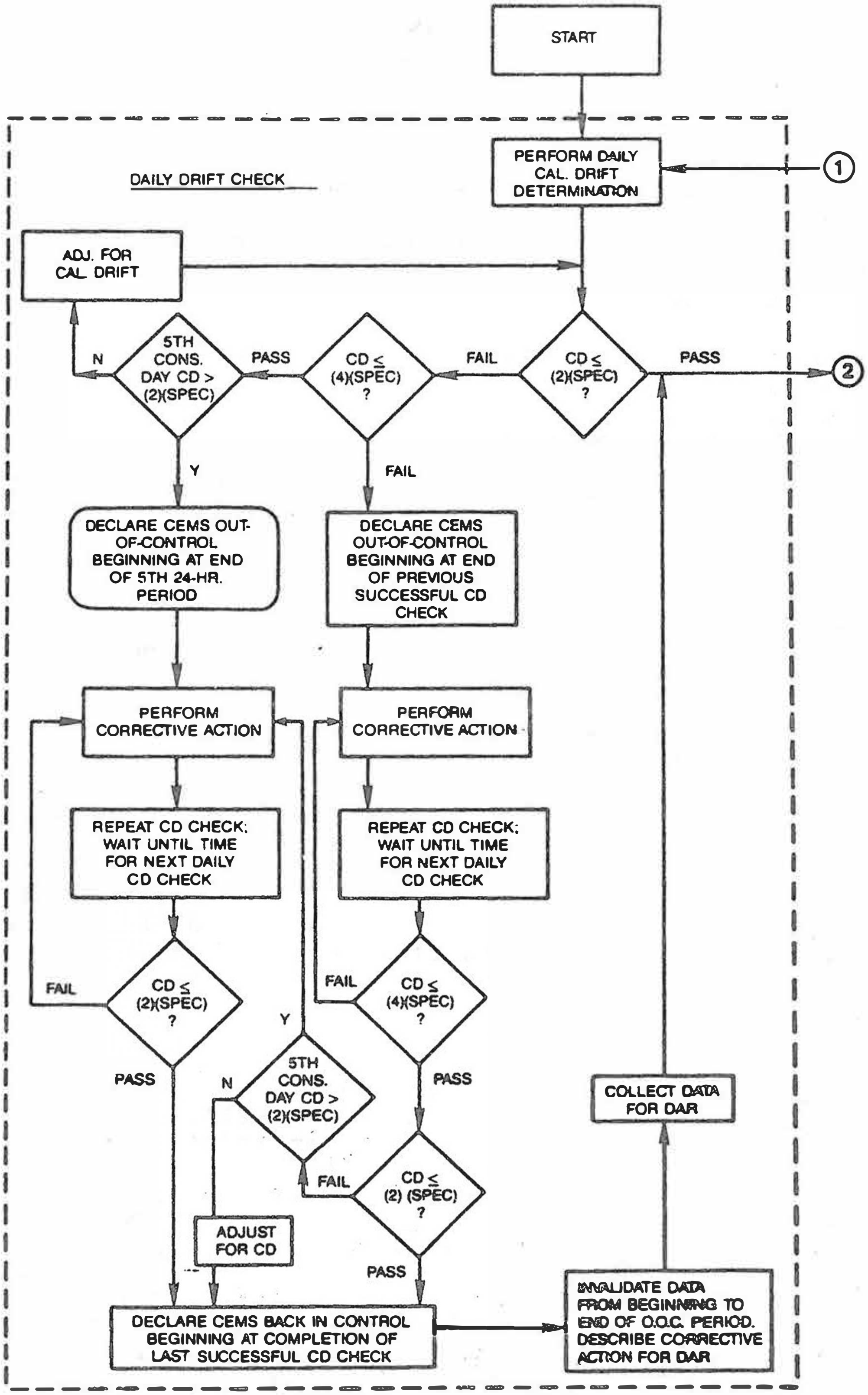
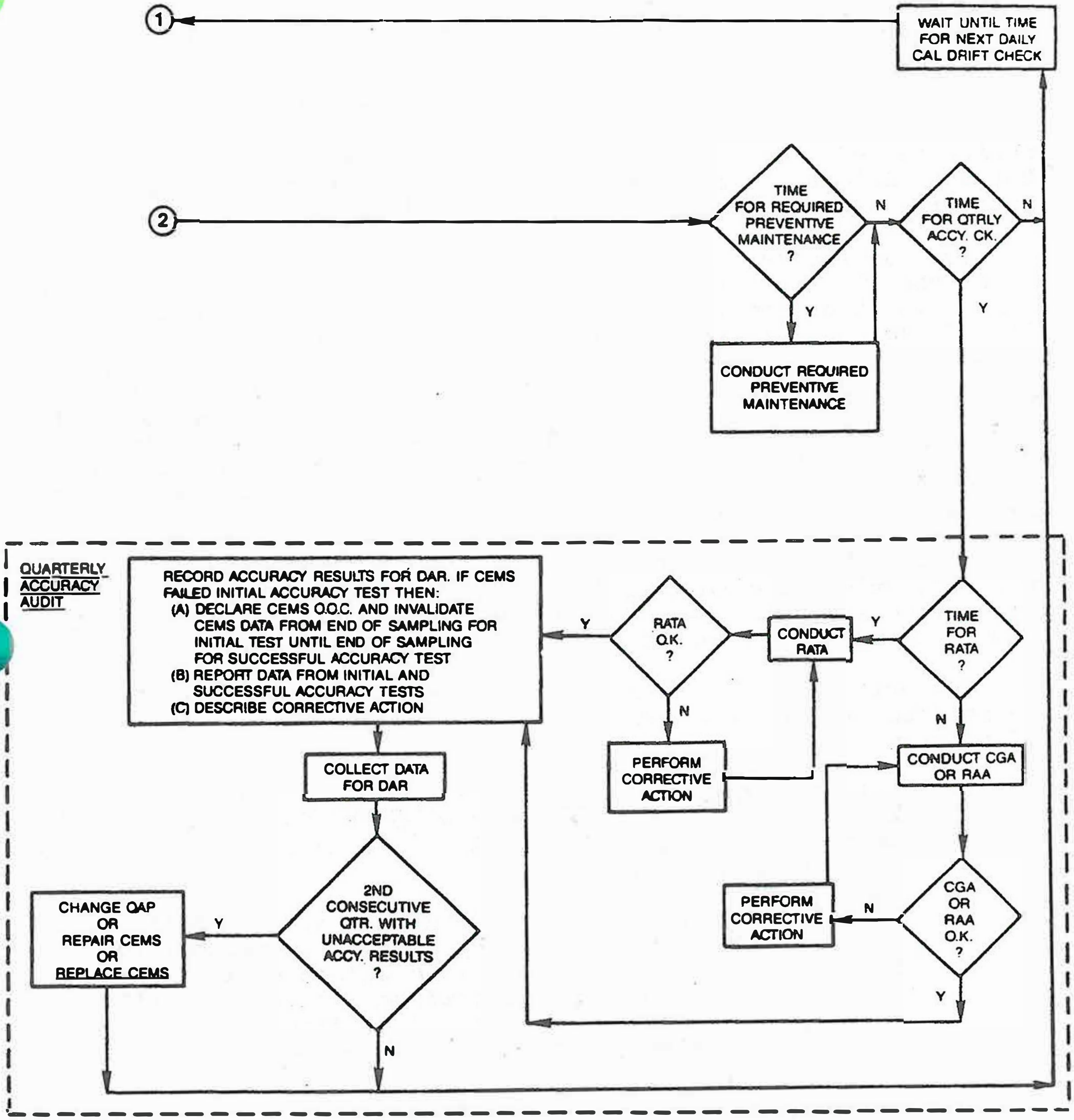


Figure 1. Flow Chart for Required QC Procedures.

(148)



CODE:

≤	= "EQUAL TO OR LESS THAN"	N	= NO
>	= "GREATER THAN"	O.O.C.	= OUT-OF-CONTROL
CD	= CALIBRATION DRIFT	QCP	= QUALITY CONTROL PROCEDURES
CONS	= CONSECUTIVE	SPEC	= DRIFT LIMITS IN PERFORMANCE SPECIFICATIONS 2 OR 3
DAR	= DATA ASSESSMENT REPORT	Y	= YES

Figure 1. (continued)

For calibrations based on external gas cells, sufficient time should be allowed for the cell and/or analyzer cabinet to reach normal operating temperature; accordingly, it is recommended that procedures be incorporated into the QC program that ensure sufficient time for the monitor response to stabilize before it is compared to the cell's named value. Some in-situ analyzers partially or totally disable temperature compensation circuitry during cell-type calibrations. In these cases, it is recommended that additional procedures addressing the calibration of this circuitry be incorporated into the QC program.

For analyzers calibrated using calibration gases as the reference, the written procedures should specify (1) at what point in the sampling system the calibration gases are to be introduced and (2) either the specific gas flow rate to be used or how the flow rate is determined. Although current continuous emission monitoring (CEM) regulations do not require establishing the traceability of calibration gases to higher standards, it is strongly recommended that procedures be established and included within the QC program for verifying the concentrations of calibration gases. One acceptable procedure is EPA's traceability protocol 1 (Reference 1).

In cases where a portable CEMS is to be used as the reference for adjusting the installed CEMS, written procedures should specify calibration and operating procedures for the portable CEMS, including the portable CEMS sampling location.

The written calibration procedures for the installed CEMS may be incorporated into one or more of the following sections of a QC program:

1. A Stand-Alone "Calibration" Section of the QC Program. In this case, the frequency of calibration or the criteria for initiating calibration activities should be clearly specified.

2. Preventive Maintenance. Within the section delineating the preventive maintenance procedures, calibration may be specified as a routine maintenance activity to be performed at regular, specified intervals. Alternatively, calibration may be specified on an as-needed basis with stated criteria for the implementation of calibration activities.

3. Corrective Action. Calibration procedures may be included within the section delineating corrective action activities to be performed at the discretion of CEMS repair personnel in response to an out-of-control CEMS.

Regardless of how the calibration procedures are incorporated into the QC program, it is recommended that the individual or group responsible for CEMS calibration be identified within the written QC plan.

10.3 Calibration Drift and Adjustment of the CEMS

Calibration drift (CD) refers to the difference between the CEMS output reading and a reference value after a period of operation during which no unscheduled maintenance, repair, or adjustment took place. Daily zero (or low level) and span drift checks are required by 40 CFR 60.13; these checks are to be used to fulfill the calibration drift check requirement of Appendix F, Procedure 1. Appendix F, Procedure 1 requires written procedures that specify how the zero (or low level) and span calibration drift determinations are to be performed. These procedures must be consistent with the monitor vendor's prescribed method for checking CD.

Table 10.1 presents CD criteria and the corresponding required source responses. Sources may choose to establish more stringent criteria for adjustment of CEMS for zero (or low level) and/or span calibration drift. It is recommended that the CD criteria selected for adjustment of the CEMS be incorporated into the written instructions for the calibration drift check procedures, so that the need for adjustment based on calibration drift may be determined immediately.

Corrections for excessive drift may consist of any adjustments or activities that the operator or technician deems necessary to correct for the observed drift. These activities typically consist of routine checks and adjustments of calibration gas flow rates and pressures, verification of proper sample cell temperatures, verification of the status of monitor specific auxiliary monitoring parameters, and adjustment of zero and/or span potentiometers. Written procedures should be available for performing these routine activities and should include criteria for determining that adjustments have been successful.

10.4 Preventive Maintenance of the CEMS

Preventive maintenance is comprised of activities designed to detect and prevent the development of monitoring problems. These activities typically include both routine maintenance procedures and maintenance, repairs, or adjustments performed on an as-needed basis. An example of as-needed preventive maintenance would be the repairing of the protective covering of an extractive sample line following damage resulting from an accident during the construction activities. If the sample line itself were not damaged, the repair would be considered preventive maintenance and would not consititute corrective action for a malfunctioning CEMS. The importance of this type of

TABLE 10.1. CEMS CALIBRATION DRIFT CRITERIA

Parameter	Criterion*	Action Required
Zero (or low) level calibration drift	CD > 2 x (Spec)**	Adjust CEMS for calibration drift
	CD > 2 x (Spec) for 5 consecutive 24-hour periods	CEMS out-of-control period begins at end of 5th day the CD exceeds 2 x (Spec); perform corrective action and repeat CD check
	CD > 4 x (Spec)	CEMS out-of-control period begins at the time corresponding to the completion of the last acceptable CD check preceding the CD check which exceeds 4 x (Spec); perform corrective action and repeat the CD check
Span calibration drift	CD > 2 x (Spec)**	Adjust CEMS for calibration drift
	CD > 2 x (Spec) for 5 consecutive 24-hour periods	CEMS out-of-control period begins at end of 5th day the CD exceeds 2 x (Spec); perform corrective action and repeat CD check
	CD > 4 x (Spec)	CEMS out-of-control period begins at the time corresponding to the completion of the last successful CD check preceding the CD check that exceeds 4 x (Spec); perform corrective action and repeat the CD check

---

*Spec refers to the applicable performance specification in Appendix B.

**This is the minimum criterion for adjustment of the CEMS. More stringent criteria, which may be preferred by many sources, are also acceptable.

maintenance is recognized; however, it is neither practical nor necessary to develop written procedures for such needed activities.

Written procedures must be available for <u>routine</u> maintenance activities. These procedures should specify what procedures are to be conducted and the frequency with which the various activities are to be performed. The QC program should specify the individual or office responsible for ensuring that the preventive maintenance procedures are conducted at the appropriate frequencies and the individual or group who will perform the actual routine maintenance procedures.

The applicable regulations do not specify the minimum level of routine preventive maintenance. It is suggested that, at a minimum, the initial procedures should incorporate the vendor's recommendations regarding preventive maintenance activities and frequencies. These procedures may later be adjusted to reflect actual operating experience with individual CEMS installations.

A list of spare parts for the CEMS must be included in the written QC plan. At a minimum, those spare parts recommended by the monitor vendor should be available. The QC program should specify the individual or office who is responsible for maintaining the listed spare parts inventory.

10.5 Data Records, Calculations, and Reporting for the CEMS

The QA/QC program must address recordkeeping, calculations, and reporting of emissions and quality assurance data. The requirements for these activities are contained in the subparts of 40 CFR 60 that specify the use of CEM. A Data Assessment Report (DAR) must be provided with emissions reports required by the applicable subpart of 40 CFR 60. The DAR must contain, at a minimum:

1. The name and address of the source owner or operator.
2. Identification and location of each monitor in the CEMS.
3. The manufacturer and model number of each monitor in the CEMS.
4. Quarterly accuracy results, including dates, CEMS responses, and either reference method results or certified gas values; if either a RATA or a RAA was performed, the results from the EPA performance audit sample analysis must also be included.
5. A summary of corrective actions taken when the monitor was determined to be out-of-control.

For emissions data, a list or diagram should be provided indicating the offices or individuals responsible for (1) retrieving the data from the CEMS, (2) calculating emissions rates from the CEMS data, (3) compiling emissions reports, and (4) reviewing and/or approving emissions reports. Formulas and example calculations should be provided for emission rate calculations. Similar information should be provided for emissions data from alternative monitoring methods that may be necessary during CEMS out-of-control periods.

A list or diagram should also be provided indicating the offices or individuals responsible for (1) collecting quality assurance (QA) data, (2) performing applicable calculations of QA/QC results, (3) recording the QA/QC results in appropriate logs (as applicable), (4) preparing the DAR, and (5) approving and/or reviewing the DAR. Formulas and example calculations should be provided for all required QA data calculations.

10.6 Accuracy Audit Procedures Including Sampling and Analysis Methods

Appendix F, Procedure 1 requires that each CEMS be audited at least once each calendar quarter. Three audit techniques are acceptable:

1. Relative accuracy test audits (RATA's);
2. Cylinder Gas Audits (CGA's); and
3. Relative accuracy audits (RAA's).

In addition, other alternative audit procedures may be used as approved by the Administrator.

If the CEMS does not demonstrate acceptable accuracy during the quarterly audit, then corrective actions must be initiated, and the CEMS must be declared out-of-control from the time corresponding to the completion of the sampling for the unsuccessful audit until the completion of the sampling for a successful follow-up audit. If the CEMS demonstrates unacceptable accuracy for two consecutive quarters, then the QA program must be revised, or the CEMS must be modified or replaced.

Table 10.2 presents the specific requirements and the corresponding CEMS performance criteria for each of the three acceptable audit techniques.

The QC program must include written sampling and analysis procedures to be used during the required quarterly accuracy audits. At a minimum, these procedures must describe the methods to be used to conduct a RATA. Applicable sections of Appendix A (Reference Methods) and Appendix B (Performance Specifications

TABLE 10.2. REQUIREMENTS AND CRITERIA FOR APPENDIX F, PROCEDURE 1 AUDIT TECHNIQUES

Technique	Requirements	Performance Criteria
RATA	Conduct as per applicable performance specification (PS) in Appendix B (e.g., PS 2 for SO_2 and NO_x) Analyze appropriate performance audit samples from EPA	RA must not exceed 20% or 10% of applicable standard, whichever is greater For SO_2 standards from 0.20 to 0.30 lb/10^6 Btu, RA must not exceed 15% of the standard For SO_2 standards below 0.20 lb/10^6 Btu, RA must not exceed 20% of the standard
RAA	Conduct as per applicable PS in Appendix B <u>except</u> only 3 runs are required Use relative difference between the mean reference method values and the mean of the CEMS responses to assess the accuracy of the CEMS data	Inaccuracy must not exceed ± 15% or 7.5% of the applicable standard, whichever is greater
CGA	Challenge both pollutant and diluent channels (if applicable) of CEMS three times at the two points specified in Procedure 1 Use gases that have been certified by comparison to NBS SRM's or NBS/EPA approved gas manufacturer's CRM's Operate analyzer in normal sampling mode Use average difference between actual gas value and concentration indicated by CEMS to access accuracy	Inaccuracy must not exceed ± 15%

may be cited where possible to describe audit procedures. The written procedures should specify individuals or groups responsible for audit program oversight, sampling, analysis, and accuracy assessment calculations. If the source chooses to conduct RAA's and/or CGA's during quarters when RATA's are not required, the QC plan should include written procedures for these audit techniques. Again, applicable sections of Appendix A, Appendix B, and/or instrument operation manuals may be cited where possible.

Sources may choose to have an outside contractor perform some or all of the accuracy audit activities. Since contractor selection may be subject to competitive bidding, the QC program need not specify a particular contractor. However, the specific activities for which the contractor will be responsible should be listed.

10.7 Program of Corrective Action for the Malfunctioning CEMS

Appendix F, Procedure 1 specifies that corrective action must be performed when a CEMS is out-of-control. Appropriate corrective action will depend on the nature of the CEMS malfunction. At a minimum, written procedures must be available, to be applied as necessary, for instrument start-up and trouble shooting. Appropriate sections of instrument operation and/or repair manuals may be referenced to fulfill this requirement. Where possible, it is recommended that additional quality assessment procedures be provided to verify proper operation of the CEMS following repair or adjustment.

A list should be provided to indicate what alternative methods are to be used for monitoring emissions during CEMS out-of-control periods in order to fulfill the minimum data availability requirements of the applicable subpart. Written procedures should be available for operation of these alternative methods.

A list or chart should be provided to indicate the offices or individuals (1) to be contacted when a CEMS out-of-control period occurs, (2) to approve the corrective action (if applicable), and (3) to be responsible for determining when alternative monitoring procedures are to be employed. Criteria should be provided for determining when the CEMS is out-of-control. As a minimum, these must include the Appendix F, Procedure 1 criteria for excessive drift and excessive inaccuracy.

10.8 References

1. Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol Number 1). June 1978, Section 3.0.4 of the Quality Assurance Handbook for Air

Pollution Measurement Systems, Volume III, Stationary Source Specific Methods. EPA-600/4-77-027b. August 1977. U. S. Environmental Protection Agency, Office of Research and Development Publications, 26 West St. Clair Street, Cincinnati, Ohio 45268.