

Figure 14-1. Roof Monitor Sampling System.

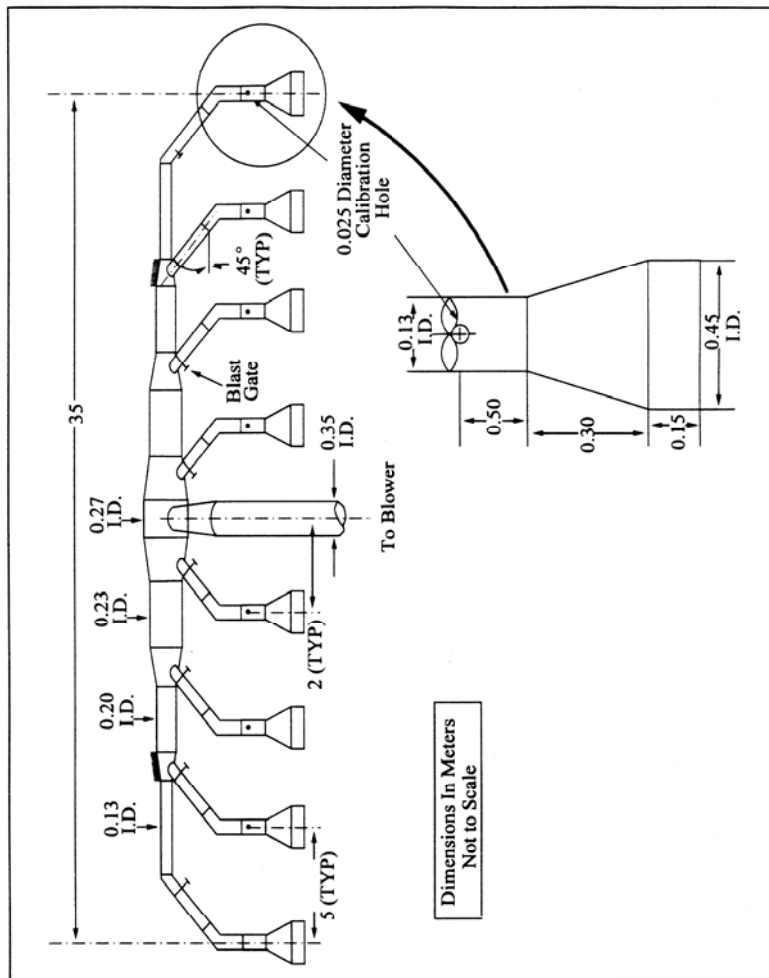


Figure 14-2. Sampling Manifold and Nozzles.

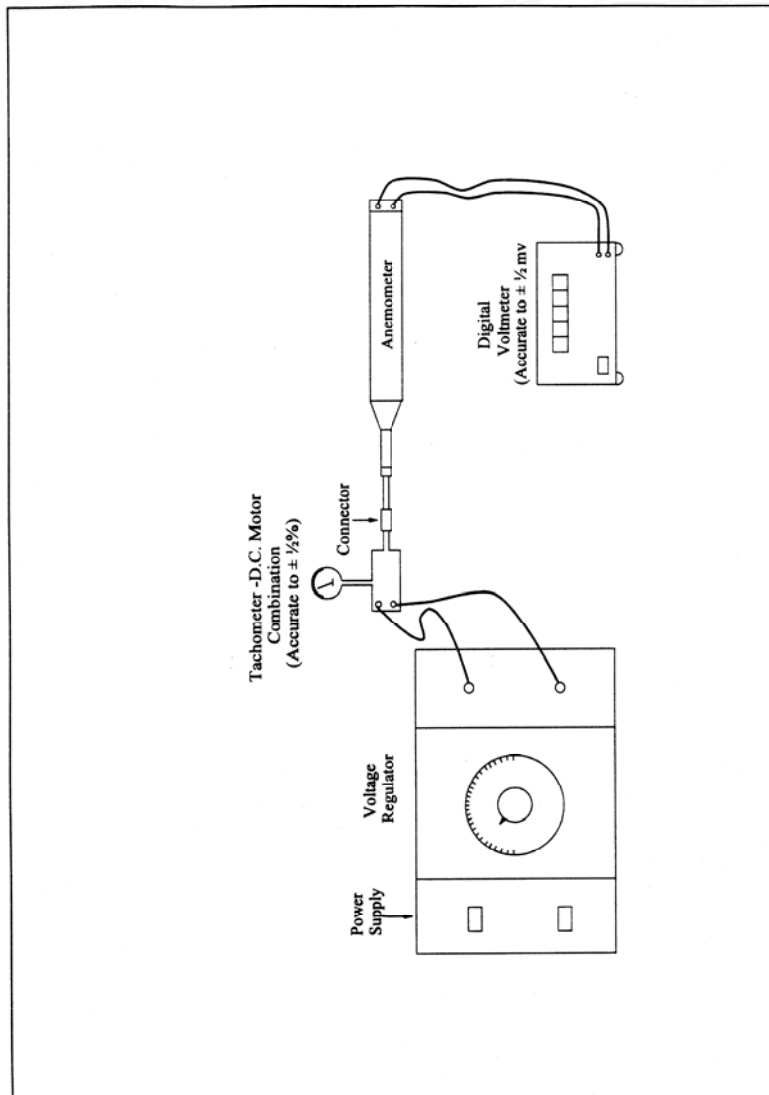


Figure 14-3. Typical RPM Generator.

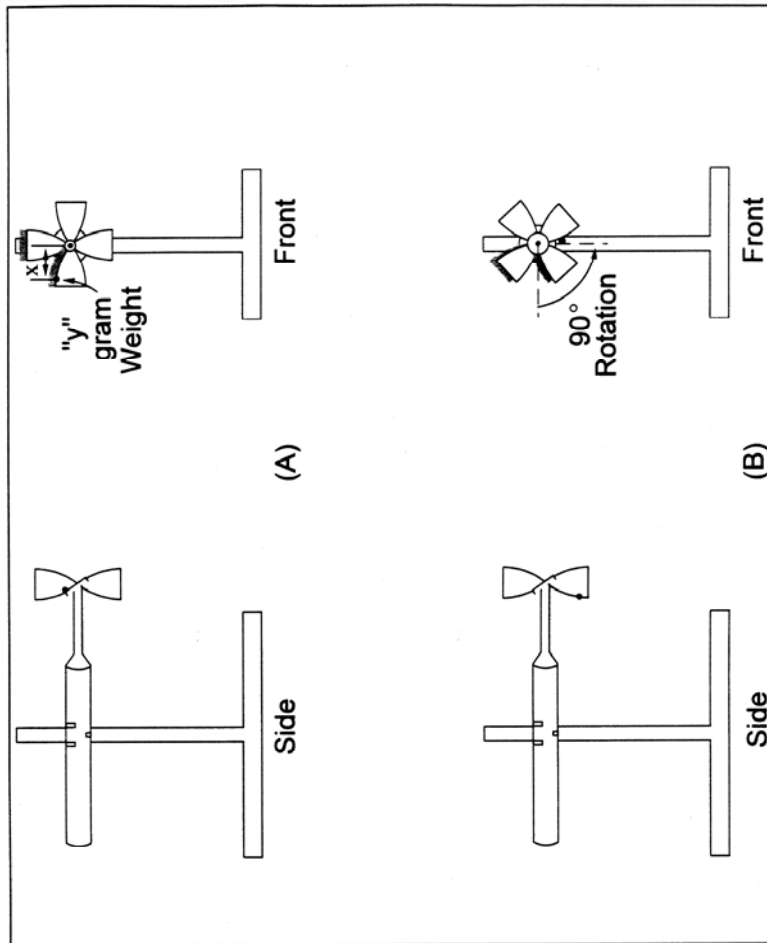


Figure 14-4. Check of Anemometer Starting Torque.

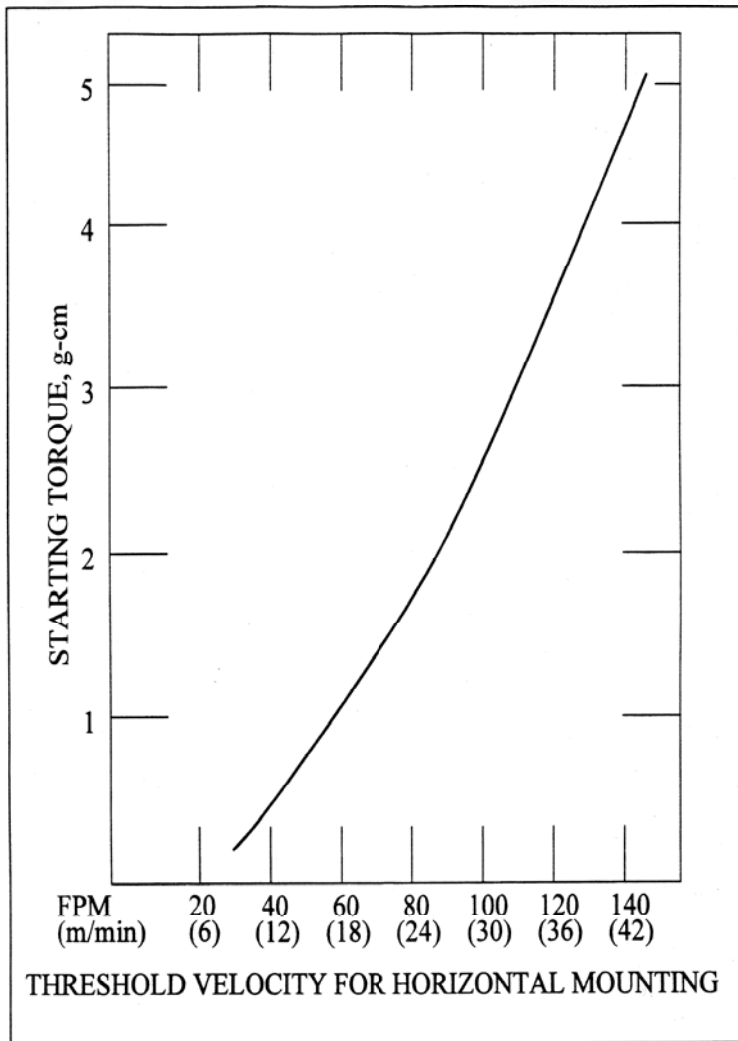


Figure 14-5. Typical Curve of Starting Torque vs. Horizontal Threshold Velocity for Propeller Anemometers.

METHOD 14A—DETERMINATION OF TOTAL FLUORIDE EMISSIONS FROM SELECTED SOURCES AT PRIMARY ALUMINUM PRODUCTION FACILITIES

NOTE: This method does not include all the specifications (e.g., equipment and supplies) and procedures (e.g., sampling) essential to its performance. Some material is incorporated by reference from other methods in

this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 5, Methods 13A and 13B, and Method 14 of this appendix.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total fluorides	None assigned	Not determined.
Includes hydrogen fluoride.	007664-39-3	Not determined.

1.2 **Applicability.** This method is applicable for the determination of total fluorides (TF) emissions from sources specified in the applicable regulation. This method was developed by consensus with the Aluminum Association and the U.S. Environmental Protection Agency (EPA).

2.0 *Summary of Method*

2.1 Total fluorides, in the form of solid and gaseous fluorides, are withdrawn from the ascending air stream inside of an aluminum reduction potroom and, prior to exiting the potroom roof monitor, into a specific cassette arrangement. The cassettes are connected by tubing to flowmeters and a manifold system that allows for the equal distribution of volume pulled through each cassette, and finally to a dry gas meter. The cassettes have a specific internal arrangement of one unaltered cellulose filter and support pad in the first section of the cassette for solid fluoride retention and two cellulose filters with support pads that are impregnated with sodium formate for the chemical absorption of gaseous fluorides in the following two sections of the cassette. A minimum of eight cassettes shall be used for a potline and shall be strategically located at equal intervals across the potroom roof so as to encompass a minimum of 8 percent of the total length of the potroom. A greater number of cassettes may be used should the regulated facility choose to do so. The mass flow rate of pollutants is determined with anemometers and temperature sensing devices located immediately below the opening of the roof monitor and spaced evenly within the cassette group.

3.0 *Definitions*

3.1 **Cassette.** A segmented, styrene acrylonitrile cassette configuration with three separate segments and a base, for the purpose of this method, to capture and retain fluoride from potroom gases.

3.2 **Cassette arrangement.** The cassettes, tubing, manifold system, flowmeters, dry gas meter, and any other related equipment associated with the actual extraction of the sample gas stream.

3.3 **Cassette group.** That section of the potroom roof monitor where a distinct group of cassettes is located.

3.4 **Potline.** A single, discrete group of electrolytic reduction cells electrically connected in series, in which alumina is reduced to form aluminum.

3.5 **Potroom.** A building unit that houses a group of electrolytic reduction cells in which aluminum is produced.

3.6 **Potroom group.** An uncontrolled potroom, a potroom that is controlled indi-

vidually, or a group of potrooms or potroom segments ducted to a common primary control system.

3.7 **Primary control system.** The equipment used to capture the gases and particulate matter generated during the reduction process and the emission control device(s) used to remove pollutants prior to discharge of the cleaned gas to the atmosphere.

3.8 **Roof monitor.** That portion of the roof of a potroom building where gases, not captured at the cell, exit from the potroom.

3.9 **Total fluorides (TF).** Elemental fluorine and all fluoride compounds as measured by Methods 13A or 13B of this appendix or by an approved alternative method.

4.0 *Interferences and Known Limitations*

4.1 There are two principal categories of limitations that must be addressed when using this method. The first category is sampling bias and the second is analytical bias. Biases in sampling can occur when there is an insufficient number of cassettes located along the roof monitor of a potroom or if the distribution of those cassettes is spatially unequal. Known sampling biases also can occur when there are leaks within the cassette arrangement and if anemometers and temperature devices are not providing accurate data. Applicable instruments must be properly calibrated to avoid sampling bias. Analytical biases can occur when instrumentation is not calibrated or fails calibration and the instrument is used out of proper calibration. Additionally, biases can occur in the laboratory if fusion crucibles retain residual fluorides over lengthy periods of use. This condition could result in falsely elevated fluoride values. Maintaining a clean work environment in the laboratory is crucial to producing accurate values.

4.2 Biases during sampling can be avoided by properly spacing the appropriate number of cassettes along the roof monitor, conducting leak checks of the cassette arrangement, calibrating the dry gas meter every 30 days, verifying the accuracy of individual flowmeters (so that there is no more than 5 percent difference in the volume pulled between any two flowmeters), and calibrating or replacing anemometers and temperature sensing devices as necessary to maintain true data generation.

4.3 Analytical biases can be avoided by calibrating instruments according to the manufacturer's specifications prior to conducting any analyses, by performing internal and external audits of up to 10 percent of all samples analyzed, and by rotating individual crucibles as the "blank" crucible to detect any potential residual fluoride carry-over to samples. Should any contamination be discovered in the blank crucible, the crucible shall be thoroughly cleaned to remove any detected residual fluorides and a "blank" analysis conducted again to evaluate the effectiveness of the cleaning. The crucible

shall remain in service as long as no detectable residual fluorides are present.

5.0 Safety

5.1 This method may involve the handling of hazardous materials in the analytical phase. This method does not purport to address all of the potential safety hazards associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.3 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.4 Perchloric Acid (HClO₄). Corrosive to eyes, skin, nose, and throat. Provide ventilation to limit exposure. Very strong oxidizer. Keep separate from water and oxidizable materials to prevent vigorous evolution of heat, spontaneous combustion, or explosion. Heat solutions containing HClO₄ only in hoods specifically designed for HClO₄.

6.0 Equipment and Supplies

6.1 Sampling.

6.1.1 Cassette arrangement. The cassette itself is a three-piece, styrene acrylonitrile cassette unit (a Gelman Sciences product), 37 millimeter (mm), with plastic connectors. In the first section (the intake section), an untreated Gelman Sciences 37 mm, 0.8 micrometer (µm) DM-800 metricel membrane filter and cellulose support pad, or equivalent, is situated. In the second and third segments of the cassette there is placed one each of Gelman Sciences 37 mm, 5 µm GLA-5000 low-ash PVC filter with a cellulose support pad or equivalent product. Each of these two filters and support pads shall have been immersed in a solution of 10 percent sodium formate (volume/volume in an ethyl alcohol solution). The impregnated pads shall be placed in the cassette segments while still wet and heated at 50 °C (122 °F) until the pad is completely dry. It is important to check for a proper fit of the filter and support pad to the cassette segment to ensure that there are no areas where gases could bypass the filter. Once all of the cassette segments have been prepared, the cassette shall be assembled and a plastic plug shall be inserted into the exhaust hole of the cassette. Prior to placing the cassette into service, the space between each segment shall be taped with an appropriately durable tape to prevent the infiltration of gases through the points of con-

nection, and an aluminum nozzle shall be inserted into the intake hole of the cassette. The aluminum nozzle shall have a short section of tubing placed over the opening of the nozzle, with the tubing plugged to prevent dust from entering the nozzle and to prepare the nozzle for the cassette arrangement leak check. An alternate nozzle type can be used if historical results or scientific demonstration of applicability can be shown.

6.1.2 Anemometers and temperature sensing devices. To calculate the mass flow rate of TF from the roof monitor under standard conditions, anemometers that meet the specifications in section 2.1.1 in Method 14 of this appendix or an equivalent device yielding equivalent information shall be used. A recording mechanism capable of accurately recording the exit gas temperature at least every 2 hours shall be used.

6.1.3 Barometer. To correct the volumetric flow from the potline roof monitor to standard conditions, a mercury (Hg), aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm [0.1 inch (in)] Hg shall be used.

NOTE: The barometric reading may be obtained from a nearby National Weather Service Station. In this case, the station value (which is absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and the sampling point shall be made at a rate of minus 2.5 mm (0.1 in) Hg per 30 meters (m) [100 feet (ft)] elevation increase or plus 2.5 mm (0.1 in) Hg per 30 m (100 ft) elevation decrease.

6.2 Sample recovery.

6.2.1 Hot plate.

6.2.2 Muffle furnace.

6.2.3 Nickel crucible.

6.2.4 Stirring rod, Teflon.

6.2.5 Volumetric flask, 50-milliliter (ml).

6.2.6 Plastic vial, 50-ml.

6.3 Analysis.

6.3.1 Primary analytical method. An automated analyzer having the following components or equivalent: a multichannel proportioning pump, multiposition sampler, voltage stabilizer, colorimeter, instrument recording device, microdistillation apparatus, flexible Teflon[®] heating bath, vacuum pump, pulse suppressers and an air flow system.

6.3.2 Secondary analytical method. Specific Ion Electrode (SIE).

7.0 Reagents and Standards

7.1 Water. Deionized distilled to conform to ASTM Specification D 1193-77, Type 3 (incorporated by reference in §60.17(a)(22) of this part). The KMnO₄ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.2 Calcium oxide.

7.3 Sodium hydroxide (NaOH). Pellets.

7.4 Perchloric acid (HClO_4). Mix 1:1 with water. Sulfuric acid (H_2SO_4) may be used in place of HClO_4 .

7.5 Audit samples. The audit samples discussed in section 9.1 shall be prepared from reagent grade, water soluble stock reagents, or purchased as an aqueous solution from a commercial supplier. If the audit stock solution is purchased from a commercial supplier, the standard solution must be accompanied by a certificate of analysis or an equivalent proof of fluoride concentration.

8.0 Sample Collection and Analysis

8.1 Preparing cassette arrangement for sampling. The cassettes are initially connected to flexible tubing. The tubing is connected to flowmeters and a manifold system. The manifold system is connected to a dry gas meter (Research Appliance Company model 201009 or equivalent). The length of tubing is managed by pneumatically or electrically operated hoists located in the roof monitor, and the travel of the tubing is controlled by encasing the tubing in aluminum conduit. The tubing is lowered for cassette insertion by operating a control box at floor level. Once the cassette has been securely inserted into the tubing and the leak check performed, the tubing and cassette are raised to the roof monitor level using the floor level control box. Arrangements similar to the one described are acceptable if the scientific sample collection principles are followed.

8.2 Test run sampling period. A test run shall comprise a minimum of a 24-hour sampling event encompassing at least eight cassettes per potline (or four cassettes per potroom group). Monthly compliance shall be based on three test runs during the month. Test runs of greater than 24 hours are allowed; however, three such runs shall be conducted during the month.

8.3 Leak-check procedures.

8.3.1 Pretest leak check. A pretest leak-check is recommended; however, it is not required. To perform a pretest leak-check after the cassettes have been inserted into the tubing, isolate the cassette to be leak-checked by turning the valves on the manifold to stop all flows to the other sampling points connected to the manifold and meter. The cassette, with the plugged tubing section securing the intake of the nozzle, is subjected to the highest vacuum expected during the run. If no leaks are detected, the tubing plug can be briefly removed as the dry gas meter is rapidly turned off.

8.3.2 Post-test leak check. A leak check is required at the conclusion of each test run for each cassette. The leak check shall be performed in accordance with the procedure outlined in section 8.3.1 of this method except that it shall be performed at a vacuum greater than the maximum vacuum reached during the test run. If the leakage rate is found to be no greater than 4 percent of the

average sampling rate, the results are acceptable. If the leakage rate is greater than 4 percent of the average sampling rate, either record the leakage rate and correct the sampling volume as discussed in section 12.4 of this method or void the test run if the minimum number of cassettes were used. If the number of cassettes used was greater than the minimum required, discard the leaking cassette and use the remaining cassettes for the emission determination.

8.3.3 Anemometers and temperature sensing device placement. Install the recording mechanism to record the exit gas temperature. Anemometers shall be installed as required in section 6.1.2 of Method 14 of this appendix, except replace the word "manifold" with "cassette group" in section 6.1.2.3. These two different instruments shall be located near each other along the roof monitor. See conceptual configurations in Figures 14A-1, 14A-2, and 14A-3 of this method. Fewer temperature devices than anemometers may be used if at least one temperature device is located within the span of the cassette group. Other anemometer location siting scenarios may be acceptable as long as the exit velocity of the roof monitor gases is representative of the entire section of the potline being sampled.

8.4 Sampling. The actual sample run shall begin with the removal of the tubing and plug from the cassette nozzle. Each cassette is then raised to the roof monitor area, the dry gas meter is turned on, and the flowmeters are set to the calibration point, which allows an equal volume of sampled gas to enter each cassette. The dry gas meter shall be set to a range suitable for the specific potroom type being sampled that will yield valid data known from previous experience or a range determined by the use of the calculation in section 12 of this method. Parameters related to the test run that shall be recorded, either during the test run or after the test run if recording devices are used, include: anemometer data, roof monitor exit gas temperature, dry gas meter temperature, dry gas meter volume, and barometric pressure. At the conclusion of the test run, the cassettes shall be lowered, the dry gas meter turned off, and the volume registered on the dry gas meter recorded. The post-test leak check procedures described in section 8.3.2 of this method shall be performed. All data relevant to the test shall be recorded on a field data sheet and maintained on file.

8.5 Sample recovery.

8.5.1 The cassettes shall be brought to the laboratory with the intake nozzle contents protected with the section of plugged tubing previously described. The exterior of cassettes shall carefully be wiped free of any dust or debris, making sure that any falling dust or debris does not present a potential laboratory contamination problem.

8.5.2 Carefully remove all tape from the cassettes and remove the initial filter, support pad, and all loose solids from the first (intake) section of the cassette. Fold the filter and support pad several times and, along with all loose solids removed from the interior of the first section of the cassette, place them into a nickel crucible. Using water, wash the interior of the nozzle into the same nickel crucible. Add 0.1 gram (g) [± 0.1 milligram (mg)] of calcium oxide and a sufficient amount of water to make a loose slurry. Mix the contents of the crucible thoroughly with a Teflon[®] stirring rod. After rinsing any adhering residue from the stirring rod back into the crucible, place the crucible on a hot plate or in a muffle furnace until all liquid is evaporated and allow the mixture to gradually char for 1 hour.

8.5.3 Transfer the crucible to a cold muffle furnace and ash at 600 °C (1,112 °F). Remove the crucible after the ashing phase and, after the crucible cools, add 3.0 g (± 0.1 g) of NaOH pellets. Place this mixture in a muffle furnace at 600 °C (1,112 °F) for 3 minutes. Remove the crucible and roll the melt so as to reach all of the ash with the molten NaOH. Let the melt cool to room temperature. Add 10 to 15 ml of water to the crucible and place it on a hot plate at a low temperature setting until the melt is soft or suspended. Transfer the contents of the crucible to a 50-ml volumetric flask. Rinse the crucible with 20 ml of 1:1 perchloric acid or 20 ml of 1:1 sulfuric acid in two (2) 10 ml portions. Pour the acid rinse slowly into the volumetric flask and swirl the flask after each addition. Cool to room temperature. The product of this procedure is particulate fluorides.

8.5.4 Gaseous fluorides can be isolated for analysis by folding the gaseous fluoride filters and support pads to approximately $\frac{1}{4}$ of their original size and placing them in a 50-ml plastic vial. To the vial add exactly 10 ml of water and leach the sample for a minimum of 1 hour. The leachate from this process yields the gaseous fluorides for analysis.

9.0 Quality Control

9.1 Laboratory auditing. Laboratory audits of specific and known concentrations of fluoride shall be submitted to the laboratory with each group of samples submitted for analysis. An auditor shall prepare and present the audit samples as a "blind" evaluation of laboratory performance with each group of samples submitted to the laboratory. The audits shall be prepared to represent concentrations of fluoride that could be expected to be in the low, medium and high range of actual results. Average recoveries of all three audits must equal 90 to 110 percent for acceptable results; otherwise, the laboratory must investigate procedures and instruments for potential problems.

NOTE: The analytical procedure allows for the analysis of individual or combined filters and pads from the cassettes provided that

equal volumes (± 10 percent) are sampled through each cassette.

10.0 Calibrations

10.1 Equipment evaluations. To ensure the integrity of this method, periodic calibrations and equipment replacements are necessary.

10.1.1 Metering system. At 30-day intervals the metering system shall be calibrated. Connect the metering system inlet to the outlet of a wet test meter that is accurate to 1 percent. Refer to Figure 5-4 of Method 5 of this appendix. The wet-test meter shall have a capacity of 30 liters/revolution [1 cubic foot (ft³)/revolution]. A spirometer of 400 liters (14 ft³) or more capacity, or equivalent, may be used for calibration; however, a wet-test meter is usually more practical. The wet-test meter shall be periodically tested with a spirometer or a liquid displacement meter to ensure the accuracy. Spirometers or wet-test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. Run the metering system pump for about 15 min. with the orifice manometer indicating a median reading as expected in field use to allow the pump to warm up and to thoroughly wet the interior of the wet-test meter. Then, at each of a minimum of three orifice manometer settings, pass an exact quantity of gas through the wet-test meter and record the volume indicated by the dry gas meter. Also record the barometric pressure, the temperatures of the wet test meter, the inlet temperatures of the dry gas meter, and the temperatures of the outlet of the dry gas meter. Record all calibration data on a form similar to the one shown in Figure 5-5 of Method 5 of this appendix and calculate Y, the dry gas meter calibration factor, and $\Delta H@$, the orifice calibration factor at each orifice setting. Allowable tolerances for Y and $\Delta H@$ are given in Figure 5-6 of Method 5 of this appendix. Allowable tolerances for Y and $\Delta H@$ are given in Figure 5-5 of Method 5 of this appendix.

10.1.2 Estimating volumes for initial test runs. For a facility's initial test runs, the regulated facility must have a target or desired volume of gases to be sampled and a target range of volumes to use during the calibration of the dry gas meter. Use Equations 14A-1 and 14A-2 in section 12 of this method to derive the target dry gas meter volume (F_v) for these purposes.

10.1.3 Calibration of anemometers and temperature sensing devices. If the standard anemometers in Method 14 of this appendix are used, the calibration and integrity evaluations in sections 10.3.1.1 through 10.3.1.3 of Method 14 of this appendix shall be used as well as the recording device described in section 2.1.3 of Method 14. The calibrations or complete change-outs of anemometers shall take place at a minimum of once per year.

The temperature sensing and recording devices shall be calibrated according to the manufacturer's specifications.

10.1.4 Calibration of flowmeters. The calibration of flowmeters is necessary to ensure that an equal volume of sampled gas is entering each of the individual cassettes and that no large differences, which could possibly bias the sample, exist between the cassettes.

10.1.4.1 Variable area, 65 mm flowmeters or equivalent shall be used. These flowmeters can be mounted on a common base for convenience. These flowmeters shall be calibrated by attaching a prepared cassette, complete with filters and pads, to the flowmeter and then to the system manifold. This manifold is an aluminum cylinder with valved inlets for connections to the flowmeters/cassettes and one outlet to a dry gas meter. The connection is then made to the wet-test meter and finally to a dry gas meter. All connections are made with tubing.

10.1.4.2 Turn the dry gas meter on for 15 min. in preparation for the calibration. Turn the dry gas meter off and plug the intake hole of the cassette. Turn the dry gas meter back on to evaluate the entire system for leaks. If the dry gas meter shows a leakage rate of less than 0.02 ft³/min at 10 in. of Hg vacuum as noted on the dry gas meter, the system is acceptable to further calibration.

10.1.4.3 With the dry gas meter turned on and the flow indicator ball at a selected flow rate, record the exact amount of gas pulled through the flowmeter by taking measurements from the wet test meter after exactly 10 min. Record the room temperature and barometric pressure. Conduct this test for all flowmeters in the system with all flowmeters set at the same indicator ball reading. When all flowmeters have gone through the procedure above, correct the volume pulled through each flowmeter to standard conditions. The acceptable difference between the highest and lowest flowmeter rate is 5 percent. Should one or more flowmeters be outside of the acceptable limit of 5 percent, repeat the calibration procedure at a lower or higher indicator ball reading until all flowmeters show no more than 5 percent difference among them.

$$F_v = \frac{(F_d)(X)}{F_c}$$

Eq. 14A-1

Where

F_v = Desired volume of dry gas to be sampled, ft³.

10.1.4.4 This flowmeter calibration shall be conducted at least once per year.

10.1.5 Miscellaneous equipment calibrations. Miscellaneous equipment used such as an automatic recorder/ printer used to measure dry gas meter temperatures shall be calibrated according to the manufacturer's specifications in order to maintain the accuracy of the equipment.

11.0 Analytical Procedure

11.1 The preferred primary analytical determination of the individual isolated samples or the combined particulate and gaseous samples shall be performed by an automated methodology. The analytical method for this technology shall be based on the manufacturer's instructions for equipment operation and shall also include the analysis of five standards with concentrations in the expected range of the actual samples. The results of the analysis of the five standards shall have a coefficient of correlation of at least 0.99. A check standard shall be analyzed as the last sample of the group to determine if instrument drift has occurred. The acceptable result for the check standard is 95 to 105 percent of the standard's true value.

11.2 The secondary analytical method shall be by specific ion electrode if the samples are distilled or if a TISAB IV buffer is used to eliminate aluminum interferences. Five standards with concentrations in the expected range of the actual samples shall be analyzed, and a coefficient of correlation of at least 0.99 is the minimum acceptable limit for linearity. An exception for this limit for linearity is a condition when low-level standards in the range of 0.01 to 0.48 µg fluoride/ml are analyzed. In this situation, a minimum coefficient of correlation of 0.97 is required. TISAB II shall be used for low-level analyses.

12.0 Data Analysis and Calculations

12.1 Carry out calculations, retaining at least one extra decimal point beyond that of the acquired data. Round off values after the final calculation. Other forms of calculations may be used as long as they give equivalent results.

12.2 Estimating volumes for initial test runs.

F_d = Desired or analytically optimum mass of TF per cassette, micrograms of TF per cassette (µg/cassette).

X = Number of cassettes used.

F_c = Typical concentration of TF in emissions to be sampled, $\mu\text{g}/\text{ft}^3$, calculated from Equation 14A-2.

$$F_c = \frac{(R_e)(R_p)(4.536 \times 10^8 \mu\text{g}/\text{lb})}{(A_r)(V_r)} \quad \text{Eq. 14A-2}$$

Where

R_e = Typical emission rate from the facility, pounds of TF per ton (lb/ton) of aluminum.

R_p = Typical production rate of the facility, tons of aluminum per minute (ton/min).

V_r = Typical exit velocity of the roof monitor gases, feet per minute (ft/min).

A_r = Open area of the roof monitor, square feet (ft^2).

12.2.1 Example calculation. Assume that the typical emission rate (R_e) is 1.0 lb TF/ton of aluminum, the typical roof vent gas exit velocity (V_r) is 250 ft/min, the typical production rate (R_p) is 0.10 ton/min, the known open area for the roof monitor (A_r) is 8,700 ft^2 , and the desired (analytically optimum) mass of TF per cassette is 1,500 μg . First calculate the concentration of TF per cassette (F_c) in $\mu\text{g}/\text{ft}^3$ using Equation 14A-2. Then calculate the desired volume of gas to be sampled (F_v) using Equation 14A-1.

$$F_c = 20.855 = \frac{(1.0 \text{ lb/ton})(0.1 \text{ tons/min})(4.536 \times 10^8 \mu\text{g}/\text{lb})}{(8,700 \text{ ft}^2)(250 \text{ ft/min})} \quad \text{Eq. 14A-3}$$

$$F_v = 575.40 \text{ ft}^3 = \frac{(1,500 \mu\text{g})(8 \text{ cassettes})}{(20.855 \mu\text{g}/\text{ft}^3)} \quad \text{Eq. 14A-4}$$

This is a total of 575.40 ft^3 for eight cassettes or 71.925 ft^3 /cassette.

12.3 Calculations of TF emissions from field and laboratory data that would yield a production related emission rate can be calculated as follows:

12.3.1 Obtain a standard cubic feet (scf) value for the volume pulled through the dry gas meter for all cassettes by using the field and calibration data and Equation 5-1 of Method 5 of this appendix.

12.3.2 Derive the average quantity of TF per cassette (in μg TF/cassette) by adding all laboratory data for all cassettes and dividing this value by the total number of cassettes used. Divide this average TF value by the corrected dry gas meter volume for each cassette; this value then becomes TF_{std} ($\mu\text{g}/\text{ft}^3$).

12.3.3 Calculate the production-based emission rate (R_e) in lb/ton using Equation 14A-5.

$$R_e = \frac{(\text{TF}_{\text{std}})(V_r)(A_r)(2.2 \times 10^{-9} \text{ lb}/\mu\text{g})}{(R_p)} \quad \text{Eq. 14A-5}$$

12.3.4 As an example calculation, assume eight cassettes located in a potline were used to sample for 72 hours during the run. The analysis of all eight cassettes yielded a total of 3,000 μg of TF. The dry gas meter volume was corrected to yield a total of 75 scf per

cassette, which yields a value for TF_{std} of $3,000/75 = 40 \mu\text{g}/\text{ft}^3$. The open area of the roof monitor for the potline (A_r) is 17,400 ft^2 . The exit velocity of the roof monitor gases (V_r) is 250 ft/min. The production rate of aluminum over the previous 720 hours was 5,000 tons,

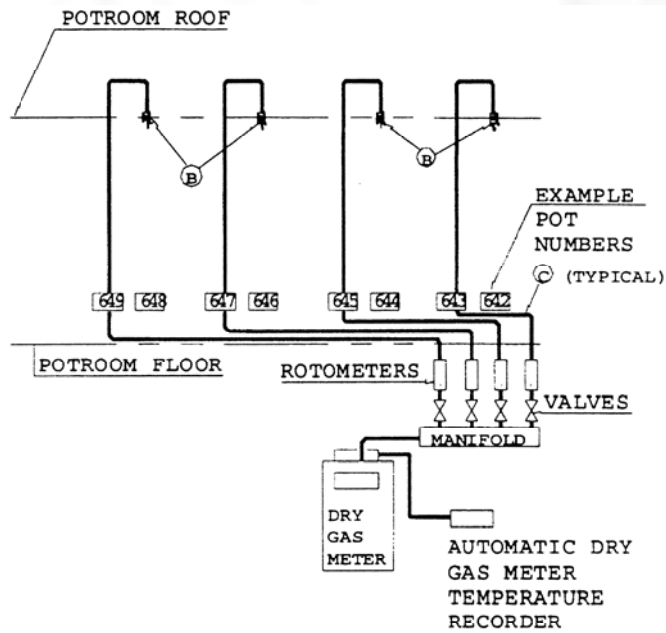
which is 6.94 tons/hr or 0.116 ton/min (R_p).
Substituting these values into Equation 14A-5 yields:

$$R_e = \frac{(5 \mu\text{g}/\text{ft}^3)(250 \text{ ft}/\text{min})(17,400 \text{ ft}^2)(2.2 \times 10^{-9} \text{ lb}/\mu\text{g})}{(0.116 \text{ ton}/\text{min})} \quad \text{Eq. 14A-6}$$

$$R_e = 0.41 \text{ lb}/\text{ton of aluminum produced.} \quad \text{Eq. 14A-7}$$

12.4 Corrections to volumes due to leakage. Should the post-test leak check leakage rate exceed 4 percent as described in section 8.3.2

of this method, correct the volume as detailed in Case I in section 6.3 of Method 5 of this appendix.



- ⓑ ALCAN CASSETTE EXAMPLE METHOD SAMPLING POINTS
- ⓒ POLYETHYLENE TUBING ENCLOSED IN CONDUIT

Figure 14A-1. Conceptual side view of arrangement of 4 cassettes for one-half of a potroom.

Note: This drawing does not reflect an equally acceptable arrangement of 8 cassettes in a cassette group located along at least 8 percent of the potroom roof.

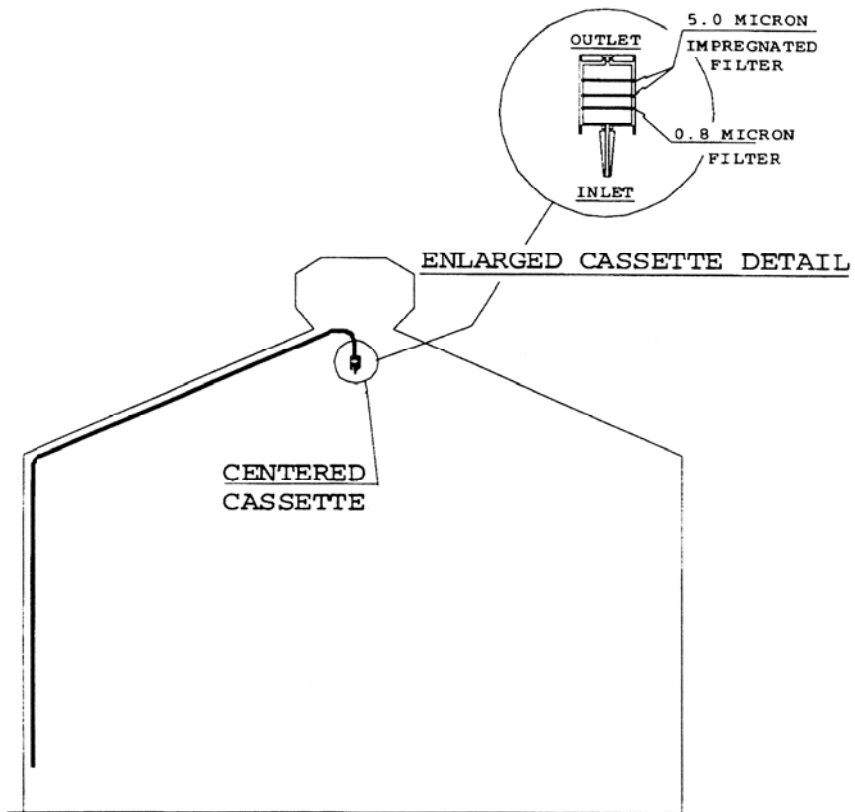


Figure 14A-2. Conceptual end view of cassette placement in a potroom roof.

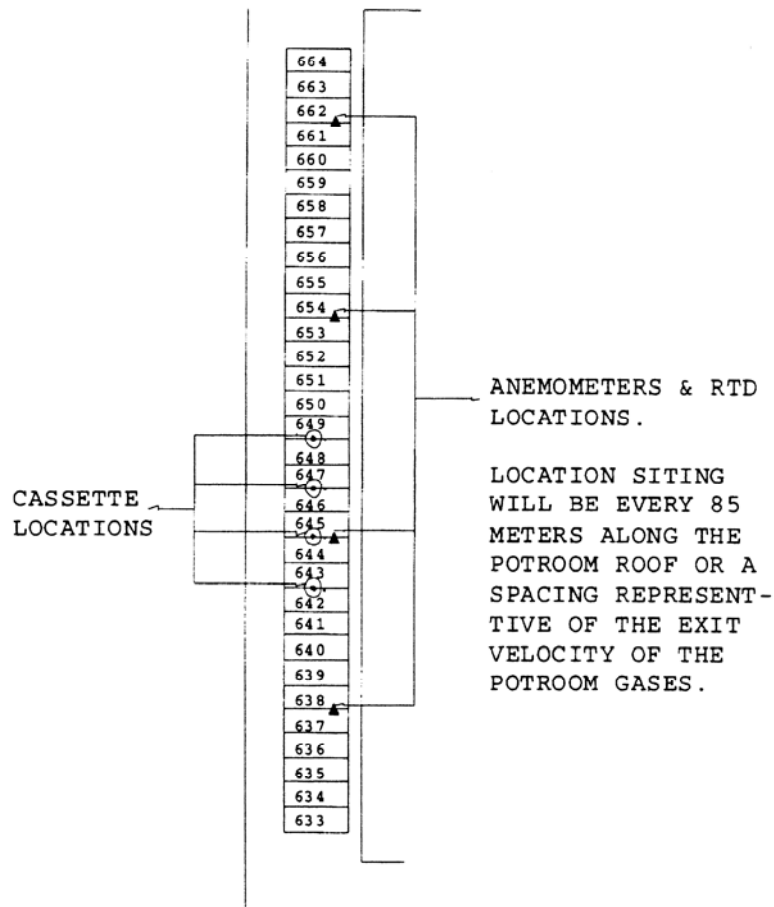


Figure 14A-3. Conceptual side view of positions of cassettes, anemometers, and RTDs in a typical half of a potroom.

Note: This drawing does not reflect other potentially acceptable arrangements.

Environmental Protection Agency

Pt. 60, App. A-5, Meth. 15

METHOD 15—DETERMINATION OF HYDROGEN SULFIDE, CARBONYL SULFIDE, AND CARBON DISULFIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method is not inclusive with respect to specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance.

Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of gas chromatography techniques.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity (See Sec 13.2)
Carbon disulfide [CS ₂]	75-15-0	0.5 ppmv
Carbonyl sulfide [COS]	463-58-1	0.5 ppmv
Hydrogen sulfide [H ₂ S]	7783-06-4	0.5 ppmv

1.2 Applicability.

1.2.1 This method applies to the determination of emissions of reduced sulfur compounds from tail gas control units of sulfur recovery plants, H₂S in fuel gas for fuel gas combustion devices, and where specified in other applicable subparts of the regulations.

1.2.2 The method described below uses the principle of gas chromatographic (GC) separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent useable methods for determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the calibration precision and sample-line loss criteria are met.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the emission source and diluted with clean dry air (if necessary). An aliquot of the diluted sample is then analyzed for CS₂, COS, and H₂S by GC/FPD.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Moisture Condensation. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This potential is eliminated by heating the probe, filter box, and connections, and by maintaining the SO₂ scrubber in an ice water bath. Moisture is removed in the SO₂ scrubber and heating the sample beyond this point is not necessary provided the ambient temperature is above 0 °C (32 °F). Alternatively, moisture may be eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the GC/FPD analytical system prior to analysis.

4.2 Carbon Monoxide (CO) and Carbon Dioxide (CO₂). CO and CO₂ have substantial desensitizing effects on the FPD even after 9:1 dilution. (Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting CO and CO₂ before any of the sulfur compounds to be measured.) Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO₂ in the diluent gas. The CO₂ level should be approximately 10 percent for the case with CO₂ present. The two chromatograms should show agreement within the precision limits of section 13.3.

4.3 Elemental Sulfur. The condensation of sulfur vapor in the sampling system can lead to blockage of the particulate filter. This problem can be minimized by observing the filter for buildup and changing as needed.

4.4 Sulfur Dioxide (SO₂). SO₂ is not a specific interferent but may be present in such large amounts that it cannot be effectively separated from the other compounds of interest. The SO₂ scrubber described in section 6.1.3 will effectively remove SO₂ from the sample.

4.5 Alkali Mist. Alkali mist in the emissions of some control devices may cause a rapid increase in the SO₂ scrubber pH, resulting in low sample recoveries. Replacing the SO₂ scrubber contents after each run will minimize the chances of interference in these cases.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test to establish appropriate safety and health practices and determine the applicability of regulatory limitations to performing this test.

6.0 Equipment and Supplies

6.1 Sample Collection. See Figure 15-1. The sampling train component parts are discussed in the following sections:

6.1.1 Probe. The probe shall be made of Teflon or Teflon-lined stainless steel and heated to prevent moisture condensation. It shall be designed to allow calibration gas to enter the probe at or near the sample point entry. Any portion of the probe that contacts the stack gas must be heated to prevent moisture condensation. The probe described in section 6.1.1 of Method 16A having a nozzle directed away from the gas stream is recommended for sources having particulate or mist emissions. Where very high stack temperatures prohibit the use of Teflon probe components, glass or quartz-lined probes may serve as substitutes.

6.1.2 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-micron porosity Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature of at least 120 °C (248 °F).

6.1.3 SO₂ Scrubber. Three 300-ml Teflon segment impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Savillex.) The first two impingers contain 100 ml of citrate buffer, and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3-mm (1/8-in.) ID and should be immersed to a depth of at least 50 cm (2 in.). Immerse the impingers in an ice water bath and maintain near 0 °C. The scrubber solution will normally last for a 3-hour run before needing replacement. This will depend upon the effects of moisture and particulate matter on the solution strength and pH. Connections between the probe, particulate filter, and SO₂ scrubber shall be made of Teflon and as short in length as possible. All portions of the probe, particulate filter, and connections prior to the SO₂ scrubber (or alternative point of moisture removal) shall be maintained at a temperature of at least 120 °C (248 °F).

6.1.4 Sample Line. Teflon, no greater than 13-mm (1/2-in.) ID. Alternative materials, such as virgin Nylon, may be used provided the line-loss test is acceptable.

6.1.5 Sample Pump. The sample pump shall be a leakless Teflon-coated diaphragm type or equivalent.

6.2 Analysis. The following items are needed for sample analysis:

6.2.1 Dilution System. The dilution system must be constructed such that all sample contacts are made of Teflon, glass, or stainless steel. It must be capable of approximately a 9:1 dilution of the sample.

6.2.2 Gas Chromatograph (see Figure 15-2). The gas chromatograph must have at least the following components:

6.2.2.1 Oven. Capable of maintaining the separation column at the proper operating temperature ± 1 °C.

6.2.2.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature ± 1 °C.

6.2.2.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

6.2.2.4 Flame Photometric Detector.

6.2.2.4.1 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

6.2.2.4.2 Power Supply. Capable of delivering up to 750 volts.

6.2.2.5 Recorder. Compatible with the output voltage range of the electrometer.

6.2.2.6 Rotary Gas Valves. Multiport Teflon-lined valves equipped with sample loop. Sample loop volumes shall be chosen to provide the needed analytical range. Teflon tubing and fittings shall be used throughout to present an inert surface for sample gas. The GC shall be calibrated with the sample loop used for sample analysis.

6.2.2.7 GC Columns. The column system must be demonstrated to be capable of resolving three major reduced sulfur compounds: H₂S, COS, and CS₂. To demonstrate that adequate resolution has been achieved, a chromatogram of a calibration gas containing all three reduced sulfur compounds in the concentration range of the applicable standard must be submitted. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Base line separation is defined as a return to zero (± 5 percent) in the interval between peaks. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Administrator.

6.3 Calibration System (See Figure 15-3). The calibration system must contain the following components:

6.3.1 Flow System. To measure air flow over permeation tubes within 2 percent. Each flowmeter shall be calibrated after each complete test series with a wet-test meter. If the flow measuring device differs from the wet-test meter by more than 5 percent, the completed test shall be discarded. Alternatively, use the flow data that will yield the lowest flow measurement. Calibration with a wet-test meter before a test is optional. Flow over the permeation device may also be determined using a soap bubble flowmeter.

6.3.2 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within 0.1 °C.