response factor (area/ppm) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation (calculated in section 12.8 of Method 25) for each set of triplicate injections is less than 2 percent. Record the overall mean of the response factor values as the calibration response factor (R).

11.0 Analytical Procedure

11.1 Preparation for Analysis. Before putting the GC analyzer into routine operation, conduct the calibration procedures listed in section 10.0. Establish an appropriate carrier flow rate and detector temperature for the specific instrument used.

11.2 Sample Analysis. Purge the sample loop with sample, and then inject the sample. Analyze each sample in triplicate, and calculate the average sample area (A). Determine the bag CO concentration according to section 12.2.

12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra significant figure beyond that of the acquired data. Round off results only after the final calculation.

12.1 Nomenclature.

- $A$ = Average sample area.
- $B_w$ = Moisture content in the bag sample, fraction.
- $C$ = CO concentration in the stack gas, dry basis, ppm.
- $C_b$ = CO concentration in the bag sample, dry basis, ppm.
- $F$ = Volume fraction of CO$_2$ in the stack, fraction.
- $P_{bar}$ = Barometric pressure, mm Hg.
- $P_v$ = Vapor pressure of the H$_2$O in the bag (from Table 10A–2, Method 10A), mm Hg.
- $R$ = Mean calibration response factor, area/ppm.

12.2 CO Concentration in the Bag. Calculate $C_b$, using Equations 10B–1 and 10B–2. If condensate is visible in the bag, calculate $B_w$, using Table 10A–2 of Method 10A and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate $B_w$ using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_v}{P_{bar}} \quad \text{Eq. 10B–1}$$

$$C_b = \frac{A}{R \left(1 - B_w\right)} \quad \text{Eq. 10B–2}$$

12.3 CO Concentration in the Stack

$$C = C_b \left(1 - F\right) \quad \text{Eq. 10B–3}$$

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13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as in Method 25, section 16.0, with the addition of the following:


17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]
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1.0 Scope and Application

1.1 Analytes.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>CAS No.</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sulfide (H₂S)</td>
<td>7783–06–4</td>
<td>8 mg/m³—740 mg/m³, (6 ppm—520 ppm).</td>
</tr>
</tbody>
</table>

1.2 Applicability. This method is applicable for the determination of the H₂S content of fuel gas streams at petroleum refineries.

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 sample is extracted from a source and passed through a series of midget impingers containing a cadmium sulfate (CdSO₄) solution; H₂S is absorbed, forming cadmium sulfide (CdS). The latter compound is then measured iodometrically.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Any compound that reduces iodine (I₂) or oxidizes the iodide ion will interfere in this procedure, provided it is collected in the CdSO₄ impingers. Sulfur dioxide in concentrations of up to 2,600 mg/m³ is removed...
with an impinger containing a hydrogen peroxide (H$_2$O$_2$) solution. Thiols precipitate with H$_2$S. In the absence of H$_2$S, only traces of thiols are collected. When methane and ethane-thiols at a total level of 300 mg/m$^3$ are present in addition to H$_2$S, the results vary from 2 percent low at an H$_2$S concentration of 400 mg/m$^3$ to 14 percent high at an H$_2$S concentration of 100 mg/m$^3$. Carbonyl sulfide at a concentration of 20 percent does not interfere. Certain carbonyl-containing compounds react with iodine and produce recurring end points. However, acetaldehyde and acetone at concentrations of 1 and 3 percent, respectively, do not interfere.

4.2 Entrained H$_2$O$_2$ produces a negative interference equivalent to 100 percent of that of an equimolar quantity of H$_2$S. Avoid the ejection of H$_2$O$_2$ into the CdSO$_4$ impingers.

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 method 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 burns as thermal burns.

5.2.1 Hydrogen Peroxide. Irritating to eyes, skin, nose, and lungs. 30% H$_2$O$_2$ is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Hydrochloric Acid. Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal in minutes. Will react with metals, producing hydrogen.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are needed for sample collection:

6.1.1 Sampling Line. Teflon tubing, 6- to 7-mm (‘‘-in.’’) ID, to connect the sampling train to the sampling valve.

6.1.2 Impingers. Five midget impingers, each with 30-ml capacity. The internal diameter of the impinger tip must be 1 mm ±0.05 mm. The impinger tip must be positioned 4 to 6 mm from the bottom of the impinger.

6.1.3 Tubing. Glass or Teflon connecting tubing for the impingers.

6.1.4 Ice Water Bath. To maintain absorbing solution at a low temperature.

6.1.5 Drying Tube. Tube packed with 6- to 16-mesh indicating-type silica gel, or equivalent, to dry the gas sample and protect the meter and pump. If the silica gel has been used previously, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to approval of the Administrator.

Note: Do not use more than 30 g of silica gel. Silica gel absorbs gases such as propane from the fuel gas stream, and use of excessive amounts of silica gel could result in errors in the determination of sample volume.

6.1.6 Sampling Valve. Needle valve, or equivalent, to adjust gas flow rate. Stainless steel or other corrosion-resistant material.

6.1.7 Volume Meter. Dry gas meter (DGM), sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate (about 1.0 liter/min) and conditions actually encountered during sampling. The meter shall be equipped with a temperature sensor (dial thermometer or equivalent) capable of measuring temperature to within 3 °C (5.4 °F). The gas meter should have a petcock, or equivalent, on the meter and pump. If the silica gel has been used previously, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to approval of the Administrator.

6.1.8 Rate Meter. Rotameter, or equivalent, to measure flow rates in the range from 0.5 to 2 liters/min (1 to 4 ft$^3$/hr).

6.1.9 Graduated Cylinder. 25-ml size.

6.1.10 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice-versa for elevation decrease.

6.1.11 U-tube Manometer. 0- to 30-cm water column, for leak-check procedure.

6.1.12 Rubber Squeeze Bulb. To pressurize train for leak-check.

6.1.13 Tee, Pinchclamp, and Connecting Tubing. For leak-check.

6.1.14 Pump. Diaphragm pump, or equivalent. Insert a small surge tank between the pump and rate meter to minimize the pulsation effect of the diaphragm pump on the rate meter. The pump is used for the air purge at the end of the sample run; the pump is not ordinarily used during sampling, because fuel gas streams are usually sufficiently pressurized to force sample gas...
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through the train at the required flow rate. The pump need not be leak-free unless it is used for sampling.

6.1.15 Needle Valve or Critical Orifice. To set air purge during purge.

6.1.16 Tube Packaged with Active Carbon. To filter air during purge.

6.1.17 Volumetric Flask. One 1000-ml.

6.1.18 Volumetric Pipette. One 15-ml.

6.1.19 Pressure-Reduction Regulator. Depending on the sampling stream pressure, a pressure-reduction regulator may be needed to reduce the pressure of the gas stream entering the Teflon sample line to a safe level.

6.1.20 Cold Trap. If condensed water or amine is present in the sample stream, a corrosion-resistant cold trap shall be used immediately after the sample tap. The trap shall not be operated below 0 °C (32 °F) to avoid condensation of C₂ or C₃ hydrocarbons.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Sample Container. Iodine flask, glass-stoppered, 500-ml size.

6.2.2 Volumetric Pipette. One 50-ml.

6.2.3 Graduated Cylinders. One each 25- and 250-ml.

6.2.4 Erlenmeyer Flasks. 125-ml.

6.2.5 Wash Bottle.

6.2.6 Volumetric Flasks. Three 1000-ml.

6.2.7 Sample Analysis. The following items are needed for sample analysis:

6.3.1 Flask. Glass-stoppered iodine flask, 500-ml.

6.3.2 Burette. 50-ml.

6.3.3 Erlenmeyer Flask. 125-ml.

6.3.4 Volumetric Pipettes. One 25-ml; two each 50- and 100-ml.

6.3.5 Volumetric Flasks. One 1000-ml; two 500-ml.

6.3.6 Graduated Cylinders. One each 10- and 100-ml.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Cadmium (CdSO₄) Absorbing Solution. Dissolve 41 g of CdSO₄·H₂O and 15 ml of 0.1 M sulfuric acid in a 1-liter volumetric flask that contains approximately 4/5 liter of water. Dilute to volume with distilled water. Mix thoroughly. The pH should be 2 ± 0.1. Add 10 drops of Dow-Corning Antifoam B. Shake well before use. This solution is stable for at least one month. If Antifoam B is not used, a more labor-intensive sample recovery procedure is required (see section 11.2).

7.1.2 Hydrogen Peroxide, 3 Percent. Dilute 30 percent H₂O₂ to 3 percent as needed. Prepare fresh daily.

7.1.3 Water. Deionized distilled to conform to ASTM D 1193-77 or 91. Type 3 (incorporated by reference—see §60.17). The KMnO₄ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.2 Sample Recovery. The following reagents are needed for sample recovery:

7.2.1 Water. Same as section 7.1.3.

7.2.2 Hydrochloric Acid (HCl) Solution, 3 M. Add 240 ml of concentrated HCl (specific gravity 1.19) to 500 ml of water in a 1-liter volumetric flask. Dilute to 1 liter with water. Mix thoroughly.

7.2.3 Iodine (I₂) Solution, 0.1 N. Dissolve 24 g of potassium iodide (KI) in 30 ml of water. Add 12.7 g of resublimed iodine (I₂) to 15 ml of KI solution. Shake the mixture until the I₂ is completely dissolved. If possible, let the solution stand overnight in the dark. Slowly dilute the solution to 1 liter with water, with swirling. Filter the solution if it is cloudy. Store solution in a brown-glass reagent bottle.

7.2.4 Standard I₂ Solution. 0.01 N. Pipette 100.0 ml of the 0.1 N iodine solution into a 1-liter volumetric flask, and dilute to volume with water. Standardize daily as in section 10.2.1. This solution must be protected from light. Reagent bottles and flasks must be kept tightly stoppered.

7.3 Sample Analysis. The following reagents and standards are needed for sample analysis:

7.3.1 Water. Same as in section 7.1.3.

7.3.2 Standard Sodium Thiosulfate Solution, 0.1 N. Dissolve 24.8 g of sodium thiosulfate pentahydrate (Na₂S₂O₃·5H₂O) or 15.8 g of anhydrous sodium thiosulfate (Na₂S₂O₃) in 1 liter of water, and add 0.01 g of anhydrous sodium carbonate (Na₂CO₃) and 0.4 ml of chloroform (CHCl₃) to stabilize. Mix thoroughly by shaking or by aerating with nitrogen for approximately 15 minutes, and store in a glass-stoppered, reagent bottle.

7.3.3 Standard Sodium Hypochlorite Solution, 0.01 N. Pipette 50.0 ml of the standard 0.1 N Na₂S₂O₃ solution into a volumetric flask, and dilute to 500 ml with water.

NOTE: A 0.01 N phenylarsine oxide (C₆H₅AsO) solution may be prepared instead of 0.1 N Na₂S₂O₃ (see section 7.3.4).

7.3.4 Standard Phenylarsine Oxide Solution, 0.01 N. Dissolve 1.80 g of (C₆H₅AsO) in 1 liter of water. Dilute the solution to pH 4.7 with 6 N HCl, and dilute to 1 liter with water. Standardize as in section 10.2.2.

7.3.5 Standard Sodium Thiosulfate Solution, 0.01 N. Pipette 50.0 ml of the standard 0.1 N Na₂S₂O₃ solution into a volumetric flask, and dilute to 500 ml with water.
indicates paper similar to Alkacid test ribbon, then add 2 ml of glacial acetic acid as a preservative.

**Note:** Test starch indicator solution for decomposition by titrating with 0.01 N I$_2$, 4 ml of starch solution in 200 ml of water that contains 1 g of KI. If more than 4 drops of the 0.01 N I$_2$ solution are required to obtain the blue color, a fresh solution must be prepared.

### 8.0 Sample Collection, Preservation, Storage, and Transport

#### 8.1 Sampling Train Preparation

Assemble the sampling train as shown in Figure 11–1, connecting the five midget impingers in series. Place 15 ml of 3 percent H$_2$O$_2$ solution in the first impinger. Leave the second impinger empty. Place 15 ml of the CdSO$_4$ solution in the third, fourth, and fifth impingers. Place the impinger assembly in an ice water bath container, and place water and crushed ice around the impingers. Add more ice during the run, if needed.

#### 8.2 Leak-Check Procedure

8.2.1 Connect the rubber bulb and manometer to the first impinger, as shown in Figure 11–1. Close the petcock on the DGM outlet. Pressurize the train to 25 cm water with the bulb, and close off the tubing connected to the rubber bulb. The train must hold 25 cm of water pressure with not more than a 1 cm drop in pressure in a 1-minute interval. Stopcock grease is acceptable for sealing ground glass joint.

8.2.2 If the pump is used for sampling, it is recommended, but not required, that the pump be leak-checked separately, either prior to or after the sampling run. To leak-check the pump, proceed as follows: Disconnect the drying tube from the impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump, pull a vacuum of 250 mm Hg (10 in. Hg), plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 seconds. If performed prior to the sampling run, the pump leak-check should precede the leak-check of the sampling train described immediately above; if performed after the sampling run, the pump leak-check should follow the sampling train leak-check.

8.3 Purge the connecting line between the sampling valve and the first impinger by disconnecting the line from the first impinger, opening the sampling valve, and allowing process gas to flow through the line for one to two minutes. Then, close the sampling valve, and reconnect the line to the impinger train. Open the petcock on the dry gas meter outlet. Record the initial DGM reading.

8.4 Open the sampling valve, and then adjust the valve to obtain a rate of approximately 1 liter/min (0.035 cfm). Maintain a constant ±10 percent flow rate during the test. Record the DGM temperature.

8.5 Sample for at least 10 minutes. At the end of the sampling time, close the sampling valve, and record the final volume and temperature readings. Conduct a leak-check as described in Section 8.2. A yellow color in the final cadmium sulfate impinger indicates depletion of the absorbing solution. An additional cadmium sulfate impinger should be added for subsequent samples and the sample with yellow color in the final impinger should be voided.

8.6 Disconnect the impinger train from the sampling line. Connect the charcoal tube and the pump as shown in Figure 11–1. Purge the train [at a rate of 1 liter/min (0.035 cfm)] with clean ambient air for 15 minutes to ensure that all H$_2$S is removed from the H$_2$O$_2$. For sample recovery, cap the open ends, and remove the impinger train to a clean area that is away from sources of heat. The area should be well lighted, but not exposed to direct sunlight.

8.7 Sample Recovery

8.7.1 Discard the contents of the H$_2$O$_2$ impinger. Carefully rinse with water the contents of the third, fourth, and fifth impingers into a 500-ml iodine flask.

**Note:** The impingers normally have only a thin film of CdS remaining after a water rinse. If Antifoam B was not used or if significant quantities of yellow CdS remain in the impingers, the alternative recovery procedure in section 11.2 must be used.

8.7.2 Proceed to section 11 for the analysis.

### 9.0 Quality Control

#### 9.0.1 Initial Calibration

**Note:** Maintain a log of all calibrations.

10.1.1.1 Initial Calibration. The DGM shall be calibrated before its initial use in the field. Proceed as follows: First, assemble the following components in series: Drying tube, needle valve, pump, rotameter, and DGM.
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Then, leak-check the metering system as follows: Place a vacuum gauge (at least 760 mm Hg) at the inlet to the drying tube, and pull a vacuum of 250 mm Hg (10 in. Hg); plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum shall remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the vacuum pressure at the dry end. Next, calibrate the DGM (at the sampling flow rate specified by the method) as follows: Connect an appropriately sized wet-test meter (0.01 N Na$_2$S$_2$O$_3$ solution) as follows: Oven-dry potassium dichromate (K$_2$Cr$_2$O$_7$) at 180 to 200 °C (360 to 390 °F). To the nearest milligram, weigh 2 g of the dichromate (W). Transfer the dichromate to a 500-ml volumetric flask, dissolve in water, and dilute to exactly 500 ml. In a 500-ml iodine flask, dissolve approximately 3 g of KI in 45 ml of water, then add 10 ml of 3 M HCl solution. Pipette 50 ml of the dichromate solution into this mixture. Gently swirl the contents of the flask once, and allow it to stand in the dark for 5 minutes. Dilute the solution with 100 to 200 ml of water, washing down the sides of the flask with part of the water. Titrate with 0.1 N Na$_2$S$_2$O$_3$ solution, until the solution is light yellow. Add 4 ml of starch indicator and continue titrating slowly to a green end point. Record the volume of Na$_2$S$_2$O$_3$ solution used, V$_s$, in ml. Repeat until replicate values agree within 0.05 ml. Calculate the normality using Equation 11–1. Repeat the standardization each week or after each test series, whichever time is shorter.

10.2.3 Phenylarsine Oxide Solution Standardization. Standardize the 0.01 N C$_6$H$_5$AsO$_3$ (if applicable) as follows: Oven-dry K$_2$Cr$_2$O$_7$ at 180 to 200 °C (360 to 390 °F). To the nearest milligram, weigh 2 g of the dichromate (W). Transfer the dichromate to a 500-ml volumetric flask, dissolve in water, and dilute to exactly 500 ml. In a 500-ml iodine flask, dissolve approximately 0.3 g of KI in 45 ml of water, then add 10 ml of 3 M HCl. Pipette 5 ml of the dichromate solution into the iodine flask. Gently swirl the contents of the flask once, and allow it to stand in the dark for 5 minutes. Dilute the solution with 100 to 200 ml of water, washing down the sides of the flask with part of the water. Titrate with 0.01 N C$_6$H$_5$AsO$_3$ until the solution is light yellow. Add 4 ml of starch indicator, and continue titrating slowly to a green end point. Record the volume of C$_6$H$_5$AsO$_3$ used, V$_a$, in ml. Repeat until replicate analyses agree within 0.05 ml. Calculate the normality using Equation 11–2. Repeat the standardization each week or after each test series, whichever time is shorter.

11.0 Analytical Procedure

Conduct the titration analyses in a clean area away from direct sunlight.

11.1 Pipette exactly 50 ml of 0.01 N I$_2$ solution into a 125-ml Erlenmeyer flask. Add 10 ml of 3 M HCl to the solution. Quantitatively rinse the acidified I$_2$ into the iodine flask. Stopper the flask immediately, and shake briefly.
11.2 Use these alternative procedures if Antifoam B was not used or if significant quantities of yellow CdS remain in the impingers. Extract the remaining CdS from the third, fourth, and fifth impingers using the acidified I\textsubscript{2} solution. Immediately after pouring the acidified I\textsubscript{2} into an impinger, stopper it and shake for a few moments, then transfer the liquid to the iodine flask. Do not transfer any rinse portion from one impinger to another; transfer it directly to the iodine flask using water. Stopper the impingers, connectors, and the beaker into which the acidified I\textsubscript{2} has been poured into any glassware containing CdS, the container must be tightly stoppered at all times except when adding more solution, and take care to mix as quickly and carefully as possible. After adding any acidified I\textsubscript{2} solution to the iodine flask, allow a few minutes for absorption of the H\textsubscript{2}S before adding any further rinses. Repeat the I\textsubscript{2} extraction until all CdS is removed from the impingers. Extract that part of the connecting glassware that contains visible CdS. Quantitatively rinse all the I\textsubscript{2} from the impingers, connectors, and the beaker into the iodine flask using water. Stopper the flask and shake briefly.

11.3 Allow the iodine flask to stand about 30 minutes in the dark, and titrate it as quickly as possible. After adding any acidified I\textsubscript{2} solution to the iodine flask, allow a few minutes for absorption of the H\textsubscript{2}S before adding any further rinses. Repeat the I\textsubscript{2} extraction until all CdS is removed from the impingers. Extract that part of the connecting glassware that contains visible CdS. Quantitatively rinse all the I\textsubscript{2} from the impingers, connectors, and the beaker into the iodine flask using water. Stopper the flask and shake briefly.

NOTE: Iodine evaporates from acidified I\textsubscript{2} solutions. Samples to which acidified I\textsubscript{2} solution has been added may not be stored, but must be analyzed in the time schedule stated above.

11.4 Prepare a blank by adding 45 ml of CdSO\textsubscript{4} absorbing solution to an iodine flask. Pipette exactly 50 ml of 0.01 N I\textsubscript{2} solution into a 125-ml Erlenmeyer flask. Add 10 ml of 3 M HCl. Stopper the flask, shake briefly, let stand 30 minutes in the dark, and titrate the samples.

NOTE: The blank must be handled by exactly the same procedure as that used for the samples.

11.5 Using 0.01 N Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} solution (or 0.01 N Cd\textsubscript{2}H\textsubscript{3}AsO\textsubscript{3} if applicable), rapidly titrate each sample in an iodine flask using gentle mixing, until solution is light yellow. Add 4 ml of starch indicator solution, and continue titrating slowly until the blue color just disappears. Record the volume of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} solution used, V\textsubscript{TT}, or the volume of Cd\textsubscript{2}H\textsubscript{3}AsO\textsubscript{3} solution used, V\textsubscript{AT}, in ml.

11.6 Titrate the blanks in the same manner as the samples. Run blanks each day until replicate values agree within 0.05 ml. Average the replicate titration values which agree within 0.05 ml.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures only after the final calculation.

12.1 Nomenclature

\[ C_{\text{H}_{2}\text{S}} = \text{Concentration of } H_2S \text{ at standard conditions, mg/dscm.} \]
\[ N_A = \text{Normality of standard } C_6H_4AsO \text{ solution, g-equiv/liter.} \]
\[ N_I = \text{Normality of standard } I_2 \text{ solution, g-equiv/liter.} \]
\[ N_R = \text{Normality of standard } (=0.1 \text{ N}) Na_2S_2O_3 \text{ solution, g-equiv/liter.} \]
\[ P_{\text{bar}} = \text{Barometric pressure at the sampling site, mm Hg.} \]
\[ P_{\text{std}} = \text{Standard absolute pressure, 760 mm Hg.} \]
\[ T_T = \text{Average DGM temperature, °K.} \]
\[ T_{\text{std}} = \text{Standard absolute temperature, 293 °K.} \]
\[ V_A = \text{Volume of } C_6H_4AsO \text{ solution used for standardization, ml.} \]
\[ V_{AI} = \text{Volume of standard } C_6H_4AsO \text{ solution used for titration analysis, ml.} \]
\[ V_{TT} = \text{Volume of standard } I_2 \text{ solution used for titration analysis, ml.} \]
\[ V_m = \text{Volume of gas sample at meter conditions, liters.} \]
\[ V_{mgcd} = \text{Volume of gas sample at standard conditions, liters.} \]
\[ V_{SI} = \text{Volume of } (=0.1 \text{ N}) Na_2S_2O_3 \text{ solution used for titration analysis, ml.} \]
\[ V_{V} = \text{Volume of } (=0.1 \text{ N}) Na_2S_2O_3 \text{ solution used for titration analysis, ml.} \]
\[ W = \text{Weight of } K_2Cr_2O_7 \text{ used to standardize Na}_2\text{S}_2\text{O}_3 \text{ or } C_6\text{H}_4\text{AsO} \text{ solutions, as applicable (see sections 10.2.2 and 10.2.3), g.} \]
\[ Y = \text{DGM calibration factor.} \]

\[ C_{\text{H}_{2}\text{S}} = \frac{2.039 \times W}{V_S} \quad \text{Eq. 11-1} \]

Where:
\[ 2.039 = \text{Conversion factor} \]
\[ = (6 \text{ g-equiv/liter } K_2Cr_2O_7) \times (1,000 \text{ ml/liter}) \]
\[ (294.2 \text{ g } K_2Cr_2O_7 \text{/mole}) \times (100 \text{ aliquot factor}) \]

\[ N_A = \frac{0.2039 \times W}{V_{\lambda}} \quad \text{Eq. 11-2} \]

Where:
\[ 0.2039 = \text{Conversion factor} \]
\[ = (6 \text{ g-equiv/liter } K_2Cr_2O_7) \times (1,000 \text{ ml/liter}) \]
\[ (294.2 \text{ g } K_2Cr_2O_7 \text{/mole}) \times (10 \text{ aliquot factor}) \]

\[ N_I = \frac{N_TV_{TT}}{V_I} \quad \text{Eq. 11-3} \]
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12.5 Dry Gas Volume. Correct the sample volume measured by the DGM to standard conditions (20°C and 760 mm Hg).

\[ V_{m\text{std}} = V_m \sqrt{\frac{T_m}{T_{\text{std}}}} \frac{P_{\text{bar}}}{P_{\text{std}}} \]  
Eq. 11-4

12.6 Concentration of H₂S. Calculate the concentration of H₂S in the gas stream at standard conditions using Equation 11–5:

\[ C_{\text{H₂S}} = 17.04 \times 10^3 \frac{(V_{IT}N_1 - V_{TT}N_T)_{\text{sample}} - (V_{IT}N_1 - V_{TT}N_T)_{\text{blank}}}{V_{m\text{std}}} \]  
Eq. 11-5

Where:

17.04 \times 10^3 = Conversion factor

= (34.07 g/mole H₂S) (1,000 liters/m³) (1,000 mg/g) (1,000 ml/liter) (2H₂S eq/mole)

NOTE: If C₆H₅AsO is used instead of Na₂S₂O₃, replace Nₐ and Vₐ in Equation 11–4 with Nₐ and Vₐ, respectively (see sections 10.2.1 and 10.2.3).

13.0 Method Performance

13.1 Precision. Collaborative testing has shown the intra-laboratory precision to be 2.2 percent and the inter-laboratory precision to be 5 percent.

13.2 Bias. The method bias was shown to be -4.8 percent when only H₂S was present. In the presence of the interferences cited in section 4.0, the bias was positive at low H₂S concentrations and negative at higher concentrations. At 230 mg H₂S/m³, the level of the compliance standard, the bias was +2.7 percent. Thiols had no effect on the precision.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References


17.0 Tables, Diagrams, Flowcharts, and Validation Data
METHOD 12—DETERMINATION OF INORGANIC LEAD EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the 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 at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Application

1.1 Analytes.
1.2 Applicability. This method is applicable for the determination of inorganic lead emissions from stationary sources, only as specified in an applicable subpart of the regulations.

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 Particulate and gaseous Pb emissions are withdrawn isokinetically from the source and are collected on a filter and in dilute nitric acid. The collected samples are digested in acid solution and are analyzed by atomic absorption spectrophotometry using an air/acetylene flame.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Copper. High concentrations of copper may interfere with the analysis of Pb at 217.0 nm. This interference can be avoided by analyzing the samples at 283.3 nm.

4.2 Matrix Effects. Analysis for Pb by flame atomic absorption spectrophotometry is sensitive to the chemical composition and to the physical properties (e.g., viscosity, pH) of the sample. The analytical procedure requires the use of the Method of Standard Additions to check for these matrix effects, and requires sample analysis using the Method of Standard Additions if significant matrix effects are found to be present.

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 method to establish appropriate safety and health practices and to 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 at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrogen Peroxide (H₂O₂). Irritating to eyes, skin, nose, and lungs.

5.2.2 Nitric Acid (HNO₃). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

6.0 Equipment and Supplies

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 12–1 in section 6.2.7, respectively. It is similar to the Method 5 train. The following items are needed for sample collection:


6.1.2 Impingers. Four impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings are needed. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (½ in.) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. For the second impinger, use the Greenburg-Smith design with the standard tip.

6.1.3 Temperature Sensor. Place a temperature sensor, capable of measuring temperature to within 1 °C (2 °F) at the outlet of the fourth impinger for monitoring purposes.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes, Petri Dishes, Graduated Cylinder and/or Balance, Plastic Storage Containers, and Funnel and Rubber Police Man. Same as Method 5, sections 6.2.1 and 6.2.4 through 6.2.7, respectively.

6.2.2 Wash Bottles. Glass (2).

6.2.3 Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for 0.1 N nitric acid (HNO₃) impinger and probe solutions and washes, 1000-ml. Use screw-cap liners that are either rubber-backed Teflon or leak-free and resistant to chemical attack by 0.1 N HNO₃. (Narrow mouth glass bottles have been found to be less prone to leakage.)

6.2.4 Funnel. Glass, to aid in sample recovery.

6.3 Sample Analysis. The following items are needed for sample analysis:

6.3.1 Atomic Absorption Spectrophotometer. With lead hollow cathode lamp and burner for air/acetylene flame.

6.3.2 Hot Plate.
VerDate Sep<11>2014 12:03 Aug 09, 2019 Jkt 247159 PO 00000 Frm 00370 Fmt 8010 Sfmt 8002 Q:\40\40V9.TXT PC31kpayne on VMOFRWIN702 with $$_JOB

0.0, 4.0, 8.0, 12.0, 16.0, and 20.0 μg Pb/ml, respectively. Prepare, as needed, additional standards at other concentrations in a similar manner.

7.3.6 Air. Suitable quality for atomic absorption spectrophotometry.

7.3.7 Acetylene. Suitable quality for atomic absorption spectrophotometry.

7.3.8 Hydrogen Peroxide, 3 Percent (v/v). Dilute 10 ml of 30 percent H₂O₂ to 100 ml with water.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Follow the same general procedure given in Method 5, section 8.1, except that the filter need not be weighed.

8.2 Preliminary Determinations. Follow the same general procedure given in Method 5, section 8.2.

8.3 Preparation of Sampling Train. Follow the same general procedure given in Method 5, sections 8.3, except place 100 ml of 0.1 N HNO₃ (instead of water) in each of the first two impingers. As in Method 5, leave the third impinger empty and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. Set up the train as shown in Figure 12–1.

8.4 Leak-Check Procedures. Same as Method 5, section 8.4.

8.5 Sampling Train Operation. Same as Method 5, section 8.5.

8.6 Calculation of Percent Isokinetic. Same as Method 5, section 8.6.

8.7 Sample Recovery. Same as Method 5, sections 8.7.1 through 8.7.6.1, with the addition of the following:

8.7.1.1 Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover sample matter and any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with 0.1 N HNO₃ and placing the wash into a glass sample storage container. Measure and record (to the nearest 2 ml) the total amount of 0.1 N HNO₃ used for these rinses. Perform the 0.1 N HNO₃ rinses as follows:

8.7.1.2 Carefully remove the probe nozzle, and rinse the inside surfaces with 0.1 N HNO₃ from a wash bottle while brushing with a stainless steel, Nylon-bristle brush. Brush until the 0.1 N HNO₃ rinse shows no visible particles, then make a final rinse of the inside surface with 0.1 N HNO₃.

8.7.1.3 Brush and rinse with 0.1 N HNO₃, the inside parts of the Swagelok fitting in a similar way until no visible particles remain.

8.7.1.4 Rinse the probe liner with 0.1 N HNO₃. While rotating the probe so that all inside surfaces will be rinsed with 0.1 N HNO₃, tilt the probe, and squirt 0.1 N HNO₃ in the same general procedure given in Method 5, section 8.7.1.3, except place 100 ml of 0.1 N HNO₃, tilt the probe, and squirt 0.1 N HNO₃.
into its upper end. Let the 0.1 N HNO₃ drain from the lower end into the sample container. A glass funnel may be used to aid in transferring liquid washes to the container. Follow the rinse with a probe brush. Hold the probe in an inclined position, squirt 0.1 N HNO₃ into the upper end of the probe as the probe brush is being pushed with a twisting action through the probe; hold the sample container underneath the lower end of the probe, and catch any 0.1 N HNO₃ and sample matter that is brushed from the probe. Run the brush through the probe three times or more until no visible sample matter is carried out with the 0.1 N HNO₃ and none remains on the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times, since metal probes have small crevices in which sample matter can be entrapped. Rinse the probe with 0.1 N HNO₃, and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the brush and filter holder. After all 0.1 N HNO₃ washings and sample matter are collected in the sample container, tighten the lid on the sample container so that the fluid will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify its contents clearly.

8.7.1.5 It is recommended that two people clean the probe to minimize loss of sample. Between sampling runs, keep brushes clean and protected from contamination.

8.7.1.6 After ensuring that all joints are wiped clean of silicone grease, brush and rinse with 0.1 N HNO₃ and sample matter that is brushed from the probe. Run the brush through the probe three times or more until no visible sample matter is carried out with the 0.1 N HNO₃ and none remains on the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times, since metal probes have small crevices in which sample matter can be entrapped. Rinse the probe with 0.1 N HNO₃, and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as described above.

8.8 Blanks.

8.8.1 Nitric Acid. Save 200 ml of the 0.1 N HNO₃ used for rinsing.

8.8.2 Filter. Save two filters from each lot of impingers and connecting glassware in the following manner:

8.7.3.1. Wipe the impinger ball joints free of silicone grease, and cap the joints.

8.7.3.2. Rotate and agitate each impinger, so that the impinger contents might serve as a rinse solution.

8.7.3.3. Transfer the contents of the impingers to a 500-ml graduated cylinder. Remove the outlet ball joint cap, and drain the contents through this opening. Do not separate the impinger parts (inner and outer tubes) while transferring their contents to the cylinder. Measure the liquid volume to within 2 ml. Alternatively, determine the weight of the liquid to within 0.5 g. Record in the log the volume or weight of the liquid present, along with a notation of any color or film observed in the impinger catch. The liquid volume or weight is needed, along with the silica gel data, to calculate the stack gas moisture content (see Method 5, Figure 5–6).

8.7.3.4. Transfer the contents to Container No. 4.

Note: In sections 8.7.3.5 and 8.7.3.6, measure and record the total amount of 0.1 N HNO₃ used for rinsing.

8.7.3.5. Pour approximately 30 ml of 0.1 N HNO₃ into each of the first three impingers and agitate the impingers. Drain the 0.1 N HNO₃ through the outlet arm of each impinger into Container No. 4. Repeat this operation a second time; inspect the impingers for any abnormal conditions.

8.7.3.6. Wipe the ball joints of the glassware connecting the impingers free of silicone grease and rinse each piece of glassware twice with 0.1 N HNO₃; transfer this rinse to Container No. 4. Do not rinse or brush the glass-fritted filter support. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify its contents clearly.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.
9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardizations

NOTE: Maintain a laboratory log of all calibrations.

10.1 Sampling Equipment. Same as Method 5, section 10.0.

10.2 Spectrophotometer.

10.2.1 Measure the absorbance of the standard solutions using the instrument settings recommended by the spectrophotometer manufacturer. Repeat until good agreement (±3 percent) is obtained between two consecutive readings. Plot the absorbance (y-axis) versus concentration in μg Pb/ml (x-axis). Draw or compute a straight line through the linear portion of the curve. Do not force the calibration curve through zero, but if the curve does not pass through the origin or at least lie closer to the origin than ±0.003 absorbance units, check for incorrectly prepared standards and for curvature in the calibration curve.

10.2.2 To determine stability of the calibration curve, run a blank and a standard after calibration curve. Prepared standards and for curvature in the calibration curve. Run a blank and a standard after calibration curve. Prepared standards and for curvature in the calibration curve.

10.2.3 To determine the absorbance for each Pb concentration into the linear absorbance range of the spectrophotometer. Because instruments vary between manufacturers, no detailed operating instructions will be given here. Instead, the instructions provided with the particular instrument should be followed. If the Pb concentration of a sample is at the low end of the calibration curve and

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<th>Section</th>
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<td>11.1</td>
<td>Sample Loss Check. Prior to analysis, check the liquid level in Containers Number 2 and Number 4. Note on the analytical data sheet whether leakage occurred during transport. If a noticeable amount of leakage occurred, either void the sample or take steps, subject to the approval of the Administrator, to adjust the final results.</td>
</tr>
<tr>
<td>11.2</td>
<td>Sample Preparation.</td>
</tr>
<tr>
<td>11.2.1</td>
<td>Container No. 1 (Filter). Cut the filter into strips and transfer the strips and all loose particulate matter into a 125-ml Erlenmeyer flask. Rinse the petri dish with 10 ml of 50 percent HNO₃ to ensure a quantitative transfer, and add to the flask.</td>
</tr>
<tr>
<td>11.2.2</td>
<td>Containers No. 2 and No. 4 (Probe and Impingers). Combine the contents of Containers No. 2 and No. 4, and evaporate to dryness on a hot plate.</td>
</tr>
<tr>
<td>11.2.3</td>
<td>Sample Extraction for Lead.</td>
</tr>
<tr>
<td>11.2.3.1</td>
<td>Based on the approximate stack gas particulate concentration and the total volume of stack gas sampled, estimate the total weight of particulate sample collected. Next, transfer the residue from Containers No. 2 and No. 4 to the 125-ml Erlenmeyer flask that contains the sampling filter using a rubber policeman and 10 ml of 50 percent HNO₃ for every 100 mg of sample collected in the train or a minimum of 30 ml of 50 percent HNO₃, whichever is larger.</td>
</tr>
<tr>
<td>11.2.3.2</td>
<td>Place the Erlenmeyer flask on a hot plate, and heat with periodic stirring for 30 minutes at a temperature just below boiling. If the sample volume falls below 15 ml, add more 50 percent HNO₃. Add 10 ml of 3 percent H₂O₂, and continue heating for 10 minutes. Add 50 ml of hot (80 °C, 176 °F) water, and heat for 20 minutes. Remove the flask from the hot plate, and allow to cool. Filter the sample through a Millipore membrane filter, or equivalent, and transfer the filtrate to a 250-ml volumetric flask. Dilute to volume with water.</td>
</tr>
<tr>
<td>11.2.4</td>
<td>Filter Blank. Cut each filter into strips, and place each filter in a separate 125-ml Erlenmeyer flask. Add 15 ml of 50 percent HNO₃, and treat as described in section 11.2.3 using 10 ml of 3 percent H₂O₂ and 50 ml of hot water. Filter and dilute to a total volume of 100 ml using water.</td>
</tr>
<tr>
<td>11.2.5</td>
<td>Nitric Acid Blank. 0.1 N. Take the entire 200 ml of 0.1 N HNO₃ to dryness on a steam bath, add 15 ml of 50 percent HNO₃, and treat as described in section 11.2.3 using 10 ml of 3 percent H₂O₂ and 50 ml of hot water. Dilute to a total volume of 100 ml using water.</td>
</tr>
<tr>
<td>11.3</td>
<td>Spectrophotometer Preparation. Turn on the power; set the wavelength, slit width, and lamp current; and adjust the background corrector as instructed by the manufacturer’s manual for the particular atomic absorption spectrophotometer. Adjust the burner and flame characteristics as necessary.</td>
</tr>
<tr>
<td>11.4</td>
<td>Analysis.</td>
</tr>
</tbody>
</table>
| 11.4.1  | Lead Determination. Calibrate the spectrophotometer as outlined in section 10.2, and determine the absorbance for each sample source, the filter blank, and 0.1 N HNO₃ blank. Analyze each sample three times in this manner. Make appropriate dilutions, as needed, to bring all sample Pb concentrations into the linear absorbance range of the spectrophotometer. Because instruments vary between manufacturers, no detailed operating instructions will be given here. Instead, the instructions provided with the particular instrument should be followed. If the Pb concentration of a sample is at the low end of the calibration curve and
Environmental Protection Agency

high accuracy is required, the sample can be taken to dryness on a hot plate and the residue dissolved in the appropriate volume of water to bring it into the optimum range of the calibration curve.

11.4.2 Container No. 3 (Silica Gel). This step may be conducted in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

11.5 Check for Matrix Effects. Use the Method of Standard Additions as follows to check at least one sample from each source for matrix effects on the Pb results:

11.5.1 Add or spike an equal volume of standard solution to an aliquot of the sample.

11.5.2 Measure the absorbance of the resulting solution and the absorbance of an aliquot of unspiked sample.

11.5.3 Calculate the Pb concentration \( C_a \) in \( \mu g/ml \) of the sample solution using Equation 12–1 in section 12.5.

Volume corrections will not be required if the solutions as analyzed have been made to the same final volume. Therefore, \( C_a \) and \( C_a \) represent Pb concentration before dilutions.

11.6 Method of Standard Additions procedures described on pages 9–4 and 9–5 of the section entitled “General Information” of the Perkin Elmer Corporation Atomic Absorption Spectrophotometry Manual, Number 393–0152 (Reference 1 in section 17.0) may also be used. In any event, if the results of the Method of Standard Additions procedure used on the single source sample do not agree to within 25 percent of the value obtained by the routine atomic absorption analysis, then reanalyze all samples from the source using the Method of Standard Additions procedure.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

- \( L_i \) = Absorbance of the sample solution.
- \( A_n \) = Cross-sectional area of nozzle, \( m^2 \) (\( ft^2 \)).
- \( A_s \) = Absorbance of the spiked sample solution.
- \( B_w \) = Water in the gas stream, proportion by volume.
- \( C_a \) = Lead concentration in standard solution, \( \mu g/ml \).
- \( C_m \) = Lead concentration in sample solution analyzed during check for matrix effects, \( \mu g/ml \).
- \( C_s \) = Lead concentration in stack gas, dry basis, converted to standard conditions, \( mg/m^3 (g/ft^3) \).
- \( I \) = Percent of isokinetic sampling.
- \( L_i \) = Individual leakage rate observed during the leak-check conducted prior to the first component change, \( m^3/min (ft^3/min) \).
- \( L_{a1} \) = Maximum acceptable leakage rate for either a pretest leak-check or for a leak-check following a component change; equal to 0.00057 \( m^3/min (0.002 cfm) \) or 4 percent of the average sampling rate, whichever is less.
- \( L_o \) = Individual leakage rate observed during the leak-check conducted prior to the 'i'th component change (i = 1, 2, 3 * * * n), \( m^3/min (cfm) \).
- \( L_p \) = Leakage rate observed during the post-test leak-check, \( m^3/min (cfm) \).
- \( m_a \) = Total weight of lead collected in the sample, \( \mu g \).
- \( M \) = Molecular weight of water, 18.0 \( g/g-mole \) (18.0 \( lb/lb-mole \)).
- \( P_{bar} \) = Barometric pressure at the sampling site, mm Hg (in. Hg).
- \( P_v \) = Absolute stack gas pressure, mm Hg (in. Hg).
- \( M_{std} \) = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
- \( R \) = Ideal gas constant, \( 0.08206 [(nm Hg) (m^3)]/[{K} (g-mole)] \), \( [(R) (lb-mole)] \).
- \( T_m \) = Absolute average dry gas meter temperature (see Figure 5–3 of Method 5), °K (°R).
- \( T_{std} \) = Standard absolute temperature, 293 °K (328 °R).
- \( V_i \) = Stack gas velocity, \( m/sec (ft/sec) \).
- \( V_m \) = Volume of gas sample as measured by the dry gas meter, dry basis, \( m^3 (ft^3) \).
- \( V_{m, std} \) = Volume of gas sample as measured by the dry gas meter, corrected to standard conditions, \( m^3 (ft^3) \).
- \( Y \) = Dry gas meter calibration factor.
- \( \Delta H \) = Average pressure differential across the orifice meter (see Figure 5–3 of Method 5), mm H_2O (in. H_2O).
- \( \delta_s \) = Total sampling time, min.
- \( \delta_b \) = Sampling time interval, from the beginning of a run until the first component change, min.
- \( \delta_s \) = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.
- \( \delta_p \) = Sampling time interval, from the final (n\textsuperscript{th}) component change until the end of the sampling run, min.
- \( \rho_w \) = Density of water, 0.9982 g/ml (0.002201 lb/ ml).

12.2 Average Dry Gas Meter Temperatures \( (T_{m, std}) \) and Average Orifice Pressure Drop \( (\Delta H) \). See data sheet (Figure 5–3 of Method 5).

12.3 Dry Gas Volume, Volume of Water Vapor, and Moisture Content. Using data obtained in this test, calculate \( V_{m, std} \), \( V_{w, std} \), and \( B_s \) according to the procedures outlined in Method 5, sections 12.3 through 12.5.

12.4 Total Lead in Source Sample. For each source sample, correct the average absorbance for the contribution of the filter blank and the 0.1 N HNO\textsubscript{3} blank. Use the calibration curve and this corrected absorbance to determine the Pb concentration in the sample aspirated into the spectrophotometer.
Calculate the total Pb content $m$, (in μg) in the original source sample; correct for all the dilutions that were made to bring the Pb concentration of the sample into the linear range of the spectrophotometer.

12.5 Sample Lead Concentration. Calculate the Pb concentration of the sample using the following equation:

$$C_m = C_a \frac{A_m}{A_1 - A_m} \quad \text{Eq. 12-1}$$

12.6 Lead Concentration. Calculate the stack gas Pb concentration $C_s$, using Equation 12-2:

$$C_s = k_s \frac{m}{V_{m(\text{std})}} \quad \text{Eq. 12-2}$$

Where:
- $k_s = 0.001$ mg/μg for metric units.
- $k_s = 1.54 \times 10^{-5}$ gr/μg for English units
- $12.7$ Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate using data obtained in this method and the equations in sections 12.2 and 12.3 of Method 2.
- $12.8$ Isokinetic Variation. Same as Method 5, section 12.11.

13.0 Method Performance

13.1 Precision. The within-laboratory precision, as measured by the coefficient of variation, ranges from 0.2 to 0.5 percent relative to a run-mean concentration. These values were based on tests conducted at a gray iron foundry, a lead storage battery manufacturing plant, a secondary lead smelter, and a lead recovery furnace of an alkyl lead manufacturing plant. The concentrations encountered during these tests ranged from 0.61 to 123.3 mg Pb/m³.

13.2 Analytical Range. For a minimum analytical accuracy of ±10 percent, the lower limit of the range is 100 μg. The upper limit can be extended considerably by dilution.

13.3 Analytical Sensitivity. Typical sensitivities for a 1-percent change in absorption (0.004 absorbance units) are 0.2 and 0.5 μg Pb/ml for the 217.0 and 283.3 nm lines, respectively.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Simultaneous Determination of Particulate Matter and Lead Emissions. Method 12 may be used to simultaneously determine Pb provided:

1. Acetone is used to remove particulate from the probe and inside of the filter holder as specified by Method 5.
2. 0.1 N HNO₃ is used in the impingers.
3. A glass fiber filter with a low Pb background is used, and
4. The entire train contents, including the impingers, are treated and analyzed for Pb as described in Sections 8.0 and 11.0 of this method.

16.2 Filter Location. A filter may be used between the third and fourth impingers provided the filter is included in the analysis for Pb.

16.3 In-Stack Filter. An in-stack filter may be used provided: (1) A glass-lined probe and at least two impingers, each containing 100 ml of 0.1 N HNO₃, after the in-stack filter, are used and (2) the probe and impinger contents are recovered and analyzed for Pb. Recover sample from the nozzle with acetone if a particulate analysis is to be made.

16.4 Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) Analysis. ICP-AES may be used as an alternative to atomic absorption analysis provided the following conditions are met:

1. Sample collection, sample preparation, and analytical preparation procedures are as defined in the method except as necessary for the ICP-AES application.

2. The limit of quantitation for the ICP-AES must be demonstrated, and the sample concentrations reported should be no less than two times the limit of quantitation.

3. The limit of quantitation is defined as ten times the standard deviation of the blank value. The standard deviation of the blank value is determined from the analysis of seven blanks. It has been reported that for mercury and those elements that form hydrides, a continuous-flow generator coupled to an ICP-AES offers detection limits comparable to cold vapor atomic absorption.

4. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) Analysis. ICP-MS may be used as an alternative to atomic absorption analysis.

5. Cold Vapor Atomic Fluorescence Spectrometry (CVAFS) Analysis. CVAFS may be used as an alternative to atomic absorption analysis.

17.0 References

Same as Method 5, section 17.0. References 2, 3, 4, 5, and 7, with the addition of the following:


18.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 12-1. Inorganic Lead Sampling Train.
**Pt. 60, App. A–5, Meth. 13A**

**METHOD 13A—DETERMINATION OF TOTAL FLUORIDE EMISSIONS FROM STATIONARY SOURCES (SPADNS ZIRCONIUM LAKE METHOD)**

**NOTE:** This method does not include all of the 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 at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

### 1.0 Scope and Application

#### 1.1 Analytes

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<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total fluorides as Fluorine</td>
<td>7782–41–4</td>
<td>Not determined</td>
</tr>
</tbody>
</table>

#### 1.2 Applicability

This method is applicable for the determination of fluoride (F⁻) emissions from sources as specified in the regulations. It does not measure fluorocarbons, such as Freons.

#### 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

Gaseous and particulate F⁻ are withdrawn isokinetically from the source and collected in water and on a filter. The total F⁻ is then determined by the SPADNS Zirconium Lake Colorimetric method.

### 3.0 Definitions [Reserved]

### 4.0 Interferences

1. **Chloride.** Large quantities of chloride will interfere with the analysis, but this interference can be prevented by adding silver sulfate into the distillation flask (see section 11.3). If chloride ion is present, it may be easier to use the specific ion electrode method of analysis (Method 13B).

2. **Grease.** Grease on sample-exposed surfaces may cause low F⁻ results due to adsorption.

### 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 method to establish appropriate safety and health practices and to 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 at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

1. **Hydrochloric Acid (HCl).** Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal in minutes. Will react with metals, producing hydrogen.

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

3. **Sulfuric Acid (H₂SO₄).** Rapidly destructive to body tissue. Will cause third-degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m³ for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

### 6.0 Equipment and Supplies

#### 6.1 Sample Collection

A schematic of the sampling train used in performing this method is shown in Figure 13A–1; it is similar to the Method 5 sampling train except that the filter position is interchangeable. The sampling train consists of the following components:

1. **Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Filter Heating System, Temperature Sensor, Metering System, Barometer, and Gas Density Determination Equipment.** Same as Method 5, sections 6.1.1.1, 6.1.1.3 through 6.1.1.7, 6.1.1.9, 6.1.2, and 6.1.3, respectively. The filter heating system and temperature sensor are needed only when moisture condensation is a problem.

2. **Probe Liner.** Borosilicate glass or 316 stainless steel. When the filter is located immediately after the probe, a probe heating system may be used to prevent filter plugging resulting from moisture condensation, but the temperature in the probe shall not be allowed to exceed 120 ± 14 °C (248 ± 25 °F).

3. **Filter Holder.** With positive seal against leakage from the outside or around the filter. If the filter is located between the probe and first impinger, use borosilicate...
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glass or stainless steel with a 20-mesh stainless steel screen filter support and a silicone rubber gasket; do not use a glass frit or a sintered metal filter support. If the filter is located between the third and fourth impingers, borosilicate glass with a glass frit filter support and a silicone rubber gasket may be used. Other materials of construction may be used, subject to the approval of the Administrator.

6.1.4 Impingers. Four impingers connected as shown in Figure 13A-1 with ground-glass (or equivalent), vacuum-tight fittings. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3-cm (1/2 in.) ID glass tube extending to 1.3 cm (1/2 in.) from the bottom of the flask. For the second impinger, use a Greenburg-Smith impinger with the standard tip. Modifications (e.g., flexible connections between the impingers or materials other than glass) may be used, subject to the approval of the Administrator. Place a temperature sensor, capable of measuring temperature to within 1 °C (2 °F), at the outlet of the fourth impinger for monitoring purposes.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Probe-liner and Probe-Nozzle Brushes.
6.2.2 Sample Storage Container. Wide-mouth, high-density polyethylene bottles for impinger water samples, 1 liter.
6.3 Sample Preparation and Analysis. The following items are needed for sample preparation and analysis:

6.3.1 Distillation Apparatus. Glass distillation apparatus assembled as shown in Figure 13A-2.
6.3.2 Bunsen Burner.
6.3.3 Electric Muffle Furnace. Capable of heating to 600 °C (1100 °F).
6.3.4 Crucibles. Nickel, 75- to 100-ml.
6.3.5 Boakers. 500-ml and 1500-ml.
6.3.6 Volumetric Flasks. 50-ml.
6.3.7 Erlenmeyer Flasks or Plastic Bottles. 500-ml.
6.3.8 Constant Temperature Bath. Capable of maintaining a constant temperature of ±0.1 °C at room temperature conditions.
6.3.9 Balance. 300-g capacity, to measure to ±0.5 g.
6.3.10 Spectrophotometer. Instrument that measures absorbance at 570 nm and provides at least a 1-cm light path.
6.3.11 Spectrophotometer Cells. 1-cm path length.

7.0 Reagents and Standards

Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are needed for sample collection:

7.1.1 Filters.
7.1.1.1 If the filter is located between the third and fourth impingers, use a Whatman No. 1 filter, or equivalent, sized to fit the filter holder.
7.1.1.2 If the filter is located between the probe and first impinger, use any suitable medium (e.g., paper, organic membrane) that can withstand prolonged exposure to temperatures up to 135 °C (275 °F), and has at least 95 percent collection efficiency (<5 percent penetration) for 0.3 μm dioctyl phthalate smoke particles. Conduct the filter efficiency test before the test series, using ASTM D 2986-71, 78, or 95a (incorporated by reference—see § 60.17), or use test data from the supplier's quality control program. The filter must also have a low F⁻ blank value (<0.015 mg F⁻/cm² of filter area). Before the test series, determine the average F⁻ blank value of at least three filters (from the lot to be used for sampling) using the applicable procedures described in sections 8.3 and 8.4 of this method. In general, glass fiber filters have high and/or variable F⁻ blank values, and will not be acceptable for use.
7.1.2 Water. Deionized distilled, to conform to ASTM D 1193-77 or 91. Type 3 (incorporated by reference—see § 60.17). If high concentrations of organic matter are not expected to be present, the potassium permanganate test for oxidizable organic matter may be deleted.
7.1.3 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, sections 7.1.2, 7.1.4, and 7.1.5, respectively.
7.2 Sample Recovery. Water, as described in section 7.1.2, is needed for sample recovery.
7.3 Sample Preparation and Analysis. The following reagents and standards are needed for sample preparation and analysis:

7.3.1 Calcium Oxide (CaO). Certified grade containing 0.005 percent F⁻ or less.
7.3.2 Phenolphthalein Indicator. Dissolve 0.1 g of phenolphthalein in a mixture of 50 ml of 90 percent ethanol and 50 ml of water.
7.3.3 Silver Sulfate (Ag₂SO₄). Concentrated.
7.3.4 Sodium Hydroxide (NaOH), Pellets. Same as ASTM D 1193-77, 78, or 95a (incorporated by reference—see § 60.17), or use test data from the supplier's quality control program.
7.3.5 Sulfuric Acid (H₂SO₄), Concentrated.
7.3.6 Sulfuric Acid, 25 Percent (v/v). Mix 1 part of concentrated H₂SO₄ with 3 parts of water.
7.3.7 Filters. Whatman No. 541, or equivalent.
7.3.8 Hydrochloric Acid (HCl). Concentrated.
7.3.9 Water. Same as in section 7.1.2.
7.3.10 Fluoride Standard Solution. 0.01 mg F⁻/ml. Dry approximately 0.5 g of sodium fluoride (NaF) in an oven at 110 °C (230 °F) for at least 2 hours. Dissolve 0.2210 g of NaF in...
8.5 Sampling Train Operation. Follow the general procedure given in Method 5, section 8.3, except that the nozzle size must be selected such that isokinetic sampling rates below 28 liters/min (1.0 cfm) can be maintained.

8.6 Sample Recovery. Proper cleanup procedures begin as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

8.6.1 When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle, and place a cap over it to keep from losing part of the sample. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing water from the impingers into the filter holder.

8.6.2 Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off any silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Remove the filter assembly, wipe off any silicone grease from the filter holder inlet, and cap this inlet. Remove the umbilical cord from the last impinger, and cap the impinger. After wiping off any silicone grease, cap off the filter holder outlet and any open impinger inlets and outlets. Ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

8.6.3 Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.6.4 Inspect the train prior to and during disassembly, and note any abnormal conditions. Treat the samples as follows:

8.6.4.1 Container No. 1 (Probe, Filter, and Impinger Catches).

8.6.4.1.1 Using a graduated cylinder, measure to the nearest ml, and record the volume of the water in the first three impingers; include any condensate in the probe in this determination. Transfer the impinger water from the graduated cylinder into a polyethylene container. Add the filter to this container. (The filter may be handled separately using procedures subject to the Administrator’s approval.) Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, clean all sample-exposed surfaces (including the probe nozzle, probe fitting, probe liner, first three impingers, impinger connectors, and filter holder) with water. Use less than 500 ml for the entire wash. Add the washings to the sample container. Perform the water rinses as follows:

8.6.4.1.2 Carefully remove the probe nozzle and rinse the inside surface with water from a wash bottle. Brush with a Nylon bristle brush, and rinse until the rinse shows no visible particles, after which make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok fitting with water in a similar way.

8.6.4.1.3 Rinse the probe liner with water. While squirting the water into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with water. Let the water drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring the liquid washes to the container. Follow the rinse with a probe brush. Hold the probe in an inclined position, and squirt water into...
the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe, and catch any water and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with water, and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as described above.

8.6.4.1.4 After ensuring that all joints have been wiped clean of the silicone grease, brush and rinse with water the inside of the filter holder (front-half only, if filter is positioned between the third and fourth impingers). Brush and rinse each surface three times or more if needed. Make a final rinse of the brush and filter holder.

8.4.10.1 Sampling equipment leak-check and calibration, Spectrophotometer calibration, Interference/recovery efficiency check during distillation.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Sampling Equipment. Calibrate the probe nozzle, pitot tube, metering system, probe heater, temperature sensors, and barometer according to the procedures outlined in Method 5, sections 10.1 through 10.6. Conduct the leak-check of the metering system according to the procedures outlined in Method 5, section 8.4.1.

10.2 Spectrophotometer.

10.2.1 Prepare the blank standard by adding 10 ml of SPADNS mixed reagent to 50 ml of water.

10.2.2 Accurately prepare a series of standards from the 0.01 mg F⁻/ml standard fluoride solution (Section 7.3.10) by diluting 0, 2, 4, 6, 8, 10, 12, and 14 ml to 100 ml with deionized, distilled water. Pipet 50 ml from each solution, and transfer each to a separate 100-ml beaker. Then add 10 ml of SPADNS mixed reagent (Section 7.3.13) to each. These standards will contain 0, 10, 20, 30, 40, 50, 60, and 70 μg F⁻(0 to 1.4 μg/ml), respectively.

10.2.3 After mixing, place the blank and calibration standards in a constant temperature bath for 30 minutes before reading the absorbance with the spectrophotometer. Adjust all samples to this same temperature before analyzing.

10.2.4 With the spectrophotometer at 570 nm, use the blank standard to set the absorbance to zero. Determine the absorbance of the standards.

10.2.5 Prepare a calibration curve by plotting μg F⁻/50 ml versus absorbance on linear graph paper. Prepare the standard curve initially and thereafter whenever the SPADNS mixed reagent is newly made. Also, run a
calibration standard with each set of samples and, if it differs from the calibration curve by more than 22 percent, prepare a new standard curve.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the liquid levels in Containers No. 1 and No. 2. Determine whether leakage occurred during transport, and note this finding on the analytical data sheet. If noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Treat the contents of each sample container as described below:

11.2.1 Container No. 1 (Probe, Filter, and Impinger Catches). Filter this container’s contents, including the sampling filter, through Whatman No. 541 filter paper, or equivalent, into a 1500-ml beaker.

11.2.1.1 If the filtrate volume exceeds 900 ml, make the filtrate basic with NaOH, and evaporate to less than 900 ml.

11.2.1.2 Place the filtered material (including sampling filter) in a nickel crucible, add some soft glass beads and several small pieces of broken glass tubing, and assemble the apparatus as shown in Figure 1A-2. Heat the flask until it reaches a temperature of 175°C (347°F) to adjust the acid/water ratio for subsequent distillations. Discard the distillate. 

CAUTION: Use a protective shield when carrying out this procedure. Observe standard precautions when mixing H₂SO₄ with water. Slowly add the acid to the flask with constant swirling.

11.3 Distillation.

11.3.1 Cool the contents of the distillation flask to below 80°C (180°F). Pipet an aliquot of sample containing less than 10.0 mg F⁻ directly into the distillation flask, and add water to make a total volume of 220 ml added to the distillation flask. (To estimate the appropriate aliquot size, select an aliquot of the solution, and treat as described in section 11.4.1. This will be an approximation of the F⁻ content because of possible interfering ions.)

NOTE: If the sample contains chloride, add 5 mg of Ag₂SO₄ to the flask for every mg of chloride.

11.3.2 Place a 250-ml volumetric flask at the condenser exit. Heat the flask as rapidly as possible with a Bunsen burner, and collect all the distillate up to 175°C (347°F). During heating, play the burner flame up and down the side of the flask to prevent bumping. Conduct the distillation as rapidly as possible (15 minutes or less). Slow distillations have been found to produce low F⁻ recoveries. Be careful not to exceed 175°C (347°F) to avoid causing H₂SO₄ to distill over. If F⁻ distillation in the mg range is to be followed by a distillation in the fractional mg range, add 220 ml of water and distill it over as in the acid adjustment step to remove residual F⁻ from the distillation system.

11.3.3 The acid in the distillation flask may be used until there is carry-over of interferences or poor F⁻ recovery. Check for interference and for recovery efficiency every tenth distillation using a water blank and a standard solution. Change the acid whenever the F⁻ recovery is less than 90 percent or the blank value exceeds 0.1 μg/ml.

11.4 Sample Analysis.

11.4.1 Containers No. 1 and No. 2.

11.4.1.1 After distilling suitable aliquots from Containers No. 1 and No. 2 according to section 11.3, dilute the distillate in the volumetric flask to exactly 250 ml with water, and mix thoroughly. Pipet a suitable aliquot
of each sample distillate (containing 10 to 40 μg F⁻/ml) into a beaker, and dilute to 50 ml with water. Use the same aliquot size for the blank. Add 10 ml of SPADNS mixed reagent (Section 7.3.13), and mix thoroughly.

11.4.1.2 After mixing, place the sample in a constant-temperature bath containing the standard solutions for 30 minutes before reading the absorbance on the spectrophotometer.

NOTE: After the sample and colorimetric reagent are mixed, the color formed is stable for approximately 2 hours. Also, a 3 °C (5.4 °F) temperature difference between the sample and standard solutions produces an error of approximately 0.005 mg F⁻/liter. To avoid this error, the absorbencies of the sample and standard solutions must be measured at the same temperature.

11.4.1.3 Set the spectrophotometer to zero absorbance at 570 nm with the zero reference solution (Section 7.3.12), and check the spectrophotometer calibration with the standard solution (Section 7.3.10). Determine the absorbance of the samples, and determine the concentration from the calibration curve. If the concentration does not fall within the range of the calibration curve, repeat the procedure using a different size aliquot.

11.4.2 Container No. 3 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation. Other forms of the equations may be used, provided that they yield equivalent results.

12.1 Nomenclature.

A₆ = Aliquot of distillate taken for color development, ml.
A₄ = Aliquot of total sample added to still, ml.
B₆₄ = Water vapor in the gas stream, portion by volume.
C₆ = Concentration of F⁻ in stack gas, mg/decml (gr/decfl).
F₆ = F⁻ concentration from the calibration curve, μg.
F₁ = Total F⁻ in sample, mg.
T₆ = Absolute average dry gas meter (DGM) temperature (see Figure 5–3 of Method 5), °K (°R).
T₄ = Absolute average stack gas temperature (see Figure 5–3 of Method 5), °K (°R).
V₆₄ = Volume of distillate as diluted, ml.
V₄₆ = Volume of gas sample as measured by DGM at standard conditions, decml (decfl).
V₆ = Total volume of F⁻ sample, after final dilution, ml.
V₆₄ₐ₠ = Volume of water vapor in the gas sample at standard conditions, scm (scf)

12.2 Average DGM Temperature and Average Orifice Pressure Drop (see Figure 5–3 of Method 5).

12.3 Dry Gas Volume. Calculate V₄₆ and adjust for leakage, if necessary, using Equation 5–1 of Method 5.

12.4 Volume of Water Vapor and Moisture Content. Calculate V₆₄ and B₆₄ from the data obtained in this method. Use Equations 5–2 and 5–3 of Method 5.

12.5 Total Fluoride in Sample. Calculate the amount of F⁻ in the sample using the following equation:

\[ C_f = \frac{F_1}{V_{m(\text{std})}} \]  

Eq. 13A-2

Where:

1. **K** \(= 10^{-3} \text{ mg/μg (metric units)} = 1.54 \times 10^{-3} \text{ gr/μg (English units)}

12.6 Fluoride Concentration in Stack Gas. Determine the F⁻ concentration in the stack gas using the following equation:

\[ F_1 = \frac{K V_6 V_6' C_6}{A_1 A_4} \]  

Eq. 13A-1

12.7 Isokinetic Variation. Same as Method 5, section 12.11.

13.0 Method Performance

The following estimates are based on a collaborative test done at a primary aluminum smelter. In the test, six laboratories each sampled the stack simultaneously using two sampling trains for a total of 12 samples per sampling run. Fluoride concentrations encountered during the test ranged from 0.1 to 1.4 mg F⁻/m³.

13.1 Precision. The intra- and inter-laboratory standard deviations, which include sampling and analysis errors, were 0.94 mg F⁻/m³ with 60 degrees of freedom and 0.964 mg F⁻/m³ with five degrees of freedom, respectively.

13.2 Bias. The collaborative test did not find any bias in the analytical method.

13.3 Range. The range of this method is 0 to 1.4 μg F⁻/ml.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Compliance with ASTM D 3270–73T, 80, 91, or 95 (incorporated by reference—see §60.17 “Analysis of Fluoride Content of the Atmosphere and Plant Tissues (Semiautomated Method) is an acceptable alternative for the requirements specified in sections 12.2, 11.3, and 11.4.1 when applied to suitable aliquots of Containers 1 and 2 samples.
17.0 References


18.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 13A-1. Fluoride Sampling Train.
METHOD 13B—DETERMINATION OF TOTAL FLUORIDE EMISSIONS FROM STATIONARY SOURCES (SPECIFIC ION ELECTRODE METHOD)

NOTE: This method does not include all of the 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 at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 13A.

1.0 Scope and Application

1.1 Analytes.

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<th>Analyte</th>
<th>CAS No.</th>
<th>Sensitive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total fluorides as Fluorine</td>
<td>7782-41-4</td>
<td>Not determined.</td>
</tr>
</tbody>
</table>

1.2 Applicability. This method is applicable for the determination of fluoride (F⁻) emissions from sources as specified in the regulations. It does not measure fluorocarbons, such as Freons.

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

Gaseous and particulate F⁻ are withdrawn isokinetically from the source and collected in water and on a filter. The total F⁻ is then determined by the specific ion electrode method.

3.0 Definitions [Reserved]

4.0 Interferences

Grease on sample-exposed surfaces may cause low F⁻ results because of adsorption.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the
user of this test method to establish appropriate safety and health practices and to 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 at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

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

5.2.2 Sulfuric Acid (H₂SO₄). Rapidly destructive to body tissue, will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m³ for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. Same as Method 13A, sections 6.1 and 6.2, respectively.

6.2 Sample Preparation and Analysis. The following items are required for sample preparation and analysis:

6.2.1 Distillation Apparatus, Bunsen Burner, Electric Muffle Furnace, Crucibles, Beakers, Volumetric Flasks, Erlenmeyer Flasks or Plastic Bottles, Constant Temperature Bath, and Balance. Same as Method 13A, sections 6.3.1 to 6.3.9, respectively.

6.2.2 Fluoride Ion Activity Sensing Electrode.

6.2.3 Reference Electrode. Single junction, sleeve type.

6.2.4 Electrometer. A pH meter with millivolt-scale capable of ±0.1-mv resolution, or a specific ion meter made specifically for specific ion electrode use.

6.2.5 Magnetic Stirrer and Tetrafluoroethylene (TFE) Fluorocarbon-Coated Stirring Bars.

6.2.6 Beakers. Polyethylene, 100-ml.

7.0 Reagents and Standards

Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection and Sample Recovery. Same as Method 13A, sections 7.1 and 7.2, respectively.

7.2 Sample Preparation and Analysis. The following reagents and standards are required for sample analysis:

7.2.1 Calcium Oxide (CaO). Certified grade containing 0.005 percent F⁻ or less.

7.2.2 Phenolphthalein Indicator. Dissolve 0.1 g phenolphthalein in a mixture of 50 ml of 90 percent ethanol and 50 ml water.

7.2.3 Sodium Hydroxide (NaOH), Pellets.

7.2.4 Sulfuric Acid (H₂SO₄), Concentrated.

7.2.5 Filters. Whatman No. 541, or equivalent.

7.2.6 Water. Same as section 7.1.2 of Method 13A.

7.2.7 Sodium Hydroxide, 5 M. Dissolve 20 g of NaOH in 100 ml of water.

7.2.8 Sulfuric Acid, 25 Percent (v/v). Mix 1 part of concentrated H₂SO₄ with 3 parts of water.

7.2.9 Total Ionic Strength Adjustment Buffer (TISAB). Place approximately 500 ml of water in a 1-liter beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride, and 4 g of cyclohexylene dinitrilo tetraacetic acid. Stir to dissolve. Place the beaker in a water bath and cool to 20 °C (68 °F). Slowly add 5 M NaOH to the solution, measuring the pH continuously with a calibrated pH reference electrode pair, until the pH is 5.3. Pour into a 1-liter volumetric flask, and dilute to volume with deionized, distilled water. Commercially prepared TISAB may be substituted for the above.

7.2.10 Fluoride Standard Solution, 0.1 M. Oven dry approximately 10 g of sodium fluoride (NaF) for a minimum of 2 hours at 110 °C (230 °F), and store in a desiccator. Then add 4.2 g of NaF to a 1-liter volumetric flask, and add enough water to dissolve. Dilute to volume with water.

8.0 Reagents and Standards

8.1 Sample Collection, Preservation, Storage, and Transport

Same as Method 13A, section 8.0.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.
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9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardizations

NOTE: Maintain a laboratory log of all calibrations.

10.1 Sampling Equipment. Same as Method 13A, section 10.1.

10.2 Fluoride Electrode. Prepare fluoride standardizing solutions by serial dilution of the 0.1 M fluoride standard solution. Pipet 10 ml of 0.1 M fluoride standard solution into a 100-ml volumetric flask, and make up to the mark with water for a 10⁻² M standard solution. Use 10 ml of 10⁻² M solution to make a 10⁻³ M solution in the same manner. Repeat the dilution procedure, and make 10⁻⁴ and 10⁻⁵ M solutions.

10.2.1 Pipet 50 ml of each standard into a separate beaker. Add 50 ml of TISAB to each beaker. Place the electrode in the most dilute standard solution. When a steady millivolt reading is obtained, plot the value on the linear axis of semilog graph paper versus concentration on the log axis. Plot the nominal value for concentration of the standard on the log axis, e.g., when 50 ml of 10⁻² M standard is diluted with 50 ml of TISAB, the concentration is still designated “10⁻² M”.

10.2.2 Between measurements, soak the fluoride sensing electrode in water for 30 seconds, and then remove and blot dry. Analyze the standards going from dilute to concentrated standards. A straight-line calibration curve will be obtained, with nominal concentrations of 10⁻¹, 10⁻², 10⁻³, 10⁻⁴ fluoride molarity on the log axis plotted versus electrode potential (in mv) on the linear scale. Some electrodes may be slightly nonlinear between 10⁻¹ and 10⁻⁴ M. If this occurs, use additional standards between these two concentrations.

10.2.3 Calibrate the fluoride electrode daily, and check it hourly. Prepare fresh fluoride standardizing solutions daily (10⁻² M or less). Store fluoride standardizing solutions in polyethylene or polypropylene containers.

NOTE: Certain specific ion meters have been designed specifically for fluoride electrode use and give a direct readout of fluoride ion concentration. These meters may be used in lieu of calibration curves for fluoride measurements over a narrow concentration ranges. Calibrate the meter according to the manufacturer’s instructions.

10.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.0 Nomenclature. Same as Method 13A, section 12.1, with the addition of the following:

\[ M = F^- \] concentration from calibration curve, molarity

12.2 Average DGM Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor and Moisture Content, Fluoride Concentration in Stack Gas, and Isokinetic Variation. Same as Method 13A, sections 12.2 to 12.4, 12.6, and 12.7, respectively.

12.3 Total Fluoride in Sample. Calculate the amount of F⁻ in the sample using Equation 13B–1:

\[ F_i = \frac{K V_i V_A M}{A_i} \]  

\[ \text{Eq. 13B–1} \]

Where:

\[ K = 19 \text{ [(mg·l)/(mole·ml)] (metric units)} \]
\[ = 0.292 \text{ [(gr·l)/(mole·ml)] (English units)} \]

13.0 Method Performance

The following estimates are based on a collaborative test done at a primary aluminum smelter. In the test, six laboratories each sampled the stack simultaneously using two sampling trains for a total of 12 samples per...
sampling run. Fluoride concentrations encountered during the test ranged from 0.1 to 1.4 mg F⁻/m³.

13.1 Precision. The intra-laboratory and inter-laboratory standard deviations, which include sampling and analysis errors, are 0.037 mg F⁻/m³ with 60 degrees of freedom and 0.056 mg F⁻/m³ with five degrees of freedom, respectively.

13.2 Bias. The collaborative test did not find any bias in the analytical method.

13.3 Range. The range of this method is 0.02 to 2,000 μg F⁻/ml; however, measurements of less than 0.1 μg F⁻/ml require extra care.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Compliance with ASTM D 3270–73T, 91, 95 “Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Semiautomated Method)” is an acceptable alternative for the distillation and analysis requirements specified in sections 11.1 and 11.2 when applied to suitable aliquots of Containers 1 and 2 samples.

17.0 References

Same as Method 13A, section 16.0, References 1 and 2, with the following addition:


18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 14—DETERMINATION OF FLUORIDE EMISSIONS FROM POTROOM ROOF MONITORS FOR PRIMARY ALUMINUM PLANTS

NOTE: This method does not include all of the 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 at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 13A, and Method 13B.

1.0 Scope and Application

1.1 Analytes.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>CAS No.</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total fluorides as Fluorine</td>
<td>7782–41–4</td>
<td>Not determined.</td>
</tr>
</tbody>
</table>

1.2 Applicability. This method is applicable for the determination of fluoride emissions from roof monitors at primary aluminum reduction plant potroom groups.

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 Gaseous and particulate fluoride roof monitor emissions are drawn into a permanent sampling manifold through several large nozzles. The sample is transported from the sampling manifold to ground level through a duct. The fluoride content of the gas in the duct is determined using either Method 13A or Method 13B. Effluent velocity and volumetric flow rate are determined using anemometers located in the roof monitor.

3.0 Definitions

Potroom means a building unit which houses a group of electrolytic cells in which aluminum is produced.

Potroom group means an uncontrolled potroom, a potroom which is controlled individually, or a group of potrooms or potroom segments ducted to a common control system.

Roof monitor means that portion of the roof of a potroom where gases not captured at the cell exit from the potroom.

4.0 Interferences

Same as section 4.0 of either Method 13A or Method 13B, with the addition of the following:

4.1 Magnetic Field Effects. Anemometer readings can be affected by potroom magnetic field effects. section 6.1 provides for minimization of this interference through proper shielding or encasement of anemometer components.

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 method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. Same as section 5.2 of either Method 13A or Method 13B.
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6.0 Equipment and Supplies

Same as section 6.0 of either Method 13A or Method 13B, as applicable, with the addition of the following:

6.1 Velocity Measurement Apparatus.

6.1.1 Anemometer Specifications. Propeller anemometers, or equivalent. Each anemometer shall meet the following specifications:

6.1.1.1 Its propeller shall be made of polyvinyl chloride or similar material of uniform density. To ensure uniformity of performance among propellers, it is desirable that all propellers be made from the same mold.

6.1.1.2 The propeller shall be properly balanced, to optimize performance.

6.1.1.3 When the anemometer is mounted horizontally, its threshold velocity shall not exceed 15 m/min (50 ft/min).

6.1.1.4 The measurement range of the anemometer shall extend to at least 600 m/min (2,000 ft/min).

6.1.1.5 The anemometer shall be able to withstand prolonged exposure to dusty and corrosive environments; one way of achieving this is to purge the bearings of the anemometer continuously with filtered air during operation.

6.1.1.6 All anemometer components shall be properly shielded or encased, such that the performance of the anemometer is uninfluenced by potroom magnetic field effects.

6.1.1.7 A known relationship shall exist between the electrical output signal from the anemometer generator and the propeller shaft rpm (see section 10.2.1). Anemometers having other types of output signals (e.g., optical) may be used, subject to the approval of the Administrator. If other types of anemometers are used, there must be a known relationship between output signal and shaft rpm (see section 10.2.2).

6.1.1.8 Each anemometer shall be equipped with a suitable readout system (see section 6.1.3).

6.1.2 Anemometer Installation Requirements.

6.1.2.1 Single, Isolated Potroom. If the affected facility consists of a single, isolated potroom (or potroom segment), install at least one anemometer for every 85 m (280 ft) of roof monitor length. If the length of the roof monitor divided by 85 m (280 ft) is not a whole number, round the fraction to the nearest whole number to determine the number of anemometers needed. For monitors that are less than 130 m (430 ft) in length, use at least two anemometers. Divide the potroom (or segment) monitor cross-section into as many equal areas as anemometers, and locate an anemometer at the centroid of each equal area. See exception in section 6.1.2.3.

6.1.2.2 Two or More Potrooms. If the affected facility consists of two or more potrooms (or potroom segments) ducted to a common control device, install anemometers in each potroom (or segment) that contains a sampling manifold. Install at least one anemometer for every 85 m (280 ft) of roof monitor length of the potroom (or segment). If the potroom (or segment) length divided by 85 m (280 ft) is not a whole number, round the fraction to the nearest whole number to determine the number of anemometers needed. If the potroom (or segment) length is less than 130 m (430 ft), use at least two anemometers. Divide the potroom (or segment) monitor cross-section into as many equal areas as anemometers, and locate an anemometer at the centroid of each equal area. See exception in section 6.1.2.3.

6.1.2.3 Placement of Anemometer at the Center of Manifold. At least one anemometer shall be installed in the immediate vicinity (i.e., within 10 m (33 ft)) of the center of the manifold (see section 6.2.1). For its placement in relation to the width of the monitor, there are two alternatives. The first is to make a velocity traverse of the width of the roof monitor where an anemometer is to be placed and install the anemometer at a point of average velocity along this traverse. The traverse may be made with any suitable low velocity measuring device, and shall be made during normal process operating conditions. The second alternative is to install the anemometer half-way across the width of the roof monitor. In this latter case, the velocity traverse need not be conducted.

6.1.3 Recorders. Recorders that are equipped with suitable auxiliary equipment (e.g., transducers) for converting the output signal from each anemometer to a continuous recording of air flow velocity or to an integrated measure of volumetric flowrate shall be used. A suitable recorder is one that allows the output signal from the propeller anemometer to be read to within 1 percent when the velocity is between 100 and 120 m/min (330 and 390 ft/min). For the purpose of recording velocity, “continuous” shall mean one readout per 15-minute or shorter time interval. A constant amount of time shall elapse between readings. Volumetric flow rate may be determined by an electrical count of anemometer revolutions. The recorders or counters shall permit identification of the velocities or flowrates measured by each individual anemometer.

6.1.4 Pitot Tube. Standard-type pitot tube, as described in section 6.7 of Method 2, and having a known coefficient, determined as outlined in section 4.1 of Method 2.

6.1.5 Pitot Tube (Optional). Isolated, Type S pitot, as described in section 6.1 of Method 2, and having a known coefficient, determined as outlined in section 4.1 of Method 2.

6.1.6 Differential Pressure Gauge. Inclined manometer, or equivalent, as described in section 6.1.2 of Method 2.

6.2 Roof Monitor Air Sampling System.

6.2.1 Manifold System and Ductwork. A minimum of one manifold system shall be installed for each potroom group. The manifold
the sample ports shall be situated so that such as a bend or contraction. The two samplers upstream from any flow disturbance of the Administrator, that there is no through comparative testing, to the satisfaction of the Administrator.

6.2.2 Exhaust Fan. An industrial fan or blower shall be attached to the sample duct at ground level (see Figure 14-1). This exhaust fan shall have a capacity such that a large enough volume of air can be pulled through the ductwork to maintain an isokinetic sampling rate in all the sample nozzles for all flow rates normally encountered in the roof monitor. The exhaust fan volumetric flow rate shall be adjustable so that the roof monitor gases can be drawn isokinetically into the sample nozzles. This control of flow may be achieved by a damper on the inlet to the exhaustor or by any other workable method.

6.3 Temperature Measurement Apparatus. To monitor and record the temperature of the roof monitor effluent gas, and consisting of the following:

6.3.1 Temperature Sensor. A temperature sensor shall be installed in the roof monitor near the sample duct. The temperature sensor shall conform to the specifications outlined in Method 2, section 6.3.

6.3.2 Signal Transducer. Transducer, to change the temperature sensor voltage output to a temperature readout.

6.3.3 Thermocouple Wire. To reach from roof monitor to signal transducer and recorder.

6.3.4 Recorder. Suitable recorder to monitor the output from the thermocouple signal transducer.

7.0 Reagents and Standards

Same as section 7.0 of either Method 13A or Method 13B, as applicable.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Roof Monitor Velocity Determination.

8.1.1 Velocity Estimate(s) for Setting Isokinetic Flow. To assist in setting isokinetic flow in the manifold sample nozzles, the anticipated average velocity in the section of the roof monitor containing the sampling manifold may be continuously monitored during the 24-hour period before the test run. Any convenient means to make this estimate may be used (e.g., the velocity indicated by the anemometer in the section of the roof monitor containing the sampling manifold may be continuously monitored during the 24-hour period before the test run). If there is question as to whether a single estimate of average velocity is adequate for an entire test run (e.g., if velocities are anticipated to be significantly different during different potroom operations), the test run may be divided into two or more “sub-runs,” and a different estimated average velocity may be used for each sub-run (see section 8.4.2).

8.1.2 Velocity Determination During a Test Run. During the actual test run, record the
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8.0, 10.0 ............ Sampling equipment leak-check and calibration.
10.3, 10.4 ........ Initial and periodic performance checks of roof monitor effluent gas characterization apparatus.
11.0 ................ Interference/recovery efficiency check during distillation.

Ensure accurate measurement of gas flow rate in duct and of sample volume.
Ensure accurate and precise measurement of roof monitor effluent gas temperature and flow rate.
Minimize negative effects of used acid.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as section 10.0 of either Method 13A or Method 13B, as applicable, with the addition of the following:

10.1 Manifold Intake Nozzles. The manifold intake nozzles shall be calibrated when the manifold system is installed or, alternatively, the manifold may be preassembled and the nozzles calibrated on the ground just before the start of a sub-run, using the procedure outlined in section 8.4.1 above.

Note: Isokinetic rate adjustments are not permissible during a sub-run.

8.5 Pretest Preparation, Preliminary Determinations, Preparation of Sampling Train, Leak-Check Procedures, Sampling Train Operation, and Sample Recovery. Same as Method 13A, sections 8.1 through 8.6, with the exception of the following:

8.5.1 A single train shall be used for the entire sampling run. Alternatively, if two or more sub-runs are performed, a separate train may be used for each sub-run; note, however, that if this option is chosen, the area of the sampling nozzle shall be the same (±2 percent) for each train. If the test run is divided into sub-runs, a complete traverse of the duct shall be performed during each sub-run.

8.5.2 Time Per Run. Each test run shall last 8 hours or more; if more than one run is to be performed, all runs shall be of approximately the same (±10 percent) length. If questions exist as to the representativeness of an 8-hour test, a longer period should be selected. Conduct each run during a period when all normal operations are performed underneath the sampling manifold. For most recently-constructed plants, 24 hours are required for all potroom operations and events to occur in the area beneath the sampling manifold. During the test period, all pots in the potroom group shall be operated such that emissions are representative of normal operating conditions in the potroom group.

10.1.1 Adjust the exhaust fan to draw a volumetric flow rate (refer to Equation 14-1) such that the entrance velocity into each manifold nozzle approximates the average effluent velocity in the roof monitor.

10.1.2 Measure the velocity of the air entering each nozzle by inserting a standard pitot tube into a 2.5 cm or less diameter hole (see Figure 14-2) located in the manifold between each blast gate (or valve) and nozzle. Note that a standard pitot tube is used, rather...
than a type S, to eliminate possible velocity measurement errors due to cross-section blockage in the small (0.13 m diameter) manifold leg ducts. The pitot tube tip shall be located in the center of each manifold leg duct. Take care to ensure that there is no leakage around the pitot tube, which could affect the indicated velocity in the manifold leg.

10.1.3 If the velocity of air being drawn into each nozzle is not the same, open or close each blast gate (or valve) until the velocity in each nozzle is the same. Fasten each blast gate (or valve) so that it will remain in position, and close the pitot port holes.

10.2 Initial Calibration of Propeller Anemometers.

10.2.1 Anemometers that meet the specifications outlined in section 6.1.1 need not be calibrated, provided that a reference performance curve relating anemometer signal output to air velocity (covering the velocity range of interest) is available from the manufacturer. If a reference performance curve is not available from the manufacturer, such a curve shall be generated.

For the purpose of this method, a “reference” performance curve is defined as one that has been derived from primary standard calibration data, with the anemometer mounted vertically. “Primary standard” data are obtainable by: (a) direct calibration of one or more of the anemometers by the National Institute of Standards and Technology (NIST); (b) NIST-traceable calibration; or (c) Calibration by direct measurement of fundamental parameters such as length and time (e.g., by moving the anemometers through still air at measured rates of speed, and recording the output signals).

10.2.2 Anemometers having output signals other than electrical (e.g., optical) may be used, subject to the approval of the Administrator. If other types of anemometers are used, a reference performance curve shall be generated, using procedures subject to the approval of the Administrator.

10.2.3 The reference performance curve shall be derived from at least the following three points: 60 ±15, 900 ±100, and 1800 ±100 rpm.

10.3 Initial Performance Checks. Conduct these checks within 60 days before the first performance test.

10.3.1 Anemometers. A performance-check shall be conducted as outlined in sections 10.3.1.1 through 10.3.1.3. Alternatively, any other suitable method that takes into account the signal output, propeller condition, and threshold velocity of the anemometer may be used, subject to the approval of the Administrator.

10.3.1.1 Check the signal output of the anemometer by using an accurate rpm generator (see Figure 14–3) or synchronous motors to spin the propeller shaft at each of the three rpm settings described in section 10.2.3, and measuring the output signal at each setting. If, at each setting, the output signal is within 5 percent of the manufacturer’s value, the anemometer can be used. If the anemometer performance is unsatisfactory, the anemometer shall either be replaced or repaired.

10.3.1.2 Check the propeller condition, by visually inspecting the propeller, making note of any significant damage or warpage; damaged or deformed propellers shall be replaced.

10.3.1.3 Check the anemometer threshold velocity as follows: With the anemometer mounted as shown in Figure 14–4(A), fasten a known weight (a straight-pin will suffice) to the anemometer propeller at a fixed distance from the center of the propeller shaft. This will generate a known torque; for example, a 0.1-g weight, placed 10 cm from the center of the shaft, will generate a torque of 1.0 g-cm. If the known torque causes the propeller to rotate downward, approximately 90° (see Figure 14–4(B)), then the known torque is greater than or equal to the starting torque; if the propeller fails to rotate approximately 90°, the known torque is less than the starting torque. By trying different combinations of weight and distance, the starting torque of a particular anemometer can be satisfactorily estimated. Once an estimate of the starting torque has been obtained, the threshold velocity of the anemometer (for horizontal mounting) can be estimated from a graph such as Figure 14–5 (obtained from the manufacturer). If the horizontal threshold velocity is acceptable (<15 m/min [50 ft/min]), when this technique is used, the anemometer can be used. If the threshold velocity of an anemometer is found to be unacceptably high, the anemometer shall either be replaced or repaired.

10.3.2 Recorders and Counters. Check the calibration of each recorder and counter (see section 6.1.2) at a minimum of three points, approximately spanning the expected range of velocities. Use the calibration procedures recommended by the manufacturer, or other suitable procedures (subject to the approval of the Administrator). If a recorder or counter is found to be out of calibration by an average amount greater than 5 percent for the three calibration points, replace or repair the system; otherwise, the system can be used.

10.3.3 Temperature Measurement Apparatus. Check the calibration of the Temperature Measurement Apparatus, using the procedures outlined in section 10.3 of Method 2, at temperatures of 0, 100, and 150 °C (32, 212, and 302 °F). If the calibration is off by more than 5 °C (9 °F) at any of the temperatures, repair or replace the apparatus; otherwise, the apparatus can be used.

10.4 Periodic Performance Checks. Repeat the procedures outlined in section 10.3 no
more than 12 months after the initial performance checks. If the above systems pass the performance checks (i.e., if no repair or replacement of any component is necessary), continue with the performance checks on a 12-month interval basis. However, if any of the above systems fail the performance checks, repair or replace the system(s) that failed and conduct the periodic performance checks on a 3-month interval basis, until sufficient information (to the satisfaction of the Administrator) is obtained to establish a modified performance check schedule and calculation procedure.

NOTE: If any of the above systems fails the 12-month periodic performance checks, the data for the past year need not be recalculated.

12.0 Analytical Procedures

Same as section 11.0 of either Method 13A or Method 13B.

12.1 Nomenclature

A = Roof monitor open area, m² (ft²).
Bₐ = Water vapor in the gas stream, portion by volume.
Cᵢ = Average fluoride concentration in roof monitor air, mg F/dscm (gr/dscf).
Dₙ = Diameter of duct at sampling location, m (ft).
D₀ = Diameter of a roof monitor manifold nozzle, m (ft).
F = Emission Rate multiplication factor, dimensionless.
Fᵢ = Total fluoride mass collected during a particular sub-run (from Equation 13A–1 of Method 13A or Equation 13B–1 of Method 13B), mg F⁻¹ (gr F⁻¹).
Mᵢ = Mole fraction of dry gas, dimensionless.
Pᵢ = Pressure in the roof monitor; equal to barometric pressure for this application.
Qᵢ = Average volumetric flow from roof monitor at standard conditions on a dry basis, m³/min.
Tᵢ = Average roof monitor temperature (from section 8.2), °C (°F).
Vᵢ = Desired velocity in duct at sampling location, m/sec.
Vₙ = Anticipated average velocity (from section 8.1.1) in sampling duct, m/sec.
Vₐ = Arithmetic mean roof monitor effluent gas velocity, m/sec.
Vᵣ = Actual average velocity in the sampling duct (from Equation 2–9 of Method 2 and data obtained from Method 13A or 13B), m/sec.
Vₐ = Average roof monitor effluent gas velocity readings (vᵢ) as measured by the anemometer in the section of the roof monitor containing the sampling manifold. If two or more sub-runs have been performed, the average velocity for each sub-run may be calculated separately.

12.2 Calculate the expected average velocity (v̄ᵢ) in the duct, corresponding to each value of Vᵢ obtained under section 12.2.1, using Equation 14–1.

\[ V_d = \frac{8D_n^2 V_{a}}{60D_d^3} \]  
\[ \text{Eq. 14-1} \]

Where:
8 = number of required manifold nozzles.
60 = sec/min.

12.2.3 Calculate the actual average velocity (vᵢ) in the sampling duct for each run or sub-run according to Equation 2–9 of Method 2, using data obtained during sampling (Section 8.0 of Method 13A).

12.2.4 Express each vᵢ value from section 12.2.3 as a percentage of the corresponding Vᵢ value from section 12.2.2.

12.2.4.1 If vᵢ is less than or equal to 120 percent of v̄ᵢ, the results are acceptable (note that in cases where the above calculations have been performed for each sub-run, the results are acceptable if the average percentage for all sub-runs is less than or equal to 120 percent).

12.2.4.2 If vᵢ is more than 120 percent of v̄ᵢ, multiply the reported emission rate by the following factor:

\[ F = 1 + \frac{100 V_i - 120}{200} \]  
\[ \text{Eq. 14-2} \]

12.3 Average Velocity of Roof Monitor Effluent Gas. Calculate the arithmetic mean roof monitor effluent gas velocity (Vᵢ) using all the velocity or volumetric flow readings from section 8.1.2.

12.4 Average Temperature of Roof Monitor Effluent Gas. Calculate the arithmetic mean roof monitor effluent gas temperature (Tᵢ) using all the temperature readings recorded in section 8.2.

12.5 Concentration of Fluorides in Roof Monitor Effluent Gas.

12.5.1 If a single sampling train was used throughout the run, calculate the average fluoride concentration for the roof monitor using Equation 13A–2 of Method 13A.

12.5.2 If two or more sampling trains were used (i.e., one per sub-run), calculate the average fluoride concentration for the run using Equation 14–3:

\[ C_i = \frac{\sum_{i=1}^{n} (F_i) v_i}{\sum_{i=1}^{n} (V_{a(i)})} \]  
\[ \text{Eq. 14-3} \]
Where:

12.6 Mole Fraction of Dry Gas.

\[ M_d = 1 - B_{w5} \quad \text{Eq. 14-4} \]

12.7 Average Volumetric Flow Rate of Roof Monitor Effluent Gas. Calculate the arithmetic mean volumetric flow rate of the roof monitor effluent gases using Equation 14-5.

\[ Q_{sd} = \frac{K_1 V_{mt} M_d P_m A}{T_{rm}} \quad \text{Eq. 14-5} \]

Where:

- \( K_1 = 0.3858 \text{ K/mm Hg for metric units} \)
- \( = 17.64 \text{ °R/in. Hg for English units} \).
Figure 14-2. Sampling Manifold and Nozzles.
Figure 14-3. Typical RPM Generator.
Figure 14-4. Check of Anemometer Starting Torque.
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.
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 individually, 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-480 metrical 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 a 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 connection, 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.

5.1.2 Barometer. To correct the volumetric flow from the point of roof monitor to 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 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.

6.2 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 (HClO₄). Mix 1:1 with water. Sulfuric acid (H₂SO₄) may be used in place of HClO₄.

7.5 Audit samples. The audit samples discussed shall be prepared 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.

8.1 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 area 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 on.

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.
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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 shall be submitted to the laboratory must investigate procedures and for potential problems. Average recoveries of all three audits shall be prepared to represent concentrations of fluoride that could take place at a minimum of once per year.

9.0 Quality Control

9.1 Laboratory auditing. Laboratory audits of specific and known concentrations of fluoride 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 shall be submitted to the laboratory must investigate procedures and for potential problems. Average recoveries of all three audits shall be prepared to represent concentrations of fluoride that could take place at a minimum of once per year.

10.0 Calibrations

10.1 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 spiro meter of 400 liters (14 ft³) or more capacity, or equivalent, may be used; however, a wet-test meter is usually more practical. The wet-test meter shall be periodically tested with a spiro meter 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 ΔHg, the orifice calibration factor at each orifice setting. Allowable tolerances for Y and ΔHg are given in Figure 5–6 of Method 5 of this appendix. Allowable tolerances for Y and ΔHg 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 (Fv) 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.

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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 until all flowmeters show no more than 5 percent difference among them.

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.

\[ F_v = \frac{(F_d)(X)}{F_c} \]  

\[ \text{Eq. 14A-1} \]

Where

- \( F_v \) = Desired volume of dry gas to be sampled, ft³.
- \( F_d \) = Desired or analytically optimum mass of TF per cassette, micrograms of TF per cassette (μg/cassette).
- \( F_c \) = Number of cassettes used.
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F_e = Typical concentration of TF in emissions to be sampled, μg/ft³, calculated from Equation 14A–2.

\[
F_e = \frac{(R_e)(R_p)(4.536 \times 10^8 \mu g/lb)}{(A_r)(V_r)}
\]

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 (ft²).

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 ft², and the desired (analytically optimum) mass of TF per cassette is 1,500 μg. First calculate the concentration of TF per cassette (\( F_e \)) in μg/ft³ using Equation 14A–2. Then calculate the desired volume of gas to be sampled (\( F_v \)) using Equation 14A–3.

\[
F_e = 20.855 = \frac{(1.0 \text{ lb/ton})(0.1 \text{ tons/min})(4.536 \times 10^8 \mu g/lb)}{(8,700 \text{ ft}^2)(250 \text{ ft/min})}
\]

\[
F_e = 575.40 \text{ ft}^3 = \frac{(1,500 \mu g)(8 \text{ cassettes})}{(20.855 \mu g/\text{ft}^3)}
\]

This is a total of 575.40 ft³ for eight cassettes or 71.925 ft³/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_\text{std} (μg/ft³).

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

\[
R_e = \frac{(\text{TF}_\text{std})(V_r)(A_r)(2.2 \times 10^{-9} \text{ lb}/\mu g)}{(R_p)}
\]

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_\text{std} of 3,000/75 = 5 μg/ft³. The open area of the roof monitor for the potline (\( A_r \)) is 17,400 ft². 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:

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

$$R_e = 0.41 \text{ lb/ton of aluminum produced.}$$

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.
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.
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.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>CAS No.</th>
<th>Sensitivity (ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon disulfide [CS₂]</td>
<td>75–15–0</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbonyl sulfide [COS]</td>
<td>463–58–1</td>
<td>0.5</td>
</tr>
<tr>
<td>Hydrogen sulfide [H₂S]</td>
<td>7783–06–4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

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 a substantial desensitizing effects on the FPD. Compliance with this requirement is 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 build-up 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, 3325 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 constructed to be less than 3-mm (½-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 (½-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 approximated 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 10⁻⁸ 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.
6.3.3 Temperature Sensor, Thermometer or equivalent to monitor bath temperature within 0.1 °C.

7.0 Reagents and Standards

7.1 Fuel. Hydrogen gas (H₂). Prepurified grade or better.
7.2 Combustion Gas. Oxygen (O₂) or air, re-search purity or better.
7.3 Carrier Gas. Prepurified grade or better.
7.4 Diluent. Air containing less than 0.5 ppmv total sulfur compounds and less than 10 ppmv each of moisture and total hydrocarbons.

7.5 Calibration Gases.
7.5.1 Permeation Devices. One each of H₂S, CO, and SO₂. Gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquefied gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.
7.5.2 Cylinder Gases. Cylinder gases may be used as alternatives to permeation devices. The gases must be traceable to a primary standard (such as permeation tubes) and not used beyond the certification expiration date.
7.6 Citrate Buffer. Dissolve 300 g of potassium citrate and 41 g of anhydrous citric acid in 1 liter of water. Alternatively, 294 g of sodium citrate may be substituted for the potassium citrate. Adjust the pH to between 5.4 and 5.6 with potassium citrate or citric acid, as required.

8.0 Sample Collection, Preservation, Transport, and Storage
8.1 Pretest Procedures. After the complete measurement system has been set up at the site and deemed to be operational, the following procedures should be completed before sampling is initiated. These procedures are not required, but would be helpful in preventing any problem which might occur later to invalidate the entire test.
8.1.1 Leak-Check. Appropriate leak-check procedures should be employed to verify the integrity of all components, sample lines, and connections. The following procedure is suggested: For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull a vacuum greater than 50 mm (2 in.) Hg, close off the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid (detergent in water, for example) at each joint. Bubbling indicates the presence of a leak. As an alternative to the initial leak-test, the sample line loss test described in section 8.3.1 may be performed to verify the integrity of components.
8.1.2 System Performance. Since the complete system is calibrated at the beginning and end of each day of testing, the precise calibration of each component is not critical. However, these components should be verified to operate properly. This verification can be performed by observing the response of flowmeters or of the GC output to changes in flow rates or calibration gas concentrations, respectively, and ascertaining the response to be within predicted limits. If any component or the complete system fails to respond in a normal and predictable manner, the source of the discrepancy should be identified and corrected before proceeding.
8.2 Sample Collection and Analysis.
8.2.1 After performing the calibration procedures outlined in section 10.0, insert the sampling probe into the test port ensuring that no dilution air enters the stack through the port. Begin sampling and dilute the sample approximately 9:1 using the dilution system. Note that the precise dilution factor is the one determined in section 10.1. Condition the entire system with sample for a minimum of 15 minutes before beginning the analysis. Inject aliquots of the sample into the GC/FPD analyzer for analysis. Determine the concentration of each reduced sulfur compound directly from the calibration curves or from the equation for the least-squares line.
8.2.2 If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if the probe or filter is clogged with particulate matter. If either is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning or replacing the probe and filter. After each run, the probe and filter shall be inspected and, if necessary, replaced.
8.2.3 A sample run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours.

8.3 Post-Test Procedures.
8.3.1 Sample Line Loss. A known concentration of H₂S at the level of the applicable standard, ±20 percent, must be introduced into the sampling system at the opening of the probe in sufficient quantities to ensure that there is an excess of sample which must be vented to the atmosphere. The sample must be transported through the entire sampling system to the measurement system in the same manner as the emission samples. The resulting measured concentration is compared to the known value to determine
the sampling system loss. For sampling losses greater than 20 percent, the previous sample run is not valid. Sampling losses of 0–20 percent must be corrected by dividing the resulting sample concentrations by the fraction of recovery. The known gas sample may be calibration gas as described in section 7.5. Alternatively, cylinder gas containing H₂S mixed in nitrogen and verified according to section 7.1.4 of Method 16A may be used. The optional pretest procedures provide a good guideline for determining if there are leaks in the sampling system.

8.3.2 Determination of Calibration Drift. After each run, or after a series of runs made within a 24-hour period, perform a partial recalibration using the procedures in section 10.0. Only H₂S (or other permeant) need be used to recalibrate the GC/FPD analysis system and the dilution system. Partial recalibration may be performed at the mid-level calibration gas concentration or at a concentration measured in the samples but not less than the lowest calibration standard used in the initial calibration. Compare the calibration curves obtained after the runs to the calibration curves obtained under section 10.3. The calibration drift should not exceed the limits set forth in section 13.4. If the drift exceeds this limit, the intervening run or runs should be considered invalid. As an option, the calibration data set that gives the highest sample values may be chosen by the tester.

9.0 Quality Control

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<tr>
<td>8.3.1</td>
<td>Sample line loss check</td>
<td>Ensures that uncorrected negative bias introduced by sample loss is no greater than 20 percent, and provides for correction of bias of 20 percent or less.</td>
</tr>
<tr>
<td>8.3.2</td>
<td>Calibration drift test</td>
<td>Ensures that bias introduced by drift in the measurement system output during the run is no greater than 5 percent.</td>
</tr>
<tr>
<td>10.0</td>
<td>Analytical calibration</td>
<td>Ensures precision of analytical results within 5 percent.</td>
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10.0 Calibration and Standardization

Prior to any sampling run, calibrate the system using the following procedures. (If more than one run is performed during any 24-hour period, a calibration need not be performed prior to the second and any subsequent runs. However, the calibration drift must be determined as prescribed in section 8.3.2 after the last run is made within the 24-hour period.)

NOTE: This section outlines steps to be followed for use of the GC/FPD and the dilution system. The calibration procedure does not include detailed instructions because the operation of these systems is complex, and it requires an understanding of the individual system being used. Each system should include a written operating manual describing in detail the operating procedures associated with each component in the measurement system. In addition, the operator should be familiar with the operating principles of the components, particularly the GC/FPD. The references in section 16.0 are recommended for review for this purpose.

10.1 Calibration Gas Permeation Tube Preparation.

10.1.1 Insert the permeation tubes into the tube chamber. Check the bath temperature to assure agreement with the calibration temperature of the tubes within 0.1 °C. Allow 24 hours for the tubes to equilibrate. Alternatively, equilibration may be verified by injecting samples of calibration gas at 1-hour intervals. The permeation tubes can be assumed to have reached equilibrium when consecutive hourly samples agree within 5 percent of their mean.

10.1.2 Vary the amount of air flowing over the tubes to produce the desired concentrations for calibrating the analytical and dilution systems. The air flow across the tubes must at all times exceed the flow requirement of the analytical systems. The concentration in ppmv generated by a tube containing a specific permeant can be calculated using Equation 15–1 in section 12.2.

10.2 Calibration of Analytical System. Generate a series of three or more known concentrations spanning the linear range of the FPD (approximately 0.5 to 10 ppmv for a 1-ml sample) for each of the three major sulfur compounds. Bypassing the dilution system, inject these standards into the GC/FPD and monitor the responses until three consecutive injections for each concentration agree within 5 percent of their mean. Failure to attain this precision indicates a problem in the calibration or analytical system. Any such problem must be identified and corrected before proceeding.

10.3 Calibration Curves. Plot the GC/FPD response in current (amperes) versus their causative concentrations in ppmv on log-log coordinate graph paper for each sulfur compound. Alternatively, a least-squares equation may be generated from the calibration data using concentrations versus the appropriate instrument response units.

10.4 Calibration of Dilution System. Generate a known concentration of H₂S using the permeation tube system. Adjust the flow rate of diluent air for the first dilution stage
so that the desired level of dilution is approximated. Inject the diluted calibration gas into the GC/FPD system until the results of three consecutive injections for each dilution agree within 5 percent of their mean. Failure to attain this precision in this step is an indication of a problem in the dilution system. Any such problem must be identified and corrected before proceeding. Using the calibration data for H$_2$S (developed under section 10.3), determine the diluted calibration gas concentration in ppmv. Then calculate the dilution factor as the ratio of the calibration gas concentration before dilution to the diluted calibration gas concentration determined under this section. Repeat this procedure for each stage of dilution required. Alternatively, the GC/FPD system may be calibrated by generating a series of three or more concentrations of each sulfur compound and diluting these samples before injecting them into the GC/FPD system. These data will then serve as the calibration data for the unknown samples and a separate determination of the dilution factor will not be necessary. However, the precision requirements are still applicable.

**11.0 Analytical Procedure**

Sample collection and analysis are concurrent for this method (see section 8.0).

**12.0 Data Analysis and Calculations**

12.1 Nomenclature.

- $C = \text{Concentration of permeant produced, ppmv.}$
- $\text{COS} = \text{Carbonyl sulfide concentration, ppmv.}$
- $\text{CS}_2 = \text{Carbon disulfide concentration, ppmv.}$
- $d = \text{Dilution factor, dimensionless.}$
- $\text{H}_2\text{S} = \text{Hydrogen sulfide concentration, ppmv.}$
- $K = 24.04 \, \text{L/g mole. (Gas constant at 20 °C and 760 mm Hg)}$
- $L = \text{Flow rate, L/min, of air over permeant 20 °C, 760 mm Hg.}$
- $M = \text{Molecular weight of the permeant, g/g-mole.}$
- $N = \text{Number of analyses performed.}$
- $P_r = \text{Permeation rate of the tube, µg/min.}$

12.2 Permeant Concentration. Calculate the concentration generated by a tube containing a specific permeant (see section 10.1) using the following equation:

$$C = \frac{KP_r}{ML} \quad \text{Eq. 15-1}$$

12.3 Calculation of SO$_2$ Equivalent. SO$_2$ equivalent will be determined for each analysis made by summing the concentrations of each reduced sulfur compound resolved during the given analysis. The SO$_2$ equivalent is expressed as SO$_2$ in ppmv.

$$\text{SO}_2\text{ equivalent}_i = \sum (\text{H}_2\text{S, COS, 2CS}_2)d \quad \text{Eq. 15-2}$$

12.4 Average SO$_2$ Equivalent. This is determined using the following equation. Systems that do not remove moisture from the sample but condition the gas to prevent condensation must correct the average SO$_2$ equivalent for the fraction of water vapor present. This is not done under applications where the emission standard is not specified on a dry basis.

$$\text{Avg SO}_2\text{ equivalent} = \frac{\sum_{i=1}^{n} \text{SO}_2\text{ equivalent}_i}{N} \quad \text{Eq. 15-3}$$

Where:

- $\text{Avg SO}_2\text{ equivalent} = \text{Average SO}_2\text{ equivalent in ppmv, dry basis.}$
- $\text{Average SO}_2\text{ equivalent}_i = \text{SO}_2$ in ppmv as determined by Equation 15-2.

**13.0 Method Performance**

13.1 Range. Coupled with a GC system using a 1-ml sample size, the maximum limit of the FPD for each sulfur compound is approximately 10 ppmv. It may be necessary to
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dilute samples from sulfur recovery plants a hundredfold (99:1), resulting in an upper limit of about 1000 ppmv for each compound.

13.2 Sensitivity. The minimum detectable concentration of the FPD is also dependent on sample size and would be about 0.5 ppmv for a 1-ml sample.

13.3 Calibration Precision. A series of three consecutive injections of the same calibration gas, at any dilution, shall produce results which do not vary by more than 5 percent from the mean of the three injections.

13.4 Calibration Drift. The calibration drift determined from the mean of three injections made at the beginning and end of any run or series of runs within a 24-hour period shall not exceed 5 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References.


17.0 Tables, Diagrams, Flowcharts, and Validation Data
Figure 15-1. Sampling and Dilution Apparatus.
Figure 15-2. Gas Chromatographic Flame Photometric Analyzer.
METHOD 15A—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM SULFUR RECOVERY PLANTS IN PETROLEUM REFINERIES

NOTE: This method does not include all of the 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 at least the following additional test methods: Method 1, Method 6, Method 15, and Method 16A.

1.0 Scope and Application

1.1 Analytes.
1.2 Applicability. This method is applicable for the determination of emissions of reduced sulfur compounds from sulfur recovery plants where the emissions are in a reducing atmosphere, such as in Stretford units.

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 An integrated gas sample is extracted from the stack, and combustion air is added to the oxygen (O₂)-deficient gas at a known rate. The reduced sulfur compounds (including carbon disulfide (CS₂), carbonyl sulfide (COS), and hydrogen sulfide (H₂S)) are thermally oxidized to sulfur dioxide (SO₂), which is then collected in hydrogen peroxide as sulfate ion and analyzed according to the Method 6 barium-thorin titration procedure.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Reduced sulfur compounds, other than CS₂, COS, and H₂S, that are present in the emissions will also be oxidized to SO₂, causing a positive bias relative to emission standards that limit only the three compounds listed above. For example, thiophene has been identified in emissions from a Stretford unit and produced a positive bias of 30 percent in the Method 15A result. However, these biases may not affect the outcome of the test at units where emissions are low relative to the standard.

4.2 Calcium and aluminum have been shown to interfere in the Method 6 titration procedure. Since these metals have been identified in particulate matter emissions from Stretford units, a Teflon filter is required to minimize this interference.

4.3 Dilution of the hydrogen peroxide (H₂O₂) absorbing solution can potentially reduce collection efficiency, causing a negative bias. When used to sample emissions containing 7 percent moisture or less, the mid-derm impingers have sufficient volume to contain the condensate collected during sampling. Dilution of the H₂O₂ does not affect the collection of SO₂. At higher moisture contents, the potassium citrate-citric acid buffer system used with Method 16A should be used to collect the condensate.

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 method 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. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H₂O₂). Irritating to eyes, skin, nose, and lungs.

5.2.2 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.

5.2.3 Sulfuric Acid (H₂SO₄). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m³ will cause lung damage in uninitiated. 1 mg/m³ for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train used in performing this method is shown in Figure 15A-1, and component parts are discussed below. Modifications to this sampling train are acceptable provided that the system performance check is met.

6.1.1 Probe. 6.4-mm (¼-in.) OD Teflon tubing sequentially wrapped with heat-resistant fiber strips, a rubberized heating tape (with a plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or some other suitable temperature-measuring device shall be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored. The probe should be sheathed in stainless steel to provide in-stack rigidity. A series of bored-out stainless steel fittings placed at the front of the sheath will prevent fine gas from entering between the probe and sheath. The sampling probe is depicted in Figure 15A-2.

6.1.2 Particulate Filter. A 50-mm Teflon filter holder and a 1- to 2-mm porosity Teflon filter (available through Savillex Corporation, 5225 Highway 101, Minnetonka, Minnesota 55345). The filter holder must be

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<tr>
<th>Analyte</th>
<th>CAS No.</th>
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<tbody>
<tr>
<td>Reduced sulfur compounds</td>
<td>None assigned</td>
<td>Not determined.</td>
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maintained in a hot box at a temperature high enough to prevent condensation.

6.1.3 Combustion Air Delivery System. As shown in the schematic diagram in Figure 15A–3. The rate meter should be selected to measure an air flow rate of 0.5 liter/min (0.02 ft³/min).

6.1.4 Combustion Tube. Quartz glass tubing with an expanded combustion chamber 2.54 cm (1 in.) in diameter and at least 30.5 cm (12 in.) long. The tube ends should have an outside diameter of 0.6 cm (¼ in.) and be at least 15.3 cm (6 in.) long. This length is necessary to maintain the quartz-glass connector near ambient temperature and thereby avoid leaks. Alternatively, the outlet may be constructed with a 90 degree glass elbow and socket that would fit directly onto the inlet of the first peroxide impinger.

6.1.5 Furnace. Of sufficient size to enclose the combustion tube. The furnace must have a temperature regulator capable of maintaining the temperature at 1100 ±50 °C (2012 ±90 °F). The furnace operating temperature must be checked with a thermocouple to ensure accuracy. Lindberg furnaces have been found to be satisfactory.

6.1.6 Peroxide Impingers, Stopcock Grease, Temperature Sensor, Drying Tube, Valve, Pump, and Barometer. Same as in Method 6, sections 6.1.1.2, 6.1.1.4, 6.1.1.5, 6.1.1.6, 6.1.1.7, 6.1.1.8, and 6.1.2, respectively, except that the midget bubbler of Method 6, section 6.1.1.2 is not required.

6.1.7 Vacuum Gauge and Rate Meter. At least 760 mm Hg (30 in. Hg) gauge and rotameter, or equivalent, capable of measuring flow rate to ±5 percent of the selected flow rate and calibrated as in section 10.2.

6.1.8 Volume Meter. Dry gas meter capable of measuring the sample volume under the particular sampling conditions with an accuracy of 2 percent.

6.1.9 U-tube manometer. To measure the pressure at the exit of the combustion gas dry gas meter.

6.2 Sample Recovery and Analysis. Same as Method 6, sections 6.2 and 6.3, except a 10-ml buret with 0.05-ml graduations is required for titrant volumes of less than 10.0 ml, and the spectrophotometer is not needed.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. When the specifications are not available, the best available grade shall be used.

7.1 Sample Collection. The following reagents and standards are required for sample analysis:

7.1.1 Water. Same as Method 6, section 7.1.1.

7.1.2 Hydrogen Peroxide (H₂O₂). 3 Percent by Volume. Same as Method 6, section 7.1.3 (40 ml is needed per sample).

7.1.3 Recovery Check Gas. Carbonyl sulfide in nitrogen (100 parts per million by volume (ppmv) or greater, if necessary) in an aluminum cylinder. Concentration certified by the manufacturer with an accuracy of ±2 percent or better, or verified by gas chromatography where the instrument is calibrated with a COS permeation tube.

7.1.4 Combustion Gas. Air, contained in a gas cylinder equipped with a two-stage regulator. The gas shall contain less than 50 ppb of reduced sulfur compounds and less than 10 ppm total hydrocarbons.

7.2 Sample Recovery and Analysis. Same as Method 6, sections 7.2 and 7.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train. For the Method 6 part of the train, measure 20 ml of 3 percent H₂O₂ into the first and second midget impingers. Leave the third midget impinger empty and add silica gel to the fourth impinger. Alternatively, a silica gel drying tube may be used in place of the fourth impinger. Place crushed ice and water around all impingers. Maintain the oxidation furnace at 1100 ±50 °C (2012 ±90 °F) to ensure 100 percent oxidation of COS. Maintain the probe and filter temperatures at a high enough level (no visible condensation) to prevent moisture condensation and monitor the temperatures with a thermocouple.

8.2 Leak-Check Procedure. Assemble the sampling train and leak-check as described in Method 6, section 8.2. Include the combustion air delivery system from the needle valve forward in the leak-check.

8.3 Sample Collection. Adjust the pressure on the second stage of the regulator on the combustion air cylinder to 15 psig. Adjust the combustion air flow rate to 0.5 ±0.05 L/min (1.1 ±0.1 ft³/hr) before injecting combustion air into the sampling train. Then inject combustion air into the sampling train, start the sample pump, and open the stack sample gas valve. Carry out these operations within 15 to 30 seconds to avoid pressurizing the sampling train. Adjust the total sample flow rate to 2.0 ±0.2 L/min (4.2 ±0.4 ft³/hr). These flow rates produce an O₂ concentration of 5.0 percent in the stack gas, which must be maintained constantly to allow oxidation of reduced sulfur compounds to SO₂. Adjust these flow rates during sampling as necessary. Monitor and record the combustion air manometer reading at regular intervals during the sampling period. Sample for 1 or 3 hours. At the end of sampling, turn off the sample pump and combustion air simultaneously (within 30 seconds of each other). All other procedures are the same as in Method 6, section 8.3, except that the sampling train should not be purged. After collecting the
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1.0 Calibration and Standardization

10.1 Metering System, Temperature Sensors, Barometer, and Barium Perchlorate Solution. Same as Method 6, sections 10.1, 10.2, 10.4, and 10.5, respectively.

10.2 Rate Meter. Calibrate with a bubble flow tube.

11.0 Analytical Procedure

11.1 Sample Loss Check and Sample Analysis. Same as Method 6, sections 11.1 and 11.2.

12.0 Data Analysis and Calculations

In the calculations, retain at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Nomenclature.

\[ \text{COS} = \text{Concentration of COS recovery gas, ppm.} \]
\[ \text{C}_{\text{RS}}^{\text{act}} = \text{Actual concentration of recovery check gas (after dilution), ppm.} \]
\[ \text{C}_{\text{RS}}^{\text{meas}} = \text{Measured concentration of recovery check gas generated, ppm.} \]
\[ \text{C}_{\text{RS}} = \text{Concentration of reduced sulfur compounds as SO}_2, \text{dry basis, corrected to standard conditions, ppm.} \]
\[ \text{N} = \text{Normality of barium perchlorate titrant, milliequivalents/ml.} \]
\[ \text{P}_{\text{bar}} = \text{Barometric pressure at exit orifice of the dry gas meter, mm Hg.} \]
\[ \text{P}_{\text{std}} = \text{Standard absolute pressure, 760 mm Hg.} \]
\[ \text{Q}_{\text{COS}} = \text{Flow rate of COS recovery gas, liters/min.} \]
\[ \text{Q}_0 = \text{Flow rate of diluent N}_2, \text{liters/min.} \]
\[ \text{R} = \text{Recovery efficiency for the system performance check, percent.} \]
\[ \text{T}_\text{m} = \text{Average dry gas meter absolute temperature, K.} \]

9.0 Quality Control

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<td>System performance check</td>
<td>Ensures validity of sampling train components and analytical procedure.</td>
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<tr>
<td>8.2, 10.0</td>
<td>Sampling equipment leak-check and calibration.</td>
<td>Ensures accurate measurement of stack gas flow rate, sample volume.</td>
</tr>
<tr>
<td>10.0</td>
<td>Barium standard solution standardization</td>
<td>Ensures precision of normality determination.</td>
</tr>
<tr>
<td>11.1</td>
<td>Replicate titrations</td>
<td>Ensures precision of titration determinations.</td>
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\[ V_{\text{ms}} = \text{dry gas volume measured by the sample train dry gas meter, corrected to standard conditions, liters.} \]

\[ V_{\text{mc}} = \text{dry gas volume measured by the combustion air dry gas meter, corrected to standard conditions, liters.} \]

\[ T_{\text{std}} = \text{standard absolute temperature, 293 °K.} \]

\[ V_{\text{soln}} = \text{total volume of solution in which the sulfur dioxide sample is contained, 100 ml.} \]

\[ V_t = \text{volume of barium perchlorate titrant used for the sample (average of replicate titrations), ml.} \]

\[ V_b = \text{volume of barium perchlorate titrant used for the blank, ml.} \]

\[ Y = \text{calibration factor for sampling train dry gas meter.} \]

\[ Y_c = \text{calibration factor for combustion air dry gas meter.} \]

\[ 32.03 = \text{equivalent weight of sulfur dioxide, mg/meq.} \]

\[ 12025 \text{ ml} \text{ meq} = \frac{(32.03 \text{ mg}) (24.051) \text{ mole}}{(64.06 \text{ g}) (10^3 \text{ ml})} \]

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

\[ V_{m(\text{std})} = V_{ms} \frac{T_{\text{std}} P_{\text{bar}}}{T_m P_{\text{std}}} \quad \text{Eq. 15A-1} \]

\[ = K_1 Y \frac{V_{mc} P_{\text{bar}}}{T_m} \]

Where:

\[ K_1 = 0.3855 \text{ °K/mm Hg for metric units,} \]

\[ = 17.65 \text{ °R/in. Hg for English units.} \]

12.3 Combustion Air Gas Volume, corrected to Standard Conditions.

\[ V_{mc(\text{std})} = K_1 Y_c \frac{(V_{mc} P_{\text{bar}})}{T_m} \quad \text{Eq. 15A-2} \]

NOTE: Correct \( P_{\text{bar}} \) for the average pressure of the manometer during the sampling period.

12.4 Concentration of reduced sulfur compounds as ppm SO₂.

\[ C_{RS} = K_2 N \frac{(V_t - V_b)(V_{soln} / V_a)}{V_{ms(\text{std})} - V_{mc(\text{std})}} \quad \text{Eq. 15A-3} \]

Where:
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\[ K_2 = \frac{32.03 \text{ mg meq}}{24.05 \text{ l mole}} \times \frac{1 \text{ mole}}{64.06 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ ml}} \times \frac{10^3 \text{ ml}}{1 \text{ l ml}} = 12025 \text{ ml meq} \]

12.5 Concentration of Generated Recovery Gas.

\[ C_{RG} = \left( \frac{C_{\cos}}{Q_{\cos}} \right) \left( \frac{Q_{\cos} + Q_{N_2}}{Q_{\cos}} \right) \quad \text{Eq. 15A-4} \]

12.6 Recovery Efficiency for the System Performance Check.

\[ R = \frac{C_{RG(m)}}{C_{RG(act)}} \times 100 \quad \text{Eq. 15A-5} \]

13.0 Method Performance

13.1 Analytical Range. The lower detectable limit is 0.1 ppmv when sampling at 2 lpm for 3 hours or 0.3 ppmv when sampling at 2 lpm for 1 hour. The upper concentration limit of the method exceeds concentrations of reduced sulfur compounds generally encountered in sulfur recovery plants.

13.2 Precision. Relative standard deviations of 2.8 and 6.9 percent have been obtained when sampling a stream with a reduced sulfur compound concentration of 41 ppmv as SO\(_2\) for 1 and 3 hours, respectively.

13.3 Bias. No analytical bias has been identified. However, results obtained with this method are likely to contain a positive bias relative to emission regulations due to the presence of nonregulated sulfur compounds (that are present in petroleum) in the emissions. The magnitude of this bias varies accordingly, and has not been quantified.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References


17.0 Tables, Diagrams, Flowcharts, and Validation Data
Figure 15A-1. Method 15A Sampling Train.
Figure 15A-2. Method 15A Sampling Probe.
Figure 15A-3. Combustion Air Delivery System.
Figure 15A-4. Recovery Gas Generator System.