SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

METHOD 6.2

DETERMINATION OF HYDROGEN SULFIDE

OFFICE OF OPERATIONS
TECHNICAL SERVICES DIVISION
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METHOD 6.2

DETERMINATION OF HYDROGEN SULFIDE

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METHOD 6.2

DETERMINATION OF HYDROGEN SULFIDE

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1. Overview

1.1 Principle

Hydrogen sulfide (H_2S) is collected from a source in a series of standard Greenburg-Smith impingers and absorbed in pH 4.0 cadmium sulfate ($CdSO_4$) solution to form cadmium sulfide (CdS), which then is measured iodometrically. An impinger containing hydrogen peroxide (H_2O_2) removes sulfur dioxide (SO_2) as an interfering species. If SO_2 is known to be absent, the first impinger containing 3 percent H_2O_2 may be eliminated.

1.2 Applicability

This method determines the hydrogen sulfide content of effluent gas streams.

1.3 Range and Sensitivity

For one cubic meter of sample, the lower limit of detection is several mg/m^3 (several ppm). The upper limit is 1000 mg/m^3 (700 ppm), which can be extended by increasing the quantity of $CdSO_4$ solution in the impingers.

1.4 Interferences

If a compound that reduces iodine or oxidizes iodide ion is collected in the cadmium sulfate impingers, it will interfere in this procedure. SO_2, in concentrations of several hundred mg/m^3, is eliminated by the H_20_2. This can be increased by adding more H_20_2 solution. Thiols precipitate with H_2S. In the absence of H_2S, only co-traces of thiols are collected. Carbon oxysulfide at a concentration of 20 percent does not interfere. Certain carbon-containing compounds react with iodine and produce recurring end points.

Entrained H_2O_2 produces a negative interference equivalent to 100 percent of that of an equimolar quantity of H_2S. Avoid entrainment of H_2O_2 into the $CdSO_4$ impingers by inserting an empty Greenburg-Smith impinger after the peroxide impinger. The empty impinger should be modified by replacing the tip with 13 mm (1/2 in.) inside diameter glass tube extending to 13 mm (1/2 in.) from the bottom of the flask.

1.5 Precision and Accuracy

Collaborative testing has shown the within-laboratory coefficient of variation to be 2.2 percent and the overall coefficient of variation to be 5 percent. The method bias was shown to be -4.8 percent when only H_2S was present.

The above figures are based on EPA Method 11, using midget impingers. Precision and accuracy using Greenburg-Smith impingers are not available.

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2. Field Procedures

2.1 Sampling Apparatus

2.1.1 Sampling Train

A schematic of the sampling train used in this method is shown in Figure 6.2-1. The sampling train has the following components:

a. Sampling Probe

Use glass or stainless steel probe for sampling standard exhaust stacks. For sampling a pressurized fuel line, connect the sampling train directly with 6 to 7 mm (1/4 in.) Teflon or equivalent tubing.

b. Impingers

Six impingers are connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings.

The first, third, and fourth impingers must be Greenburg-Smith design with the standard tip. The second, fifth, and sixth impingers must be of the Greenburg-Smith design, modified by replacing the tip with 13 mm (1/2 in.) ID glass tube extending to about 13 mm (1/2 in.) from the bottom of the flask.

c. Ice Bath Container

An ice bath maintains the absorbing solution at a low temperature ($60^{\circ}F$).

d. Volume Meter

Sample volume is measured by a dry gas meter accurate to within 2 percent and calibrated at the selected flow rate and conditions encountered during sampling. The meter must be equipped with a temperature gauge (dial thermometer or equivalent) capable of measuring temperature to within 3°C (5.4°F) or be temperature compensated.

e. Pump

Use a leak-free diaphragm pump, or equivalent. If necessary, insert a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump. A pump may not be required for sampling a pressurized fuel line because fuel gas streams are usually sufficiently pressurized to force sample gas through the train at the required flow rate.

f. Pressure Reduction Regulator

A pressure reduction regulator may be needed to reduce the pressure of the gas stream entering the sample line to a safe level.

2.1.2 Barometer

A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg is used. The barometric pressure may be obtained from a nearby National Weather Service station. Adjust for elevation difference between the station value and the sampling point at a rate of minus 2.5 mm (0.1 in.) Hg per 30 m (100 ft) elevation increase or plus the same adjustment for elevation decrease.

2.1.3 Rubber Squeeze Bulb

Bulb is used pressurize train for leak check.

2.1.4 Tee, Pinch Clamp, and Connecting Tubing

Equipment is used for leak check.

2.2 Sampling Reagents

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.

a. Cadmium Sulfate Absorbing Solution

Dissolve 246 g of $3CdSO_4.8H_2O$ in a 1 liter volumetric flask containing approximately 3/4 liter of deionized, distilled water. Adjust the pH to 4.0 ± 0.1 with sulfuric acid. Dilute to volume and mix thoroughly. Add 10 drops of Dow-Corning Antifoam B. Shake well before use.

b. Hydrogen Peroxide, (H_2O_2), 3 Percent

Dilute 30 percent H_2O_2 to 3 percent as needed. Prepare fresh daily.

c. Water

Use deionized, distilled water to conform to ASTM specifications D1193-77, Type 3. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present. Reference to water throughout this method implies deionized, distilled water.

d. Silica Gel

Indicating type, 6 to 17 mesh dried at 175°C (350°F). Silica gel may be used as received.

e. Crushed Ice or Dry Ice Pellets

f. Stopcock Grease

2.3 Preliminary Determinations

If the gas stream is homogeneous, the sampling point in the duct shall be either at the centroid or at a point no closer to the wall than 1.0 m (3.3 ft), unless otherwise specified by the

Executive Officer. If there is an uneven distribution of H_2S concentration in the effluent, traverse sampling is required.

2.4 Sample Collection Train Preparation

Assemble the sampling train with the six impingers in series, as shown in Figure 6.2-1. Place 100 ml of 3 percent H_2O_2 solution in the first impinger. Leave the second impinger empty. Place 100 ml of the cadmium sulfate absorbing solution in both the third and fourth impingers. Leave the fifth impinger empty. Place a known weight of silica gel in the sixth impinger. If a high concentration of H_2S is known to be present in the effluent gas stream, place 200 ml of $CdSO_4$ solution in both the third and fourth impingers.

In case of sewage gas sampling, a few extra impingers with $CdSO_4$ solution should be available as back-up. Place the impinger assembly in an ice bath container and add water and ice to the bath. Add more ice during the run, if needed.

During the preparation and assembly of the train cover all openings where contamination can occur until just prior to assembly or until sampling is about to begin.

The impingers containing $CdSO_4$ solution should always be covered with aluminum foil to avoid exposure to direct sunlight. Reserve 200 ml of absorbing solution as a blank.

2.5 Pretest Leak Check

Follow the basic procedures outlined in Method 5.1. If a pressurized fuel line is sampled, follow this leak check procedure.

Connect the rubber bulb and magnehelic gauge to the first impinger, as shown in Figure 6.2-2. Close the dry gas meter outlet. Pressurize the train to 25 cm water pressure with the bulb and close off the tubing connected to the rubber bulb. The train must hold a 25 cm 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 joints.

After the leak check, purge the connecting line between the sampling valve and the first impinger by disconnecting the line from the first impinger, opening the sample valve, and allowing the fuel gas to flow throughout for a minute or two. Close the valve and reconnect the line.

2.6 Meter Calibration

See Method 5.1., Section 2.

2.7 Sampling Train Operation

Follow the basic procedure outlined in Method 5.1. The sampling rate should be about 0.015 m^3/min. (0.5 cfm). If component changes become necessary during a run, a leak check should be performed immediately before and after the change. Record data on a form such as shown in Figure 6.2-3.

In case of fuel line sampling adjust the sampling valve to obtain a rate of approximately 0.015 m^3/min. (0.5 cfm). Maintain a constant flow rate (± 10 percent) and a pressure below 25 cm water during the test. Record the meter temperature and initial meter reading.

Sample for 30 minutes or until the $CdSO_4$ solution in the fourth impinger turns pale yellow, whichever occurs first. Obtain a minimum of 15 ft^3 of sample and stop the pump. In case of fuel line sampling, close the sampling valve. Record the final volume and temperature readings. Conduct a leak check and meter calibration as described in Sections 2.5 and 2.6 above.

2.8 Sample Handling

Remove the probe from the duct. In case of fuel line sampling disconnect the impinger train from the sampling line. Purge the train at a rate of 0.5 cfm with clean ambient air for 15 minutes to ensure that all H_2S is removed from the H_2O_2. For sample recovery, cap the open ends of the impinger train and move it to a clean area away from heat sources.

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3. Laboratory Procedures

3.1 Apparatus

3.1.1 Sample Collection Train Preparation

A schematic of the sampling train used in this method is shown in Figure 6.2-1. See Section 2.1.1.

3.1.2 Sample Recovery

a. Graduated Cylinder with Stopper
500 ml (1000 ml if necessary).

b. Sample Containers

Leak-free polyethylene bottles, 500 ml capacity (1000 ml, 2000 ml if necessary).

c. Policeman

Rubber or plastic.

d. Wash Bottle

e. Gloves, Waterproof

To be worn at all times when working with $CdSO_4$ solutions.

f. Balance

Accurate to 0.5 g.

3.1.3 Analysis

a. Iodine Flask

Glass stoppered, 500 ml.

b. Pipets

Several of each size; 10, 25, 50 ml, 100 ml, preferably wide-mouth.

c. Graduated Cylinders

10 ml, 250 ml.

d. Burets

25 ml, 50 ml.

e. Gloves, Waterproof

To be worn at all times when working with $CdSO_4$ solution.

3.2 Reagents

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.

3.2.1 Sample Collection Train Preparation

See Section 2.4.

3.2.2 Sample Recovery

a. Water

See Section 2.2 c.

3.2.3 Analysis

a. Iodine Solution, 0.1N

Dissolve 24 g of potassium iodide (KI) in 30 ml of water. Add 12.7 g of resublimed iodine (I_2) to the KI solution. Shake the mixture until the iodide 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.

b. Sodium Thiosulfate Solution, 0.05N

Dissolve 12.5 g of sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) or 7.9 g of anhydrous sodium thiosulfate ($Na_2S_2O_3$) in 1 liter of water and add 0.01 g of anhydrous sodium carbonate (Na_2CO_3) and 0.4 ml of chloroform ($CHCl_3$) to stabilize. Mix thoroughly by shaking, or by aerating with nitrogen for approximately 15 minutes and store in a glass-stoppered reagent bottle overnight before standardization. Standardize as in Section 3.9.

c. Hydrochloric Acid (HCl), Concentrated

d. Starch Indicator Solution

Suspend 10 g of soluble starch in 100 ml of water and add 15 g of potassium hydroxide (KOH) pellets. Stir until dissolved. Dilute with 900 ml of water and let stand for 1 hour. Neutralize the alkali with concentrated HCl, using an indicator paper similar to Alkacid test ribbon. Add 2 ml of glacial acetic acid as a preservative. Alternately, a commercial preparation may be used as an indicator solution if it passes the following test.

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

3.3 Pretest Preparation

Check all equipment and reagents for readiness before proceeding with the following procedures. Prepare the cadmium sulfate, iodine, and thiosulfate solutions at least one day in advance of the test.

3.4 Preparation of Sample Collection Train

See Section 2.4.

3.5 Leak Check

The sample collection train may be leak checked in the laboratory after assembly using the field procedure in Section 2.5.

3.6 Sample Recovery

Proceed with sample recovery on the same day that the sample train is returned to the laboratory. Otherwise cap the openings and protect the train from light inside a cooler.

Note whether the silica gel is expended and if the train or its components are sealed.

Note and record any unusual appearance of the train and its contents. Weigh each impinger plus contents to the nearest 0.5 g and record these weights.

Shake the impingers well, and pour the contents into a graduated 500 ml cylinder (1000 ml if necessary). Loosen the remaining yellow precipitate using a rubber or plastic policeman aided by a water wash bottle. Quantitatively transfer all the cadmium solution to the cylinder and dilute to the nearest 100 ml mark. Stopper the cylinder and shake well. Transfer the sample to a container. Rinse the cylinder with a known volume of water, add this rinse to the sample, and record the total volume. Seal the container, mark the level of the liquid, and label the container to clearly identify its contents.

Dilute 200 ml of the reagent blank proportionately in a graduated cylinder. Stopper the cylinder and mix well. Transfer the blank to a container. Seal the container, mark the level of the liquid, and label the container to clearly identify its contents.

3.7 Sample Analysis

Stir the sample rapidly with a magnetic stirrer. While stirring, take a 100 ml (maximum) aliquot from the middle of the sample with a wide-mouth pipet. The sample aliquot may be decreased for higher concentrations of H_2S, but must produce at least a 5 ml difference between sample and blank titration. Transfer the aliquot to an iodine flask and add 100 ml of water.

Pipet 10.0 ml of 0.1N iodine solution to the sample. Add 10 ml of concentrated HCl. Stopper the iodine flask, swirl, and store in a dark place for 30 minutes.

Titrate the excess iodine, using standardized 0.05N thiosulfate solution. Add four drops of starch solution after the iodine becomes light yellow. Slowly complete the titration to a colorless end point. Record the volume (V_S) of thiosulfate solution to the nearest 0.05 ml. Repeat the procedure with another sample aliquot and average the titration values. Results should agree to 0.2 ml.

Analyze the reagent blank using the same procedure and aliquot sizes. Calculate the average blank titration values (V_B) and record.

3.8 Calculations

Carry out calculations retaining at least one decimal figure more than that of the acquired data. Round off results only after the final calculation.

3.8.1 Normality of the Thiosulfate Solution

Normality of the Standard (0.05 N) Thiosulfate Solution:

$$N = \frac{0.05000 \text{ N} \times 25.0 \text{ ml}}{V_S}$$

where:

0.05000 N = The normality of the dichromate standard

25.0 = The volume of dichromate standard used, ml

V_S = Volume of $Na_2S_2O_3$ used, ml

Phenylarsine oxide solution may replace thiosulfate solution. Consult the literature.

3.8.2 Total H_2S in the Sample, mg

$$H_2S = (V_B - V_S) \times AF \times 17.04 \times N$$

where:

V_S = Average volume used to titrate sample $CdSO_4$, ml

V_B = Average volume used to titrate blank $CdSO_4$, ml

AF = Aliquot factor; total volume divided by aliquot volume

17.04 = H_2S, g-eq.

N = Normality of standardized thiosulfate solution (made to approximately 0.05N)

3.9 Calibration

3.9.1 Thiosulfate Standardization

Dry approximately 5 g of potassium dichromate (primary-standard grade) in an oven at 100°C for 1 hour. Cool in a desiccator. Weigh 2.452 g of the dry dichromate into a 1 liter volumetric flask and dissolve in about 500 ml of water. Dilute to 1 liter with water and mix thoroughly.

Pipet exactly 25.0 ml of the solution into a 500 ml iodine flask. Add 100 ml of water, 3 g of solid KI and 10 ml of concentrated HCl. Stopper the flask. Swirl once and place in the dark for 5 minutes. Dilute the solution in each flask with 200 ml with water and titrate with the 0.05 N sodium thiosulfate until the brown color is almost discharged. Add 3 ml of starch indicator and titrate to a green end point. Record the volume used to the nearest 0.02 ml. Repeat this procedure using another standard aliquot. Values must be within 0.05 ml. If they are, average the results. If not, repeat the procedure.

Substitute 25 ml of water for the standard solution, and repeat this procedure. Record the volumes used to the nearest 0.02 ml. Blank values must agree to within 0.05 ml. If they do, average the blank values. Subtract the volume of sodium thiosulfate required for the blank titration from the volume required for the standard titration. Record the net volume of thiosulfate solution used (V_S). Calculate the normality, N, using the equation in Section 3.8.1. Repeat the standardization each week, or after each test series, whichever time is longer.

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4. Engineering Calculations

4.1 Dry Gas Volume

Correct the sample volume measured by the dry gas meter to standard conditions 15^{O}C (60^{O}F) and 760 mm Hg.

$$V_{m(std)} = V_m Y[(T_{std}/T_m)\ (P_{bar}/P_{std})]$$

where:

$V_{m(std)}$ = Volume at standard conditions of gas sample through the dry gas meter, dscm

V_m = Volume of gas sample through the dry gas meter at meter conditions, m^3

T_{std} = Absolute temperature at standard conditions, 288^{O}K

T_m = Average absolute dry gas meter temperature, ^{o}K

P_{bar} = Barometric pressure at the sampling site, mm Hg

P_{std} = Absolute pressure at standard conditions, 760 mm Hg

Y = Dry gas meter calibration factor

4.2 Concentration of H_2S

Calculate the concentration of H_2S in the gas stream at standard conditions using the following equation:

$$C_{H_2S} = K[(V_{IT}N_I - V_{TT}N_T)\ \text{sample} - (V_{IT}N_I - V_{TT}N_T)\ \text{blank}] \cdot AF/V_{m(std)}$$

where (metric units):

C_{H_2S} = Concentration of H_2S at standard conditions, mg/dscm

K = Conversion factor = 17.04 x 10^3 (34.07 g/g-mole H_2S) (1000 liters/m^3) (1000 mg/g) = (1000 ml/liter) ($2H_2S$ eq/mole) $^{C}H_2S$ in PPM = $^{C}H_2S$ in mg/dscm x 34.07

V_{IT} = Volume of standard iodine solution = 10.0 ml

N_I = Normality of standard iodine solution, g-eq/liter

V_{TT} = Volume of standard sodium thiosulfate solution, g-eq/liter

$V_{m(std)}$ = Dry gas volume at standard conditions, dscm

AF = Aliquot Factor, total sample volume/aliquot volume, ml

4.3 Mass Emission Rate of H_2S

When mass emission rate of H_2S is required follow this calculation:

H_2S, lb/hr = $A \cdot B \cdot C \cdot D$

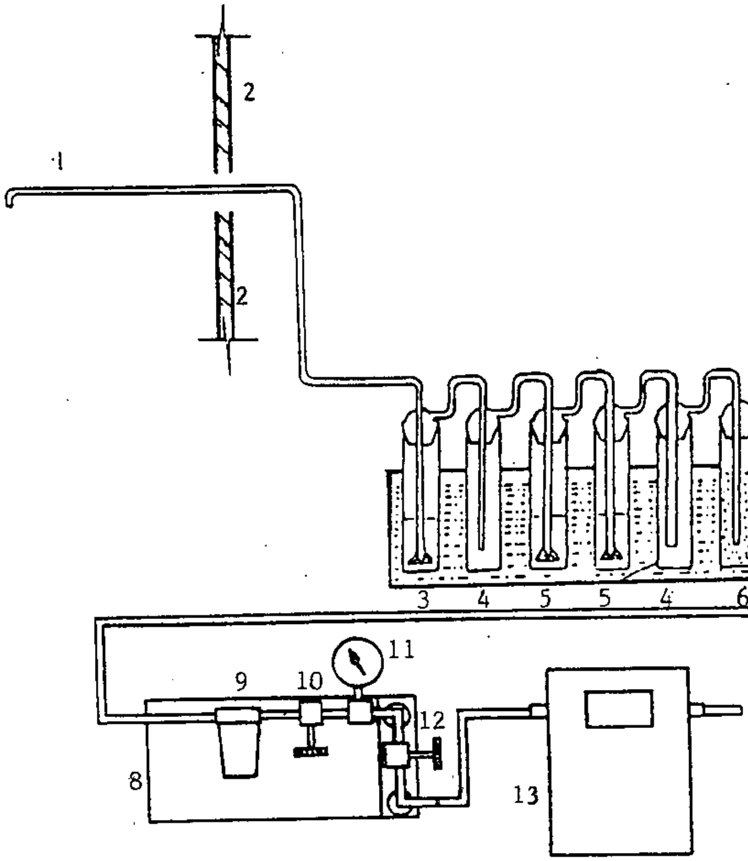
where:

A = H_2S concentration, ppm

B = Molecular weight of H_2S, 34.07 lb/lb-mole

C = Conversion factor, 1.58×10^{-7}
$(10^{-6}/\text{ppm})\ (60\ \text{min/hr})/(379\ \text{cu ft/lb-mole})$

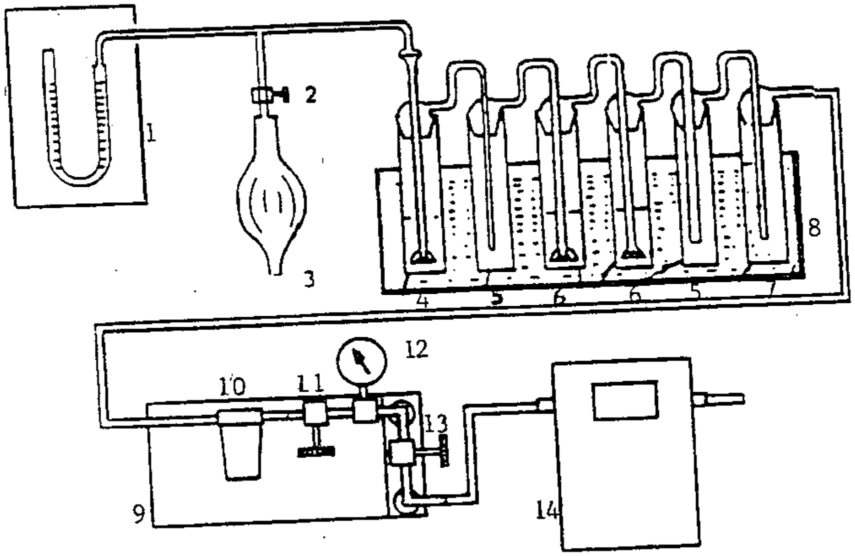
D = Dry standard stack gas flow rate per minute measured, dscfm. Follow Method 2.1



1. Probe
2. Stack Wall
3. Impinger with 100 ml H_2O_2
4. Empty Bubbler
5. Impinger with 100 ml $CdSO_4$
6. Bubbler with Silica Gel
7. Ice Bath
8. Sealed Pump (Leak Free)
9. Filter for Pump
10. Metering Value
11. Vacuum Gauge
12. By-pass Valve
13. Temperature Compensated Dry Gas Meter

Figure 6.2-1

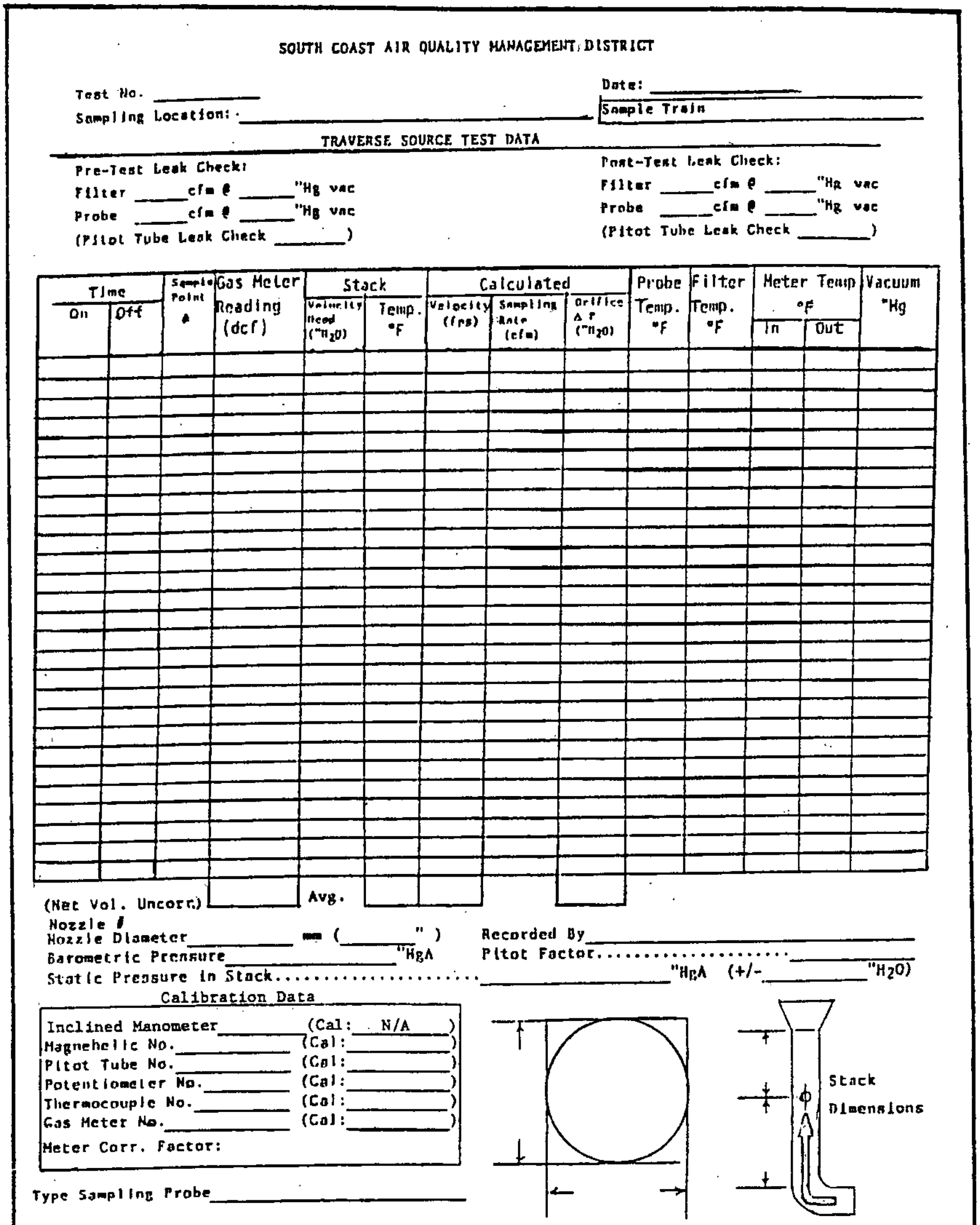
H_2S Impinger Train Setup



1. U-Tube Manometer
2. Pinch Clamp
3. Rubber Bulb
4. Impinger with 100 ml H_2O_2
5. Empty Bubbler
6. Impinger with 100 ml $CdSO_4$
7. Bubbler with Silica Gel
8. Ice Bath
9. Sealed Pump (Leak Free)
10. Filter for Pump
11. Metering Valve
12. Vacuum Gauge
13. By-pass Valve
14. Temperature Compensated Dry Gas Meter

Figure 6.2-2

Leak Check Setup for H_2S Impinger Train



SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

Test No. ____________ Date: ______________

Sampling Location: ________________________ Sample Train ______________

TRAVERSE SOURCE TEST DATA

Pre-Test Leak Check: Post-Test Leak Check:

Filter ______cfm @ ______"Hg vac Filter ______cfm @ ______"Hg vac

Probe ______cfm @ ______"Hg vac Probe ______cfm @ ______"Hg vac

(Pitot Tube Leak Check ________) (Pitot Tube Leak Check ________)

Time		Sample Point #	Gas Meter Reading (dcf)	Stack		Calculated			Probe Temp. °F	Filter Temp. °F	Meter Temp °F		Vacuum "Hg
On	Off			Velocity Head ("H_2O)	Temp. °F	Velocity (fps)	Sampling Rate (cfm)	Orifice ΔP ("H_2O)			In	Out	
		(Net Vol. Uncorr.)		Avg.									

Nozzle #

Nozzle Diameter__________ mm (________") Recorded By______________________

Barometric Pressure______________"HgA Pitot Factor.....................________

Static Pressure in Stack......................____________"HgA (+/-__________"H_2O)

Calibration Data

Inclined Manometer__________(Cal: N/A)

Magnehelic No.__________(Cal:__________)

Pitot Tube No.__________(Cal:__________)

Potentiometer No.__________(Cal:__________)

Thermocouple No.__________(Cal:__________)

Gas Meter No.__________(Cal:__________)

Meter Corr. Factor:

Type Sampling Probe______________________

Figure 6.2-3

Traverse Source Test Data Sheet