

METHOD 44

DETERMINATION OF REDUCED SULFUR GASES AND SULFUR DIOXIDE IN EFFLUENT SAMPLES BY GAS CHROMATOGRAPHIC METHOD

Ref: Reg. 7-303
Reg. 9-1-302, 304.3, 305 to 310

1. PRINCIPLE

- 1.1 Effluent samples containing reduced sulfur gases and sulfur dioxide collected in Tedlar bag, Teflon bag or "SilcoCan" canisters are analyzed using a gas chromatograph fitted with a flame photometric detector (FPD).
- 1.2 The reduced sulfur gases normally found in effluent samples are: hydrogen sulfide (H₂S), carbonyl sulfide (COS), carbon disulfide (CS₂), methyl mercaptan (MeSH), ethyl mercaptan (EtSH), and dimethyl sulfide (DMS).
- 1.3 The detection limit (LOD) of this method is 0.5 ppm (500 ppb) for all gases.
- 1.4 Interference:
 - 1.4.1 The retention times of COS and SO₂ are so close to each other that there is a possibility of one compound masking the other where the difference in their concentrations are so large with respect to each other.
 - 1.4.2 High concentrations of hydrocarbon in the sample can have a quenching effect on the detector.
 - 1.4.3 High concentrations (>10%) of carbon monoxide and carbon dioxide have desensitizing effect on the FPD.
- 1.5 This method combines the other methods for reduced sulfur determination found in the District's Manual of Procedure, Volume III, into one.

2. APPARATUS

- 2.1 Gas Chromatograph (GC). This unit is fitted with a flame photometric detector (FPD), a sampling valve with a Teflon sample loop, a compatible integrator or a data station. The GC operating parameters are as follows:

Oven Temp.	40 ^o C
Hold Time	10 min.
Injector Temp.	Unheated

Detector Temp.	200 ^o C
Carrier Gas	N ₂
Carrier Gas Flow	45 ml/min.
Sample Loop Size	0.9 ml

- 2.1.1 Analytical Column. Any column that can resolve the reduced sulfur gases and sulfur dioxide from each other is acceptable. The following analytical columns are suggested for this method:
 - 2.1.1.1 A 2 m x 2 mm ID glass column packed with 1.5% XE-60/1.0% H₃PO₄, Carbo-pack B, 60/80 mesh. (FIGURE 1)
 - 2.1.1.2 Use the following analytical column to confirm the presence of sulfur dioxide (SO₂):
 - A 36' x 0.085" ID Teflon column packed with 12% polyphenyl ether/0.5% H₃PO₄ on Chromosorb T 40/60 mesh. (FIGURE 2)
- 2.2 "SilcoCan" Canisters, 6 liter capacity, available from Restek Corp., 110 Benner Circle, Bellefonte, PA 16823-8812.
- 2.3 Syringe with luer lock, various sizes as needed.
- 2.4 Erlenmeyer Flask with ground glass gas connector, 1 liter capacity.
- 2.5 Vacuum pump. Capable of pulling a vacuum to 24 inches.
- 2.6 Mercury manometer.
- 2.7 Thick wall Tygon tubing.
- 2.8 Pinch clamp.
- 2.9 Tedlar or Teflon Bag, various sizes as needed.

3. REAGENTS

- 3.1 Cylinder Nitrogen.
- 3.2 Calibration Gas Standard, NIST traceable standard mixture of reduced sulfur gases in the 1 to 100 ppm range. This standard is commercially available from any specialty gases and equipment company capable of preparing such gas standards.
 - 3.2.1 Standard gas mixture in nitrogen containing the following: (NOTE 1)
 - Hydrogen Sulfide (H₂S)
 - Carbonyl Sulfide (COS)
 - Methyl Mercaptan (MeSH)
 - Ethyl Mercaptan (EtSH)

Carbon Disulfide (CS₂)
Dimethyl Sulfide (CH₃)₂S

3.2.2 Sulfur Dioxide (SO₂) in nitrogen, 10 ppm.

NOTE 1: The standard mixture containing the reduced sulfur gases and sulfur dioxide must be recertified at six months interval.

3.3 Cylinder air or compressed air.

3.4 Cylinder hydrogen.

4. ANALYTICAL PROCEDURE

4.1 Set up the gas chromatograph as described in (2.1).

4.2 Samples collected in Tedlar or Teflon bags must be analyzed on the same day or within 24 hours after it was collected.

4.3 Samples collected in "SilcoCan" canisters must be analyzed within five to seven days after sample collection.

4.4 Prior to sample analysis, condition the analytical system by injecting hydrogen sulfide standard (~100 ppm) into the gas chromatograph through the sample loop until a consistent area count is obtained.

4.5 Once the analytical system has been stabilized, inject room air (blank) and check the chromatogram for the presence of hydrogen sulfide. If necessary, make additional blank injections until the chromatogram is cleared of any hydrogen sulfide peak. (NOTE 2).

NOTE 2: Purge the column of any sulfur compound by injecting a blank into the gas chromatograph after each sample run.

4.6 After the analytical system has been cleared of contamination, prepare a five point calibration curve for all the gases in the standard as instructed in Section 5.

4.7 Inject the sample into the gas chromatograph in triplicate. The average peak area obtained with the triplicate injection must be within (+/-) 5% of the mean. If this is not achieved, repeat the operation.

4.8 If the concentrations of the analytes are higher than those of the standard compounds, dilute the sample in a calibrated 1 liter Erlenmeyer flask with a ground glass gas connector. (NOTE 3 & 4).

NOTE 3: Calibrate the 1 liter Erlenmeyer flask as described in ASTM 1475-90.

NOTE 4: Be sure to tape the body of the flask or wrap the flask in a plastic net in order to prevent injury to the analyst in case of explosion.

- 4.9 To dilute the sample, evacuate a clean 1 liter Erlenmeyer flask with a gas connector, and depending on the concentration of the analyte to be diluted, introduce an aliquot of the sample into the 1 liter Erlenmeyer flask using a gas tight syringe. After the sample has been introduced into the evacuated flask, release the vacuum in the flask by opening the stopcock of the gas connector. This will bring the flask to atmospheric pressure.
- 4.10 Connect the stopcock of the gas connector to a manometer using a thick wall Tygon tubing. Connect the manometer to the regulator of a nitrogen compressed gas cylinder by means of a thick wall Tygon tubing.
- 4.11 Open the main valve of the compressed gas cylinder and adjust the regulator to read between five and ten pounds of pressure.
- 4.12 Open the stopcock of the gas connector and slowly open the low pressure valve of the regulator to pressure the flask to 960 mm of Hg. Close the regulator valve as soon as the manometer reads 960 mm Hg. Close the stopcock of the gas connector. Disconnect the flask from the Tygon tubing that is connected to the manometer.
- 4.13 Allow the sample in the flask to reach equilibrium for 30 to 60 minutes, before injection into the gas chromatograph.
- 4.14 Close the main valve of the compressed gas cylinder and release the pressure from the regulator by opening the regulator valve.
- 4.15 Repeat (4.7), using the diluted sample in (4.13).
- 4.16 Confirm the identity of each analyte by comparing the chromatogram of the standard obtained in (4.6) to the sample chromatogram obtained in either (4.7) or (4.15).

5. STANDARD CURVE

- 5.1 Prepare a five point calibration curve for all the gases by making triplicate injections into the gas chromatograph. The area of each compound obtained with the triplicate injections must be within (+/-) 5% of the mean. If this is not achieved, repeat the operation. Record the retention times and peak areas of each compound.
- 5.2 Determine the average area of each compound.
- 5.3 Plot the average area of each standard compound vs concentration, using a log-log paper. (NOTE 5)

NOTE 5: A computer software such as Microsoft Excel Analysis Tools can be used to plot the standard curve and calculate the sample concentration from the regression line.

6. CALCULATION

6.1 Determine the concentration of each reduced sulfur compound and sulfur dioxide directly from the calibration curve.

6.2 If the sample was diluted, multiply (6.1) by the dilution factor, DF.

Where: $DF = V_{CEF} \text{ (ml) at 960 mm Hg} / V_s \text{ (ml)}$.

$$V_{CEF} = \frac{960 \text{ mm Hg} \times C_F}{760 \text{ mm Hg}}$$

V_{CEF} = Volume of the Calibrated Flask at 960 mm Hg. (NOTE 3)

C_F = Calibrated Volume of the Erlenmeyer Flask.

V_s = Volume (ml) of sample aliquot used in (4.8).

6.3 $TRS, \text{ ppm} = \sum (\text{ppm H}_2\text{S} + \text{ppm MeSH} + \text{ppm EtSH} + \text{ppm CS}_2 + \text{ppm COS} + \text{ppm DMS})$

Where:

TRS = Total Reduced Sulfur

H₂S = Hydrogen Sulfide

MeSH = Methyl Mercaptan

EtSH = Ethyl Mercaptan

CS₂ = Carbon Disulfide

COS = Carbonyl Sulfide

6.4 Expressing TRS as ppm SO₂ =
 $\sum [\text{ppm H}_2\text{S} + \text{ppm MeSH} + \text{ppm EtSH} + (2 \times \text{ppm CS}_2) + \text{ppm COS} + \text{ppm DMS}]$

7. REFERENCE

7.1 Kremer, L. and Spicer, L. :Gas Chromatographic Separation of Hydrogen Sulfide, Carbonyl Sulfide and Higher Sulfur Component with a Single Pass", Anal. Chem., 45, 1963, 1973.

7.2 Stevens, R.K. et al. "Gas Chromatography of Reactive Sulfur Gases in Air at the Part-per-Billion Level", Anal. Chem., 43, 827, 1971.

7.3 EPA Method 16 - "Semicontinuous Determination of Sulfur Emissions From Stationary Sources", 40 CFR Ch. 1 (7-1-88 Edition), Pt. 60, App. A

7.4 Anderson, M. and Dimmer, R.C. "Analyze Trace Sulfur Compounds in Hydrocarbon Gas Streams", Hydrocarbon Processing, April, 1997.

- 7.5 Steudler, Paul A. and Kijowski, Wojciech. "Determination of Reduced Sulfur Gases in Air by Solid Absorbent Preconcentration and Gas Chromatography," Anal. Chem. 1984, 56,. 1432-1436.

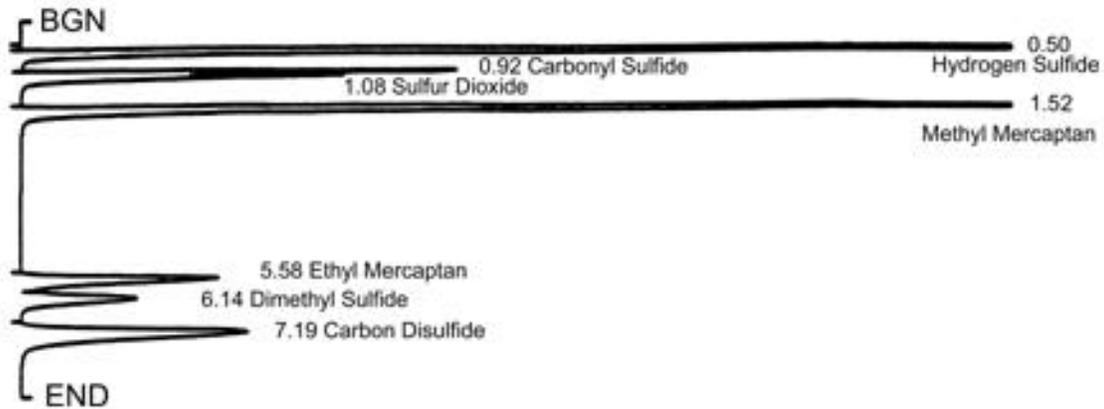


FIGURE 44-1

A Typical Chromatogram Using the Analytical Column
(2m x 2mm ID glass column packed with 1.5% XE-60/H₃PO₄,
Carbopack B, 60/80 mesh)

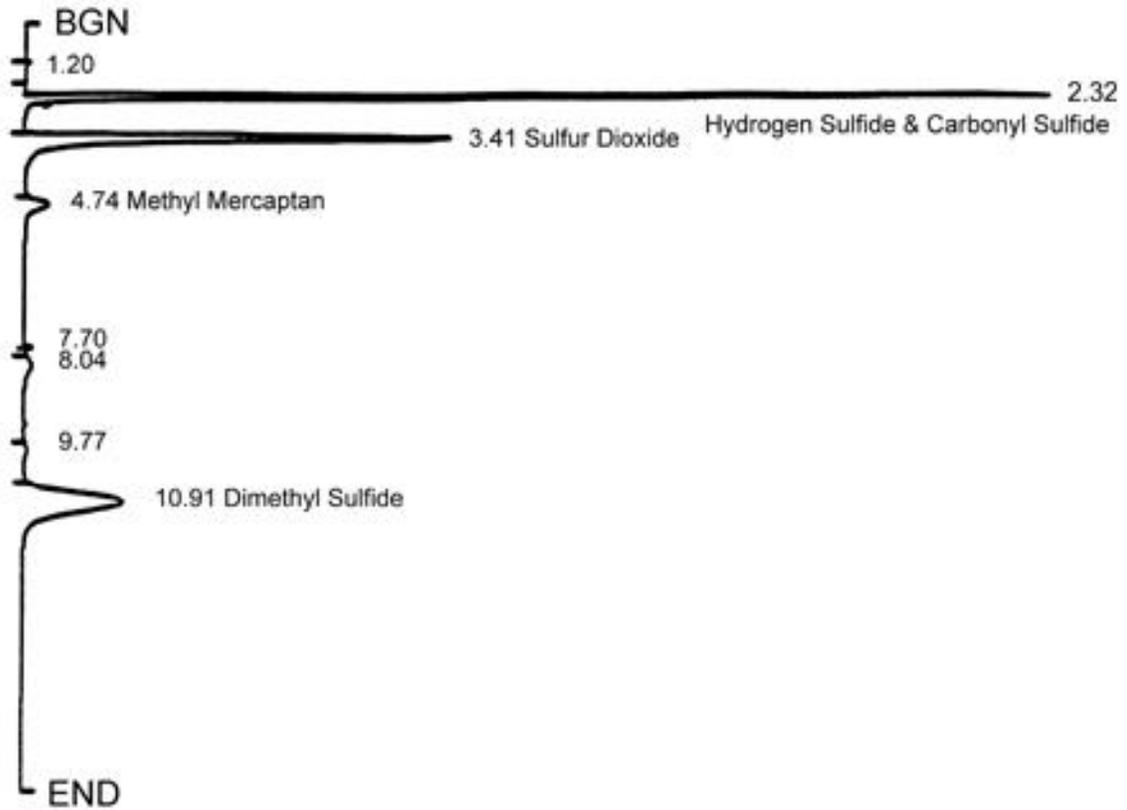


FIGURE 44-2

A Typical Chromatogram Showing the Separation of Sulfur Dioxide from Carbonyl Sulfide (36' x 0.085" ID Teflon column packed with 12% polyphenyl ether/0.5% H₃PO₄, on Chromosorb T, 40/60 mesh)