

METHOD 44A

DETERMINATION OF REDUCED SULFUR GASES AND SULFUR DIOXIDE IN A GASEOUS MATRIX USING THE SULFUR CHEMILUMINESCENCE DETECTOR

REF: Reg. 7-303
9-1-304.3
9-1-302
9-1-307 to 9-1-310

1. PRINCIPLE

- 1.1 Effluent samples containing reduced sulfur gases and sulfur dioxide are collected in Tedlar bags, Teflon bags or "SilcoCan" canisters and analyzed using a gas chromatograph equipped with a sulfur chemiluminescence detector (SCD) and a megabore analytical column.
- 1.2 The sulfur gases are combusted in a hydrogen-rich chamber yielding sulfur monoxide. The sulfur monoxide is reacted with ozone, producing sulfur dioxide, oxygen and light. The light produced is detected by a photomultiplier tube and the response is proportional to the amount of compound in the sample relative to standards.
- 1.3 The following equations show how sulfur compounds are detected in the SCD:
 - 1.3.1 $\text{S-Compound} + \text{H}_2 + \text{O}_2 \rightarrow \text{SO} + \text{Other Products}$
 - 1.3.2 $\text{SO} + \text{O}_3 \rightarrow \text{SO}_2 + \text{O}_2 + h\nu$, where $h\nu$ is light energy in the blue region of the spectrum.
- 1.4 The reduced sulfur compounds normally found in the sample are: hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), methyl mercaptan (MeSH), ethyl mercaptan (EtSH), and dimethylsulfide (DMS).
- 1.5 The detection limit for this method is 20 ppb for sulfur dioxide (SO_2) and COS , and 15 ppb for all the other reduced sulfur gases.
- 1.6 The upper limit was found to be "75" ppm for all reduced sulfur gases and can be extended by appropriate dilution.
- 1.7 This method may be used instead of Method 44, especially if the sample contains high concentrations of hydrocarbon or the concentration of the reduced sulfur compounds and sulfur dioxide are less than 500 ppb. (Note 1).

Note 1: A high concentration of hydrocarbon compounds in the sample has a quenching effect on the flame photometric detector (FPD). The FPD has a detection limit (LOD) of 500 ppb.

2. APPARATUS

- 2.1 Gas Chromatograph (GC). This unit is equipped with a sulfur chemiluminescence detector (SCD), a high nickel content sampling valve with a "SilcoSteel" sample loop, and a compatible data station. The recommended GC operating parameters are as follows:

Initial Oven Temperature (°C)	-20
Initial Hold Time (min)	2
Temperature Program Rate 1 (°C/min)	5
Oven Temperature 2 (°C)	30
Temperature Program Rate 2 (°C/min)	30
Final Oven Temperature (°C)	125
Final Hold Time (min)	5
Injector Temperature (°C)	Unheated
Sampling Valve Temperature (°C)	125
Carrier Gas Flow (ml/min)	10
Injection Sample Loop Size (ml)	1

- 2.1.1 Analytical Column: Any column that can resolve the reduced sulfur gases and sulfur dioxide from each other is acceptable. The following column is suggested for this method:

- 2.1.1.1 A 50m x 0.53 mm ID CP-SIL 5CB Column 5 μ film thickness. This column is available from Chrompack Inc., 1130 Route 202 Raritan, NJ 08869

- 2.2 Sulfur Chemiluminescence Detector (SCD) Operating Conditions:

Pressure (Torr)	150-275 (Controller)	5-10 (SCD)
Burner Temp (°C)	800	
Hydrogen Flow Rate (ml/min)	100	
Air Flow Rate (ml/min)	40	3-10 (FID Adapter)
Background Signal (mV)	0.2 – 0.8	

- 2.3 "SilcoCan" Canisters, 6 liter capacity, available from Restek Corp., 110 Benner Circle, Bellefonte, PA 16823-8812.
- 2.4 Syringe with luer lock, various sizes as needed.
- 2.5 Erlenmeyer flask, with ground glass connector, 1 liter capacity.
- 2.6 Vacuum pump.
- 2.7 Mercury manometer.
- 2.8 Thick wall Tygon tubing.
- 2.9 Pinch clamp.
- 2.10 Tedlar or Teflon bag, various sizes as needed.

- 2.11 Keck Original Standard Taper Clips, Size 24, available from Cole Parmer Instrument Co., 625 East Bunker Court, Vernon Hills, IL 60061-1844.
- 2.12 Spring, various sizes as needed.
- 2.13 Portable Hood.

3. REAGENTS

- 3.1 Carrier Gas, helium, 99.99% or higher purity. (Note 2)
- 3.2 Fuel/Detector Gas, hydrogen, 99.9% or higher purity. (Note 2)
- 3.3 Fuel/Detector Gas, oxygen, 99.9% or higher purity. (Note 2)
- 3.4 Compressed air. (Note 2)

Note 2: The carrier, fuel/detector gases are compressed under high pressure. Hydrogen is an extremely flammable gas. Oxygen and compressed air support combustion. Read the precautionary label before handling these materials.

- 3.5 Calibration Gas Standard. EPA Protocol Gas Standard or NIST traceable standard mixture of reduced sulfur gases in the 1 to 100 ppm range. These standard mixtures are commercially available from any specialty gases and equipment company capable of preparing such gas standards. (Note 3)

Note 3: The standard mixture containing the reduced sulfur gases and sulfur dioxide must be recertified at the interval recommended by the manufacturer. These are compressed gases under high pressure. Read the precautionary label before handling these materials.

- 3.5.1 Standard gas mixture in nitrogen containing the following:

- Hydrogen Sulfide (H₂S)
- Carbonyl Sulfide (COS)
- Methyl Mercaptan (MeSH)
- Ethyl Mercaptan (EtSH)
- Carbon Disulfide (CS₂)
- Dimethyl Sulfide (CH₃)₂S

- 3.5.2 Sulfur Dioxide (SO₂) in nitrogen, 1.0 to 100 ppm range.

4. ANALYTICAL PROCEDURE

- 4.1 Set up the gas chromatograph as described in Section 2.1.
- 4.2 Set up the SCD as described in Section 2.2.
- 4.3 To start up and shutdown the detector, refer to the manufacturer's instructions.

- 4.4 For a typical detector operating conditions, please refer to the manufacturer's instructions.
- 4.5 Samples in Tedlar or Teflon bags must be analyzed on the same day or within 24 hours after they were collected from the source.
- 4.6 Samples in "SilcoCan" canisters must be analyzed within five to seven days after the samples were collected.
- 4.7 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 is obtained.
- 4.8 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 injections until the chromatogram is cleared of any hydrogen sulfide peak. (Note 4).

Note 4: Purge the column of any sulfur compound by injecting a blank into the gas chromatogram after each sample run.

- 4.9 After the analytical system has been purged of contamination, prepare a five point calibration curve for all gases in the standard as instructed in Section 5.
- 4.10 Inject the sample into the gas chromatograph in duplicate. The peak areas obtained with the duplicate injection must be within $\pm 4\%$ of the mean. If this is not achieved, repeat the operation. Record the retention time and peak areas of each compound of interest. (Note 5)

Note 5: For ppb levels, record the peak height of each compound instead of the peak area. Repeat the analysis if the peak heights obtained with the duplicate injections vary by more than $\pm 6\%$ of the mean.

- 4.11 If the concentrations of the analytes are higher than those of the standard compounds, dilute the sample in a 1 liter Erlenmeyer flask with a ground glass gas connector. (Note 6).

Note 6: Calibrate the 1 liter Erlenmeyer flask as described in ASTM 1475-90. Tape or wrap the body of the flask in a plastic net in order to prevent injury in case of an explosion.

- 4.12 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. (Note 7).

Note 7: Secure the gas connector to the flask using a clamp, springs or

rubber bands.

- 4.13 Connect the tip of the gas connector to a manometer using a thick wall Tygon tubing. Connect the manometer to the regulator of a nitrogen gas cylinder by means of a thick wall Tygon tubing.
- 4.14 Open the main valve of the nitrogen gas cylinder and adjust the regulator to read between five and ten pounds/sq. inch (psi).
- 4.15 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 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.
- 4.16 Close the main regulator valve of the gas cylinder and then release the pressure by opening the low pressure valve of the regulator.
- 4.17 Allow the mixture to reach equilibrium by allowing the flask to stand undisturbed for 30 to 60 minutes. Inject an aliquot of the mixture into the GC-SCD. Retain the chromatogram.
- 4.18 Confirm the identity of the compounds in the sample by comparing the chromatogram of the standard obtained in (4.9) to the sample chromatogram obtained in (4.10) or (4.17).
- 4.19 Figure 1 shows a typical chromatogram of sulfur dioxide and reduced sulfur gases.

5. PREPARATION OF STANDARD CURVES

- 5.1 For Parts Per Million (ppm) Concentrations:
 - 5.1.1 Prepare a five point calibration curve for all gases by making duplicate injections into the gas chromatograph. The peak areas of each compound obtained with the duplicate injections must be within $\pm 4\%$ of the mean. If this is not achieved, repeat the operation. Record the retention time and peak areas of each compound of interest.
 - 5.1.2 Determine the average area of each compound.
 - 5.1.3 Plot the average area of each standard compound vs concentration in ppm, using a "square" graphing paper. (Note 8).

Note 8: 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.
- 5.2 For Parts Per Billion (ppb) Concentrations:

- 5.2.1 Repeat (5.1.1) through (5.1.3), except that the concentrations of the gases are in ppb, and instead of using the average peak area, use the average peak height of each compound to plot the standard curves. Repeat the operation if the peak heights obtained with the duplicate injections vary by more than $\pm 6\%$ of the mean. (See Note 8 & Note 9).

Note 9: Subtract the average peak height of the blank from the average peak height of the compound.

6. CALCULATION

- 6.1 Determine the concentrations of each reduced sulfur compound and sulfur dioxide directly from the calibration curve (ppm or ppb range). (Note 10).

Note 10: For ppb concentration, subtract the average peak height of the blank from the average peak height of the analyte before extrapolation.

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

Where:

$$DF = V_{CEF} \text{ (ml) at 960 mm Hg} / V_S \text{ (ml)}$$

$$V_{CEF} = 960 \times V_F / 760 \text{ mm Hg}$$

$$V_F = \text{Calibrated Volume of the Erlenmeyer Flask.}$$

$$V_S = \text{Volume of aliquot used in (4.12).}$$

- 6.3 Total Reduced Sulfur (TRS), ppm or ppb =

$$[(\text{Conc. H}_2\text{S} + \text{Conc. MeSH} + \text{Conc. EtSH} + \text{Conc. CS}_2 + \text{Conc. COS} + \text{Conc. DMS})]$$

Where:

Conc. = Concentrations of the reduced sulfur gases expressed as ppm or ppb.

- 6.4 Expressing TRS as SO₂ =

$$[(\text{Conc. H}_2\text{S} + \text{Conc. MeSH} + \text{Conc. EtSH} + 2 \times \text{Conc. CS}_2 + \text{Conc. COS} + \text{Conc. DMS})]$$

7. REFERENCES

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- 7.3 Hutte, R.S. et al. "Gas Chromatography Detectors Based on Chemiluminescence," *Journal of Chromatographic Science*, 1986, 24, 499-505.
- 7.4 Dean, C. and Stevenson D., "How to Develop Calibration Curves for Fuel Gas," *Hydrocarbon Processing*, 1994, Sept., 97 – 99.
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- 7.6 Dominguez, R. et al. "G.C. Detection of Volatile Sulfur Compounds: An Evaluation of Sulfur Chemiluminescence Detectors," *South Coast Air Quality Management District, Technical Services Division Report*, March 1990.

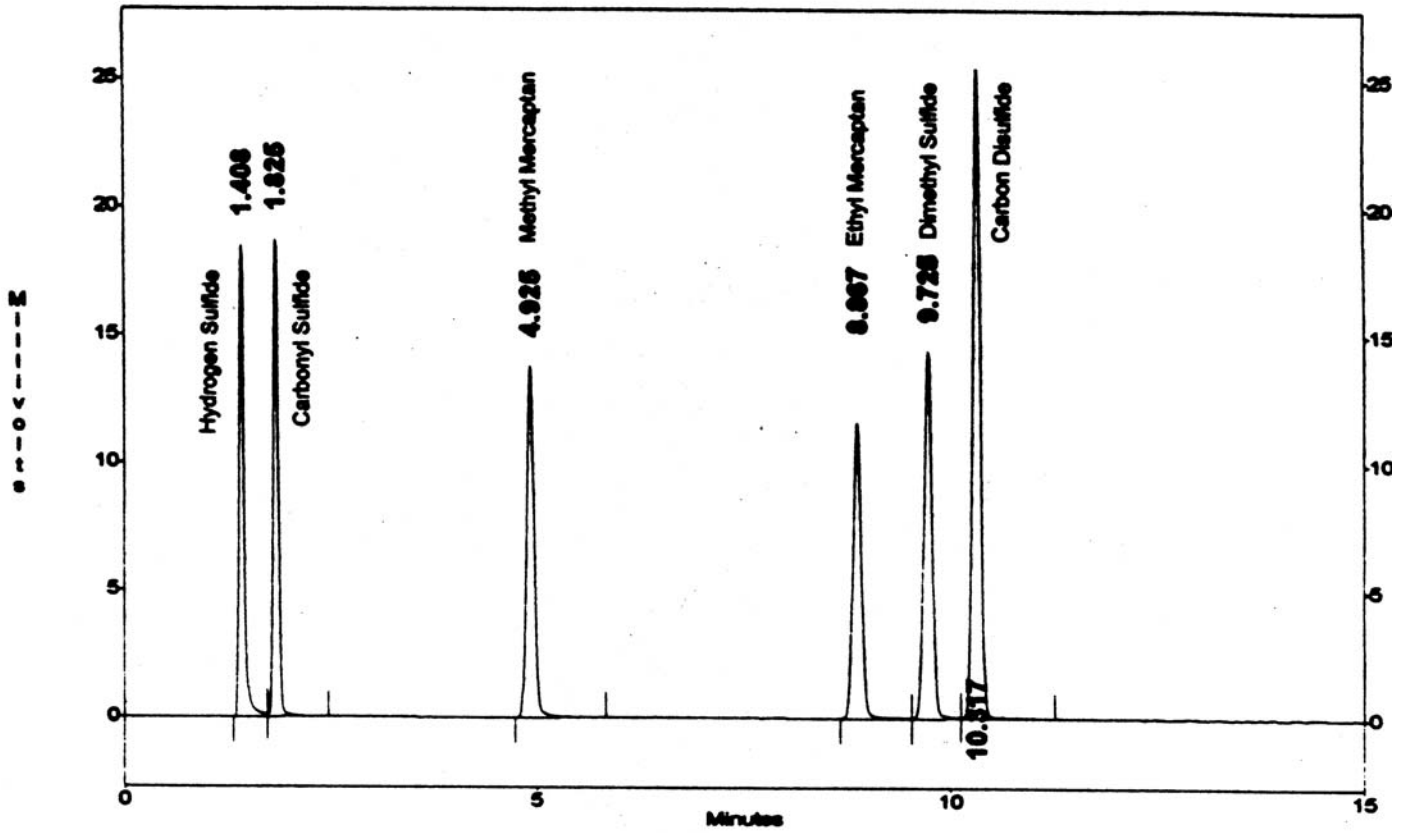


FIGURE 44A-1

A Typical Chromatogram Using the Recommended Analytical Column (50 m X 0.53 mm ID CP-SIL 5CB Column, 5 μ Film Thickness)