Revised March 1994

SCAQMD METHOD 307-91

DETERMINATION OF SULFUR IN A GASEOUS MATRIX

1. Principle

1.1 Reduced sulfur compounds and SO_2 are separated by gas chromatography. These compounds are then combusted in a hydrogen-rich flame to yield sulfur monoxide and other products. The sulfur monoxide is reacted with ozone to yield sulfur dioxide, oxygen and light. The light is detected with a photomultiplier and the response is calibrated against previously run standards.

2. Instrumentation and Equipment

2.1 Gas chromatograph, standard manufacture, with oven temperature ramp capability and hardware necessary for interfacing to a chemiluminescence detector

2.2 Detector, chemiluminescence, possessing a linear response over at least two orders of magnitude and of sufficient range and sensitivity to meet method criteria

2.3 Injection valve, six-port, gas, fitted with a sulfur conditioned sample injection loop of appropriate volume to meet the range of this method

2.4 G.C. column, Chromosil^R 310 packed in Teflon^R, 6' X 1/8" O.D. or SPB-1 Capillary Column.

2.5 Integrator, variable scale, capable of plotting full scale data over the range of this method

2.6 Syringe, gas tight, 100 mL, fitted with an inert valve

2.7 Minimum one-liter Tedlar^R bags fitted with polypropylene valves or the equivalent for sample transportation and storage

3. Gases

3.1 Helium, chromatographic grade

3.2 Hydrogen, chromatographic grade

3.3 Nitrogen, chromatographic grade

3.4 Compressed air, breathing grade

3.5 Compressed oxygen, medical grade

3.6 Standards

3.6.1 Standard gas mixtures in nitrogen containing:

Hydrogen sulfide (H_2S)
Carbonyl sulfide (COS)
Sulfur dioxide (SO_2)
Methyl mercaptan (CH_2SH)
Ethyl mercaptan (CH_3CH_2SH)
1-propanethiol ($CH_3CH_2CH_2SH$)
2-propanethiol ($CH_3CHSHCH_3$)
Carbon disulfide (CS_2)
Dimethyl sulfide (CH_3SCH_3)
Dimethyl disulfide (CH_3SSCH_3)

The concentrations range from 10 to 300 ppm (v/v). These standards are to be recertified at six (6) month intervals.

3.6.2 Alternatively, gas permeation devices containing compounds listed in 3.6.1 may be used.

4. Procedure

4.1 Many operating conditions can be used to perform sulfur gas speciation and quantitation. The following operating conditions are recommended:

Carrier Flow	35 mL/min helium
Injector Temperature	$60^{o}C$
Sample Loop Volume	1 mL
Sample Aliquot	100 mL
Column	Chromosil^R 310/Teflon^R 6' X 1/8" O.D.

Hydrogen Flow Rate	200 mL/min
Air Flow Rate	260 mL/min
Oven Program	Initial temperature 40°C for 2.5 min Ramp to 110°C at 6.0°C/min Hold at 110°C for 10 min.

4.2 Prior to analysis and on a monthly basis, a five-point calibration curve including a point for zero for each analyte must be prepared. If linearity is verified a single-point calibration may be used subsequent to preparation of those curves until a new set is necessary. If linearity is not confirmed, on a daily basis, a three-point calibration curve must be prepared bracketing anticipated analyte concentrations for each sulfur compound present in samples.

4.3 Appropriate standards are analyzed until three (3) consecutive trials yield results that are within 5% of the mean of the three (3) injections. Standard concentrations must lie within 50% of anticipated sample concentrations.

4.4 A nitrogen blank is analyzed before samples are analyzed at an integrator attenuation where the baseline noise is an average of 1 mm in height. Lack of sample carry-over is verified by a featureless baseline. Additional nitrogen blanks may be analyzed to meet this requirement.

4.5 Samples must be analyzed the same day or within 24 hours of collection in duplicate.

4.6 The response (peak area or peak height) for components of greater than 1 ppm concentration must lie within ten (10) percent of each other in duplicate samples.

4.7 Either a spiked sample or a standard is analyzed at the end of a batch run as part of a QA/QC program.

4.8 Retention times of peaks in the sample chromatogram are compared to those of peaks in the standard chromatogram in order to identify each sulfur compound.

4.9 Compounds for which a standard is not available are to be quantified using the methyl mercaptan response factor.

5. Calculations

5.1 Concentration of reduced sulfur compounds or SO_2 is by the following:

$$\text{Analyte concentration, ppm} = \frac{\text{pksamp}}{\text{pkstd}} \times \text{Std}$$

Where:

Analyte concentration = concentration of individual reduced sulfur compounds or SO_2
Pksamp = Peak area in the sample
Pkstd = Peak area in the standard
Std = concentration of analyte in the standard, ppm
Peak heights may be substituted for peak areas.

5.2 The concentrations of the monatomic sulfur compounds are added to twice the concentrations of each diatomic sulfur compound except where these substances are quantified using the response of methyl mercaptan standard. In this case total sulfur is the summation of all compounds. This value is the total sulfur content reported as H_2S in ppm by volume.

6. Range and Sensitivity

6.1 The minimum range for this method is from 0.5 ppm (v/v) to 100 ppm (v/v). The upper limit may be expanded by dilution of the sample using chromatographic grade nitrogen. With a 1 mL sample loop, a lower detection limit of at least 0.03 ppm is obtained with this method for all sulfur compounds examined.

7. Quality Control

7.1 After analysis of all samples, a final analysis of either a spiked sample or a standard is to be done. Results for spike or standard components must lie within 10% of the theoretical amounts based on the original standards.

7.2 Reproducibility
Interlaboratory studies demonstrated that the allowable range among laboratories is the greater of 4 ppm or 10% of the average value. These values were based on the Rule 431.1 limit of 40 ppm total sulfur in fuel gas and the allowed 10% variability in duplicate analyses of samples specified in Section 4.6.

8. References

8.1 EPA Method 16, "Semicontinuous Determination of Sulfur Emissions from Stationary Sources".

8.2 GC Detection of Volatile Sulfur Compounds: An Evaluation of Sulfur Chemiluminescence Detectors, SCAQMD, Technical Services Division Report, March 1990.

8.3 The Detection of Volatile Sulfur Compounds in Gas Samples, SCAQMD,. Applied Science & Technology Division Report, In Preparation.

8.4 Total Sulfur Analyzer Demonstration Project: Report of Data Collected, Western States Petroleum Association, June, 1993.

8.5 Dominguez, R. Jr. and Wadley, M.W., "The Chemiluminescent Detection of Volatile Sulfur Compounds", Sampling and Analysis of Airborne Pollutants, Lewis Publishers, Ann Arbor, MI, 1993.

Figure 1
Typical SCD Chromatogram for Reduced Sulfur Compounds

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

APPLIED SCIENCE & TECHNOLOGY DIVISION
LABORATORY SERVICES BRANCH

SCAQMD METHOD 307-91

DETERMINATION OF SULFUR IN A GASEOUS MATRIX

Approved June 1, 1991
Revised March 1994

Revised March 1994

SCAQMD METHOD 307-91

DETERMINATION OF SULFUR IN A GASEOUS MATRIX

This method defines a procedure for speciation and quantitation of reduced sulfur compounds and sulfur dioxide (SO_2) in gaseous samples including fuel gas, landfill gas, digester gas and other related sources.

The total sulfur content is reported as hydrogen sulfide (H_2S).

CONTENTS

Page

1. Principle 1
2. Instrumentation and Equipment 1
3. Gases 1
4. Procedure 2
5. Calculations 4
6. Range and Sensitivity 4
7. Quality Control 4
8. References 5
9. Figure 1: Typical SCD Chromatogram for Reduced Sulfur Compounds 6