



Dimethyl Sulfide

Method number: PV2210

Control number: T-PV2210-01-8707-CH

Target concentration: 10 ppm (No OSHA PEL or ACGIH TLV)

Procedure: Samples are collected by drawing a known volume of air through a charcoal tube. Samples are desorbed with 1 mL methylene chloride and analyzed by gas chromatography with a flame photometric detector.

Air volume and sampling rate studied: 5 liters at 0.1 Lpm (Section 2.4)

Status of method: Partially validated method. This method has been only partially evaluated and is presented for information and trial use.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA Laboratory recently received samples collected on charcoal tubes requesting analysis for dimethyl sulfide. There is no PEL or TLV for dimethyl sulfide, but it has similar toxic effects to methyl mercaptan, so a target level of 10 ppm was chosen. Samples were desorbed with 1 mL methylene chloride for 30 minutes with occasional shaking and analyzed by gas chromatography with a flame photometric detector in the sulfur mode (GC/FPD).

1.1.2 Potential workplace exposure (Ref. 5.1)

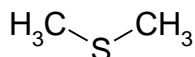
Workers are exposed to dimethyl sulfide in the paper processing industry. It is a by-product of Kraft pulp mills.

1.1.3 Toxic Effects (This section is for information only and should not be taken as the basis for OSHA policy.) (Ref. 5.2)

The LD₅₀ for rats tested was 40,250 ppm. Orally, the LD₅₀ for dimethyl sulfide in rats is 535 mg/kg.

1.1.4 Physical properties:

CAS:	75-18-3
IMIS:	D650
Compound:	(CH ₃) ₂ S
Molecular weight:	62.13
Density:	0.8458
Freezing point:	(-83 °C)
Boiling point:	38 °C
Synonyms:	methyl sulfide; methyl thiomethane
Odor:	Foul, skunk-like
Color:	Clear liquid
Autoignition Temperature:	206 °C (403 °F)
Structure:	



1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 10 ng based on a 2 uL injection volume. This is the smallest amount that could be detected.

1.3 Advantages

1.3.1 The sampling procedure is convenient.

1.3.2 The analytical method is reproducible and sensitive.

1.3.3 Reanalysis of samples is possible.

1.3.4 It may be possible to analyze other compounds at the same time.

1.3.5 Interferences may be avoided by proper selection of column and GC parameters.

1.4 Disadvantages

None known

2 Sampling procedure

2.1 Apparatus

- 2.1.1 A calibrated personal sampling pump, the flow of which can be determined within $\pm 5\%$ at the recommended flow with the sample tube in line.
- 2.1.2 Charcoal tubes, lot 120, containing a 100 mg adsorbing section with a 50 mg backup section separated by a 2-mm portion of urethane foam, with a silanized glass wool plug before the adsorbing section and a 3-mm plug of urethane foam behind the backup section. The ends are flame sealed. The glass tube containing the adsorbent is 7-cm x 6-mm o.d. and 4-mm i.d., (SKC tubes or equivalent).

2.2 Sampling technique

- 2.2.1 The ends of the charcoal tubes are opened immediately before sampling.
- 2.2.2 Connect the charcoal tube to the sampling pump with flexible tubing.
- 2.2.3 Tubes should be placed in a vertical position to minimize channeling, with the smaller section towards the pump.
- 2.2.4 Air being sampled should not pass through any hose or tubing before entering the charcoal tube.
- 2.2.5 Seal the charcoal tube with plastic caps immediately after sampling. Seal each sample lengthwise with a Form OSHA-21 seal.
- 2.2.6 With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (break ends, seal, & transport) except that no air is drawn through it.
- 2.2.7 Transport the samples and corresponding paperwork to the lab for analysis.
- 2.2.8 Bulks submitted for analysis must be shipped in a separate container from the samples.

2.3 Desorption efficiency

A solution of dimethyl sulfide in methylene chloride was prepared. This solution was spiked onto six tubes at each of four levels. The resulting mass of dimethyl sulfide on the tubes was 84.6, 169.2, 338.3, and 676.6 μg . The samples were stored in the refrigerator overnight. They were then opened, desorbed with 1 mL methylene chloride, and analyzed by GC-FPD (Table 1). The average desorption over the range is 97.5%.

Table 1
Dimethyl Sulfide
Desorption Efficiency

μg spiked	% recovered
676.6	103
676.6	104
676.6	103
676.6	103
676.6	105
676.6	lost in analysis
Average	103
338.3	93.3
338.3	94.8
338.3	97.0
338.3	96.6
338.3	94.9
338.3	93.0
Average	94.9
169.2	95.2
169.2	95.5
169.2	93.8
169.2	94.9
169.2	99.1
169.2	98.4
Average	96.2
84.6	95.4
84.6	96.1
84.6	96.8
84.6	96.1
84.6	96.6
84.6	93.5
Average	95.8
overall average	97.5%
standard deviation	± 3.98

2.4 Retention efficiency

A solution of dimethyl sulfide in methylene chloride was prepared. Twelve tubes were spiked with this solution, for a concentration 338.3- μg dimethyl sulfide. Six tubes had 5 liters of humid air (83% RH) drawn through them, and six tubes had of 10 liters humid air drawn through them. There was little loss when 5 liters of humid air were drawn, although there was significant breakthrough, but there was a significant loss with 10 liters of humid air was drawn (Table 2).

Table 2
Dimethyl Sulfide
Retention Study

liters	% recovered		% total
	'A'	'B'	
5	68.3	27.2	95.5
5	62.2	31.8	94.0
5	65.3	26.8	92.1
5	53.9	34.7	88.6
5	53.3	34.3	87.6
5	73.2	15.7	88.9
average = 91.1%			
average corrected for desorption = 96.0%			
10	22.6	40.2	62.8
10	13.8	24.9	38.7
10	12.4	18.9	31.3
10	14.7	20.9	35.6
10	12.2	19.4	31.6
10	10.5	16.3	26.8
average = 37.8%			
average corrected for desorption = 39.8%			

2.5 Storage

A solution of dimethyl sulfide in methylene chloride was prepared. Six tubes were spiked with this solution for a mass of 338.3 μg dimethyl sulfide on each tube. They were stored in the refrigerator until analyzed on day 10. There was some migration of the dimethyl sulfide onto the backup portion of the charcoal tubes, averaging 5.6%. The average recovery was 94.3% (Table 3).

Table 3
Dimethyl Sulfide
Storage Stability

tube #	% recovered
1	88.9
2	90.7
3	90.4
4	92.3
5	94.2
6	94.8
average	91.9
average corrected for desorption = 94.3%	

2.6 Air volume and sampling rate studied

2.6.1 The air volume studied was 5 liters (Section 2.4).

2.6.2 The sampling rate studied was 0.1 liters per minute.

2.7 Interferences

Suspected interferences should be listed on sample data sheets.

2.8 Safety precautions

2.8.1 Sampling equipment should be placed on an employee in a manner that does not interfere with work performance or safety.

2.8.2 Safety glasses should be worn at all times during inspection.

2.8.3 Follow all safety practices that apply to the workplace being sampled.

3 Analytical method

3.1 Apparatus

3.1.1 Gas chromatograph equipped with a flame photometric detector in the sulfur mode. A Varian 3400 gas chromatograph was used in this study.

3.1.2 GC column capable of separating the analyte from any interference. A 20' x 1/8" FFAP on 80/100 mesh Chrom WAW was used in this procedure.

3.1.3 An alternate analytical GC method is shown in Figure 2.

3.1.4 An electronic integrator or some other suitable method for measuring peak areas.

3.1.5 Two milliliter vials with PTFE-lined caps for sample desorption.

3.1.6 A 5-uL syringe or other convenient size for sample injection.

3.1.7 Pipettes for dispensing the desorbing solution.

3.1.8 Volumetric flasks - 5 mL and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 Purified GC grade helium, hydrogen, oxygen, and air.

3.2.2 dimethyl sulfide, Reagent grade

3.2.3 methylene chloride, Reagent grade

3.3 Sample preparation

3.3.1 Sample tubes are opened and the front and back section of each tube are placed in separate 2-mL vials.

3.3.2 Each section is desorbed with 1 mL methylene chloride.

3.3.3 The vials are sealed immediately and allowed to desorb for 30 minutes with occasional shaking.

3.4 Standard preparation

- 3.4.1 Standards are prepared by diluting a known quantity of dimethyl sulfide with methylene chloride.
- 3.4.2 At least two separate stock standards should be made. Dilutions of these standards are made to cover the concentration range of the samples. At least four different concentrations should be used to prepare a calibration curve. The range of standards used in this study was from 10 to 676.6 µg/mL.
- 3.4.3 A standard of dimethyl sulfide in methylene chloride at the concentration of 0.2 µL/mL is equivalent to 169.2 µg/mL or 13.3 ppm based on a 5-liter air volume.

3.5 Analysis

- 3.5.1 Gas chromatograph conditions. A Varian 3400 gas chromatograph with a flame photometric detector in the sulfur mode was used in this study.

<u>Flow rates</u>	<u>(mL/min)</u>	<u>Temperature</u>	<u>(°C)</u>
Helium:	30	Injector:	180
Hydrogen:	170	Detector:	200
Air 1:	80	Column:	80 °C for 4 min, increase
Air 2:	170		10°C/min to 160°C
Injection size:	2 µL		
Elution time:	6.8 min		
Chromatograms:	(See Figures 1 & 2)		

- 3.5.2 Peak areas are measured by an integrator or other suitable means.

3.6 Interferences (analytical)

- 3.6.1 Any compound having the general retention time of the analyte is interference. Possible interferences should be listed on the sample data sheet. GC parameters should be adjusted, if necessary, so these interferences will pose no problems.
- 3.6.2 Retention time data on a single column is not considered proof of chemical identity. Samples over the target concentration should be confirmed by GC/Mass Spec or other suitable means.

3.7 Calculations

- 3.7.1 To calculate the concentration of analyte in the air sample the following formulas are used:

$$\text{mass of analyte, } \mu\text{g} = \frac{(\mu\text{g} / \text{mL})(\text{desorption volume, mL})}{(\text{desorption efficiency, decimal})}$$

$$\text{moles of analyte} = \frac{(\text{mass of analyte, } \mu\text{g})(1\text{g})}{(\text{molecular weight})(10^6 \mu\text{g})}$$

$$\text{volume of analyte} = (\text{moles of analyte})(\text{molar volume})$$

$$ppm = \frac{(volume\ of\ analyte)(10^6)^*}{(air\ volume,\ L)}$$

* All units must cancel.

3.7.2 The above formulas can be combined to give the following formula. To calculate the ppm of analyte in the sample based on a 10-liter air sample, and a 1 mL desorbing solution:

$$ppm = \frac{(\mu g / mL)(DV)(24.46)}{(L)(DE)(MW)}$$

Where:

$\mu g/mL$ = concentration of analyte in sample
 24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg
 MW = Molecular weight (g/mole)
 DV = Desorption volume, 1.0 mL
 L = Air volume, 5 L
 DE = Desorption efficiency, decimal

3.7.3 This calculation is done for each section of the sample tube and the results are then added together.

3.8 Safety precautions

3.8.1 All handling of solvents should be done in a hood.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses at all times in laboratory.

4 Recommendations for further study

Collection efficiencies should be evaluated. While there seems to be a problem with sample retention in high humidity, a maximum air volume of 5 liters should minimize this problem. There were some samples analyzed at the lab which contained 1046 μg dimethyl sulfide on them, with no dimethyl sulfide on the backup portion of the charcoal tube. There was no indication, by the industrial hygienist, of the relative humidity when the samples were taken.

5 References

- 5.1 Grayson, M., "Encyclopedia of Chemical Technology," Third Edition, John Wiley & Son, N.Y., 1981, Vol. 16, p. 795.
- 5.2 Lewis, R., Sweet, D., "Registry of Toxic Effects of Chemical Substances," NIOSH, Cincinnati, OH, 1985, Vol. 2, p. 1205.
- 5.3 Sax, N., "Dangerous Properties of Industrial Materials," Fifth Edition, Van Nostrand Reinhold Co., New York, 1979, p. 832.

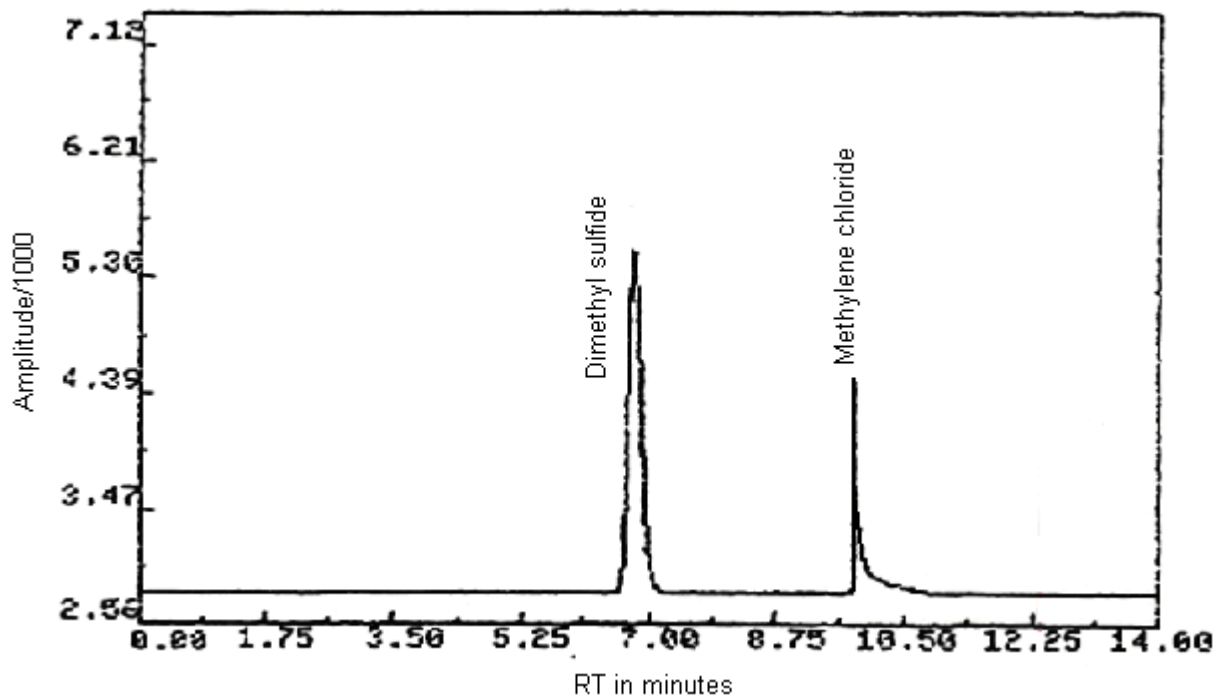


Figure 1. Dimethyl sulfide standard (135.3 $\mu\text{g}/\text{mL}$) in methylene chloride.

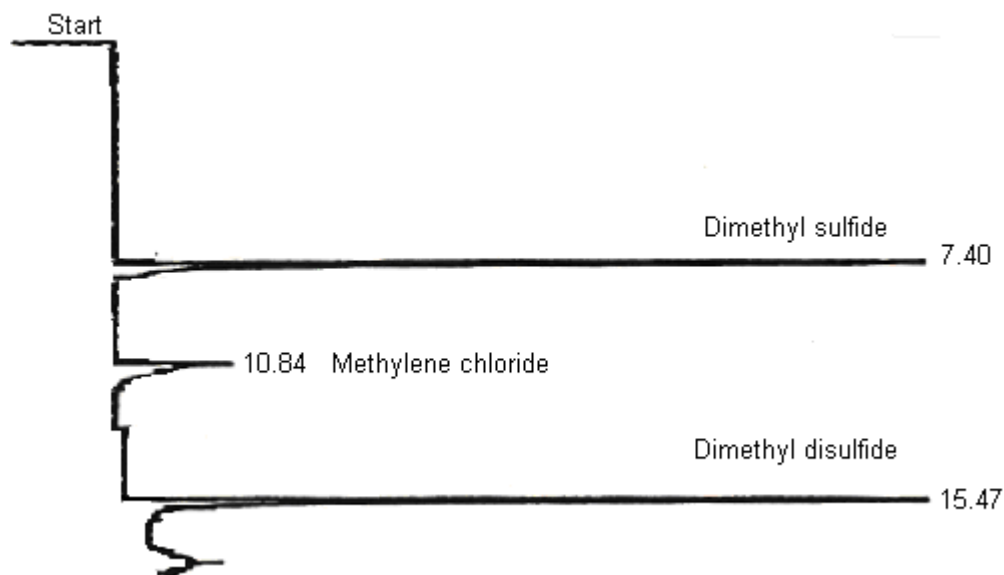


Figure 2. Chromatogram using an HP5890 GC with flame photometric detector (FPD) in the sulfur mode. Temperature program 40 $^{\circ}\text{C}$ for 5 min then increase temperature 10 $^{\circ}\text{C}/\text{min}$ to 120 $^{\circ}\text{C}$. Column was 60-m x 0.32-mm i.d. with 0.5 μm d_f DB-WAX glass capillary. Injection size 1 μL , standard was 42.8 $\mu\text{g}/\text{mL}$ dimethyl disulfide and 34.7 $\mu\text{g}/\text{mL}$ dimethyl sulfide in methylene chloride.