DIMETHYL SULFATE

Matrix:	Air
Target concentration:	1 ppm (5 mg/m^3)
OSHA PEL:	1 ppm (5 mg/m^3)
Procedure:	Samples are collected by drawing a known volume of air through glass sampling tubes containing Porapak-Q adsorbent. Samples are extracted with acetone and analyzed by GC using a flame photometric detector (GC/FPD).
Recommended sampling time and sampling rate:	100 min at 0.1 L/min (10 L)
Detection limit of the overall procedure (based on 10 L):	0.05 ppm
Status of method:	Stopgap Method: This method has been 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 received samples for dimethyl sulfate collected on Porapak-Q tubes. The need to analyze those samples prompted this work. This partially validated method was developed using Porapak-Q sampling tubes, desorption with acetone, and analysis by GC/flame photometric detector in the sulfur mode. NIOSH has published a similar method that specifies collection on Porapak-P, desorption with diethyl ether, and analysis by GC/electrolytic conductivity detector in the sulfur mode (Ref. 1).

1.1.2. Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

The OSHA PEL for dimethyl sulfate is 1 ppm, but the American Conference of Government Industrial Hygienists recommended a PEL of 0.1 ppm (Ref. 2.). The lowest dose to cause death in humans is an exposure of 97 ppm for 10 minutes (Ref. 3). Skin exposure causes blisters and necrosis. Inhalation exposure causes headaches and giddiness with burning of the eyes reaching maximum intensity two to ten hours after first eye effects. This is followed by irritation of nose and throat with hoarseness, loss of voice, cough, difficulty breathing and swallowing, vomiting, diarrhea and scalding micturition, followed by circulatory failure and death. Impairment of liver function and color blindness have been observed six years after exposure. Rats exposed to 3 and 10 ppm levels five days a week showed nose and eye irritation at both levels followed by death in some of the animals. The survivors had malignant tumors at both levels (Ref. 4.).

1.1.3. Potential workplace exposure

Dimethyl sulfate is used in the manufacturing process of many chemicals and as a war gas (Ref. 5.).

1.1.4. Physical properties (Ref. 6.)

CAS no.:	77-78-1
IMIS no.:	0960
Molecular weight:	126.13
Density:	1.3322
Boiling point:	188 °C (decomposes)
Color:	Colorless liquid
Vapor density:	4.35
Flash point:	240 °F (open cup) 182 °F (closed cup)
Odor:	Odorless except in very high concentrations, then slight onion odor
Molecular formula:	$(CH_3)_2SO_4$

1.2. Limit defining parameters

Detection limit of the analytical procedure is 2 µg/injection. This is the amount of analyte that will give a peak whose height is approximately five times the baseline noise.

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 whose flow can be determined within ±5% at the recommended flow.

2.1.2. Porapak-Q tubes containing a 150-mg adsorbing section and a 50-mg backup section, separated by silanized glass wool, with silanized glass wool before and after the adsorbing sections. The ends are flame sealed and the glass tube containing the adsorbent is 7 cm long with 6 mm O.D. and 4 mm I.D., SKC tubes or equivalent.

2.2. Sampling technique

2.2.1. The ends of the Porapak-Q tubes are opened immediately before sampling.

2.2.2. Connect the Porapak-Q tubes with flexible tubing.

2.2.3. The tube should be placed in a vertical position to minimize channeling and with the smaller section towards the pump.

2.2.4. Air being sampled should not pass through any hose or tubing before entering the pump.

2.2.5. Seal the tubes with plastic caps immediately after sampling. Seal each tube lengthwise with Form OSHA-21 seals.

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 air samples.

2.3. Desorption efficiency

2.3.1. Porapak-Q tubes were spiked with mass equivalents of 4.13 ppm, 2.07 ppm, 1.03 ppm, and 0.52 ppm dimethyl sulfate all based on 10 L air sample volumes. This was accomplished by injecting microliter volumes of solutions containing dimethyl sulfate diluted with acetone on the tubes. The following amounts were spiked on the tubes to obtain amounts equivalent to the associated air concentrations. 4.13 ppm: 5 µL of a 32 µL/mL solution; 2.07 ppm: 10 µL of 8 µL/mL solution; 1.03 ppm: 5 µL of 8 µL/mL solution; 0.52 ppm: 5 µL of 20 µL/5 mL solution. Samples were desorbed with 1 mL of acetone, allowed to desorb for about an hour, and then analyzed by gas chromatography with a FPD detector in the sulfur mode.

Desorption Efficiency
(percent recovery)

tube	4.13 ppm	2.07 ppm	1.03 ppm	0.52 ppm
1	91.37	89.75	88.21	83.92
2	94.24	92.33	87.70	85.76
3	96.48	88.83	87.70	82.67
4	94.76	87.60	88.54	87.44
5	95.61	89.98	83.62	82.46
6	93.11	91.02	lost	83.81
average	94.26	89.92	87.15	84.34

2.4. Retention efficiency

Six Porapak-Q tubes were spiked with 5 µL of a 16 µL dimethyl sulfate/mL acetone solution for a concentration of 2.07 ppm (based on 10 L) dimethyl sulfate/tube. Ten liters of humid air (80% RH) was drawn through each tube. The sampling rate was 0.1 liters per minute. The samples were then desorbed with 1 mL of acetone and analyzed by gas chromatography with a flame photometric detector.

Retention Efficiency

tube	% recovered
1	83.14
2	78.78
3	89.23
4	86.04
5	88.63
6	85.26
average	85.18

2.5. Storage

2.5.1. Twelve tubes were spiked with 5 µL of a 8 µL dimethyl sulfate/mL acetone solution for a concentration of 1.03 ppm (based on 10L) dimethyl sulfate/tube. Six of these tubes were stored at room temperature (24°C), and six were refrigerated (0°C). On day three and on day seven after preparation three tubes from each group were analyzed.

Storage Test					
sample	time (days)	refrigerated recovery (%)	refrigerated average (%)	ambient recovery (%)	ambient average (%)
1	3	87.90		90.64	
2	3	89.19		89.12	
3	3	90.70	89.26	92.60	90.79
4	7	74.90		77.56	
5	7	80.01		84.59	
6	7	80.60	78.50	83.15	78.43

2.6. Air volume and sampling rate studied

2.6.1. The air volume studied was 10 liters.

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.

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 operated in the sulfur mode.

3.1.2. GC column capable of separating the analyte from potential interferences. The column used in this work was a 10 ft x 1/8 inch stainless steel column packed with 20% SP2100 with 0.1% Carbowax 1500 on 80/100 mesh Supelcoport support.

3.1.3. An electronic integrator or some method of measuring peak areas.

3.1.4. Two-milliliter vials with PTFE-lined caps.

3.1.5. A 5-µL syringe and other convenient sizes.

3.1.6. Pipets for dispensing the desorbing solution. A Glenco 1-mL dispenser was used in this work.

3.1.7. Volumetric flasks, 5 mL and other convenient sizes for preparing standards.

3.1.8. Pipets of convenient sizes for standard preparation.

3.2. Reagents

3.2.1. Dimethyl sulfate, reagent grade.

3.2.2. Acetone, reagent grade.

3.2.3. Purified GC grade nitrogen, hydrogen, oxygen, and air.

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 of acetone.

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 sulfate in acetone.

3.4.2. A concentration of 53 µg/mL of dimethyl sulfate in acetone is approximately equivalent to 1 ppm for a 10.0 liter air sample volume.

3.4.3. Standards were prepared over the range of approximately 2 to 215 µg/mL of dimethyl sulfate in acetone.

3.4.4. At least two separate stock standards should be made.

3.5. Analysis

3.5.1. Gas Chromatograph Conditions

flow rates	(mL/min)	temperature	(°C)
Nitrogen	24	Injector:	160
Hydrogen	100	Detector:	200
Air	60	Column:	120
Oxygen	30		

Injection size:	3 µL
Retention time:	4.41 min
Chromatogram:	(See Figure 1)
Attenuation:	5

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

3.5.3. An external standard procedure was used. A standard curve was prepared and samples were bracketed with standards. (See Figure 2.)

3.6. Interferences (analytical)

3.6.1. Any compound having the same general retention time of the analyte is an 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 greater than the target concentration should be confirmed by GC/mass spectrometry or other suitable means.

3.7. Calculations

3.7.1. The amount of dimethyl sulfate in the sample is determined from the calibration curve. Air concentrations are calculated as follows:

$$\frac{\text{mg}}{\text{m}^3} = \frac{(\frac{\mu\text{g}}{\text{mL}}\ \text{sample} - \frac{\mu\text{g}}{\text{mL}}\ \text{blank}) \times (\text{desorption volume in mL})}{(\text{decimal equivalent of desorption efficiency}) \times (\text{liters of air sampled})}$$

$$\text{ppm} = \frac{\frac{\text{mg}}{\text{m}^3} \times 24.46}{126.13}$$

3.7.2. This calculation is done for each section of the sampling tube and the results are added together.

3.8. Safety reactions

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.

4. Recommendations for further study

Storage stability should be studied with tubes that have had humid air drawn through them. Water decomposes dimethyl sulfate, and the effect of water on storage stability needs to be evaluated. A longer time storage study of spiked tubes needs to be evaluated. If the PEL is lowered, lower level desorption and retention efficiency studies will need to be done. The instrument will need to be optimized to detect lower levels of dimethyl sulfate if the PEL is lowered.

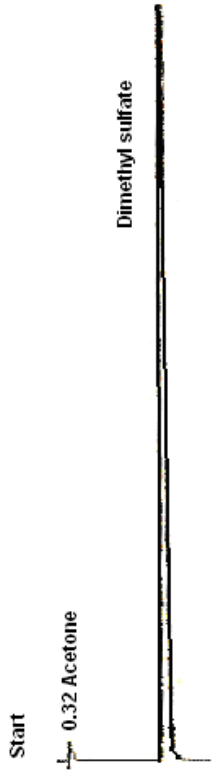

Figure 1. Standard containing 53 µg/mL of dimethyl sulfate in acetone.

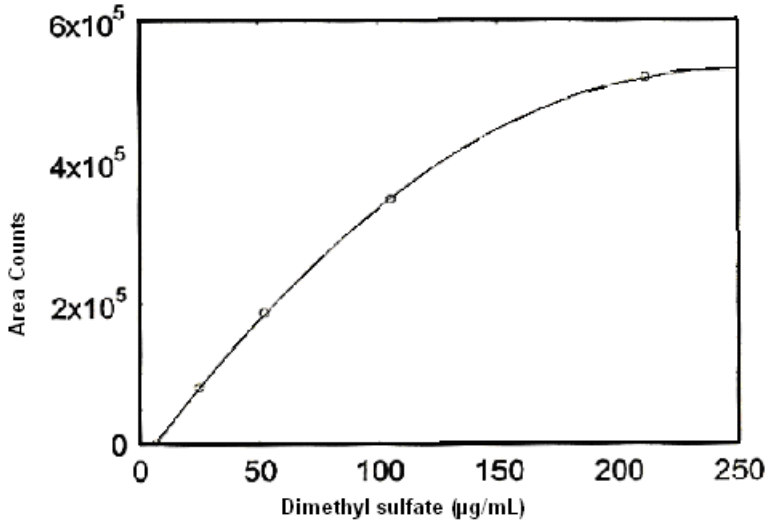

Figure 2. Calibration curve for dimethyl sulfate in acetone. Linear plots are obtained if the square of the sulfur atom concentration is used.

5. References

5.1. “NIOSH Manual of Analytical Methods”, 2nd ed.; Department of Health, Education and Welfare, National Institute for Occupational Safety and Health; Cincinnati, OH. 1979; Vol. 5, Method P&CAM 301; DHEW (NIOSH) Publ. (US), NO. 79-141.

5.2. Carter, V.L., "TLVs Threshold Limit Values for Chemical Substances in Work Air Adopted by ACGIH for 1982", American Conference of Governmental Hygienists, Cincinnati, 1982, page 17.

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5.4. Elkins, H.B., "Documentation of TLVs", American Conference of Governmental Hygienists, Cincinnati, 1980, page 150.

5.5. "Encyclopedia of Chemical Technology", 2nd Edition, vol. 19, pages 494 - 5.

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