

Note

Gas chromatographic method for the determination of dimethyl sulfate in air

KIRPAL S. SIDHU

Occupational Health Laboratory, Michigan Department of Public Health, 3500 North Logan Street, P.O. Box 30035, Lansing, MI 48909 (U.S.A.)

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Dimethyl sulfate, $(\text{CH}_3)_2\text{SO}_4$, is a colorless liquid soluble in water, alcohol and diethyl ether. It boils at 188°C^1 . Dimethyl sulfate is a highly toxic compound and can be absorbed through skin^{2,3}. It is used as a methylating agent for amines and phenols¹. It is present in fly ash and in air borne particulate matter from coal combustion processes⁴. Exposure to dimethyl sulfate can cause health problems because of its proven mutagenic⁵ and possible carcinogenic⁶ effects. The American Conference of Governmental Industrial Hygienists has tentatively adopted 0.1 ppm as a threshold limit value-time weighted average (TLV-TWA) for dimethyl sulfate⁷. At present, no standard for occupational exposure to dimethyl sulfate has been established. During 1979-1980, attempts were made at this laboratory to develop a reliable sampling technique and an analytical procedure for determination of dimethyl sulfate in air. In the meantime, two reports^{8,9} have appeared describing the analysis of dimethyl sulfate by gas chromatographic procedures. Lunsford and Fey⁸ described collection of dimethyl sulfate on Porapak Q porous polymer followed by its subsequent determination by gas chromatography using an oxidative-mode electrolytic conductivity detector. Recently, Gilland and Bright⁹ described a procedure which involves desorption of adsorbed dimethyl sulfate with acetone followed by a gas chromatographic procedure. This method requires gas chromatographic equipment with a solvent venting valve to allow the escape of a large volume of solvent (acetone) without overloading the detector⁹. The object of the present report is to describe the analysis of dimethyl sulfate by a gas chromatographic procedure developed at this laboratory. This method involves adsorption of dimethyl sulfate on silica gel followed by desorption with distilled water and analysis by a gas chromatographic procedure. The method described herein is simple, rapid and accurate.

EXPERIMENTAL

Preparation of dimethyl sulfate standards

Dimethyl sulfate (Mallinckrodt, St. Louis, MO, U.S.A.) standards ranging in concentration from 53.7 to 536.8 $\mu\text{g}/\text{ml}$ in distilled water were prepared in glass vials (Wheaton Scientific, Millville, NJ, U.S.A.).

Preparation of dimethyl sulfate standards by using silica gel tubes

Dimethyl sulfate (4 ppm) from a standard environment (50 l) was adsorbed on

silica gel (silica gel sample tubes; SKC, Eighty Four, PA, U.S.A.) by sampling 10 to 15 l of air using a personal sampler (0.48 ml/count; SKC).

Desorption efficiency study

The first section of each silica gel tube (100 mg silica gel) was loaded with dimethyl sulfate (134.2 to 402.6 $\mu\text{g}/\text{tube}$). A blank silica gel tube was included in the study. The tubes were immediately stored at 4°C for 48 h. The silica gel from the first section of each tube was then transferred to glass vials each containing 0.5 ml of distilled water. The analyte was desorbed with water using an ultrasonic bath (Branosonic 220) for 1 h. All vials were tightly capped to minimize losses from evaporation. The percentage recovery of dimethyl sulfate determined by gas chromatography was calculated by comparing the results with the standard curve. A smooth standard curve was prepared from the data obtained for dimethyl sulfate standards in distilled water.

Gas chromatography

The gas chromatographic analysis was conducted by using a gas chromatograph (Beckman GC 72-5) equipped with a flame ionization detector. The analytical column used was 3 m \times 6 mm I.D. stainless steel packed with 10% Apiezon L (Alltech Assoc., Arlington Heights, IL, U.S.A.) on a 60-80 mesh size Chromosorb P AW (Analabs, New Haven, CT, U.S.A.). The column was conditioned for 24 h at 200°C. The analytical conditions were: column temperature 100°C isothermal, inlet temperature 150°C, detector temperature 250°C, hydrogen flow 50 ml/min, air flow 250 ml/min and argon (carrier gas) flow 60 ml/min. Dimethyl sulfate adsorbed on silica gel was desorbed with 0.5 ml of distilled water as described above. An aliquot (2 μl) was injected by using the solvent flush technique. The column was primed by repeated injections of a dimethyl sulfate standard (1341.9 $\mu\text{g}/\text{ml}$) in distilled water.

RESULTS AND DISCUSSION

The results of dimethyl sulfate standards prepared in distilled water revealed that dimethyl sulfate can be analyzed by the gas chromatographic identification on Apiezon L using a flame ionization detector. The precision (coefficient of variation) for the analytical procedure was 3.54% ($n = 9$).

A chromatogram representing the results of dimethyl sulfate standards prepared by using silica gel tube is shown in Fig. 1. A sharp peak with a retention time of 1.0 min was obtained. Based on a 20-l air sample, the calculated detectable limit for dimethyl sulfate by this procedure was 0.05 ppm. In general the results are in agreement with the finding of Gilland and Bright⁹ that dimethyl sulfate can be adsorbed on silica gel.

The desorption efficiency of distilled water for desorption of dimethyl sulfate from silica gel is given in Table I. The overall mean desorption efficiency was $97.1 \pm 1.64\%$.

CONCLUSION

A simple, rapid and accurate method for the determination of dimethyl sulfate

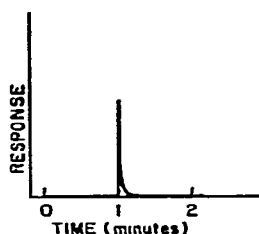


Fig. 1. Gas chromatogram of dimethyl sulfate (4 ppm). Volume of air sampled was 14.8 l. The analytical conditions were: column temperature, 100°C isothermal; inlet temperature, 150°C; flame ionization detector temperature, 250°C; carrier gas (argon) flow, 60 ml/min; and sample size, 2 μ l.

TABLE I
DESORPTION EFFICIENCY DATA

Dimethyl sulfate added (μ g)	Determination (n)	Storage (h)	Recovery (%) [*]
134.2	3	48	95.8 \pm 4.01
268.4	4	48	97.6 \pm 3.07
402.6	4	48	97.7 \pm 3.54
Overall desorption efficiency of distilled water =			97.1 \pm 1.64

* Mean \pm standard error.

is presented. The method involves adsorption of dimethyl sulfate on silica gel, desorption with distilled water and subsequent gas chromatographic identification on 10% Apiezon L using a flame ionization detector.

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