Short Communication

Determination of dimethyl sulphate in air by gas chromatography with flame photometric detection

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ABSTRACT

A rapid and precise analytical method for the determination of dimethyl sulphate in air, involving sampling with a Florisil adsorption tube and determining of the amount of desorbed dimethyl sulphate by gas chromatography using a flame photometric detector for the detection of sulphur, is described. The application of a flame photometric detector for sulphur detection serves as a simple gas chromatographic procedure which does not require the derivatization of dimethyl sulphate and solvent flashing techniques. The coefficients of variation including the desorption of dimethyl sulphate from the Florisil tube are 2.70–3.65%. The detection limit for a sample size of 10 l and an injection volume of 1.0 μl is 0.03 ppm of dimethyl sulphate in air.

INTRODUCTION

Dimethyl sulphate is commonly used as a methylating agent for amines and phenols in industry and laboratories. It is an extremely hazardous compound but it has no warning characteristics; it can be absorbed through the skin and can give serious poisoning without immediately noticeable signs [1,2]. Evidence regarding mutagenic and possible carcinogenic effects of dimethyl sulphate has been presented [3]. The American Conference of Governmental Industrial Hygienists recommended a tentative change in the threshold limit value (TLV) of dimethyl sulphate from 1.0 to 0.01 ppm in 1973. Currently, a limit of 0.1 ppm has been adopted [4].

The determination of dimethyl sulphate in air requires a sensitive and simple method for the routine determination of ppb levels of dimethyl sulphate. An obstacle to the application of gas chromatography (GC) for this purpose is the difficulty of the complete separation of the peak of dimethyl sulphate from those of solvents. Gilland and Bright [5] described a procedure which involves desorption of dimethyl sulphate adsorbed on silica gel with acetone followed by analysis using a gas chromatograph equipped with a solvent venting valve to allow the escape of acetone. Sidhu [6] report-

ed a similar method using distilled water as a solvent instead of acetone and a solvent flushing technique in GC.

Williams [7] reported a high-performance liquid chromatographic (HPLC) procedure involving sampling with a silica gel adsorption tube, reaction of the trapped dimethyl sulphate with sodium p-nitrophenoxide in acetone solution and determination of the resulting p-nitroanisole by HPLC.

In this paper we describe a procedure for the determination of dimethyl sulphate involving sampling with a Florisil adsorption tube and determination of the desorbed dimethyl sulphate by GC with flame photometric detection of sulphur, which is highly sensitive to dimethyl sulphate and poorly sensitive to non-sulphur-containing solvents. Hence no derivatization of dimethyl sulphate or venting of solvent is required.

EXPERIMENTAL

Materials

Analytical-reagent grade dimethyl sulphate was purchased from Nacalai Tesque Co. Florisil (60–80 mesh) for GC was purchased from Nacalai Tesque and was washed with 10% hydrochloric acid until the washings become colourless, washed with distilled water, then heated at 450°C for 5 h. Silica gel (60–80 mesh) for chromatography was purchased from Nacalai Tesque. Methyl isobutyl ketone (MIBK), methanol, butyl acetate and toluene were of analytical-reagent grade.

Instrumentation

GC was carried out with a Shimadzu Model GC-4CM gas chromatograph equipped with a Shimadzu Model FPD-1A flame photometric detector for sulphur and a flame ionization detector. The transmission of the optical filter attached to the flame photometric detector was maximum at 384 nm. The separation was performed on a 2 × 3 mm I.D. glass column packed with 3% silicone OV-330 on 80–100-mesh Chromosorb W AW DMSC.

Preparation of dimethyl sulphate standards

Dimethyl sulphate standards ranging in concentration from 1.0 to 20.0 μg/ml in MIBK were prepared.

Preparation of adsorption tube

A 50 mm × 3 mm I.D. glass tube was packed with 100 mg of Florisil or silica gel and both ends were stopped with glass-wool.

Sampling and analysis of dimethyl sulphate

A metered flow of air (0.5–1.0 l/min) was drawn over the adsorption tube. The adsorbent in the tube was placed in a glass vial containing 1.0 ml of solvent and the mixture was sonicated for 10 min. An aliquot of the solution was injected into the gas chromatograph. The concentration of dimethyl sulphate was determined with the aid of a calibration graph obtained as a log–log plot of peak height *versus* concentration of dimethyl sulphate. The analytical conditions were column temperature 100°C isothermal, inlet temperature 220°C, detector temperature 220°C, nitrogen carrier gas

flow-rate 60 ml/min, hydrogen pressure 0.5 kg/cm^2 and air pressure 0.6 kg/cm^2. The sensitivity and range were set at 100 MΩ and 8 × 0.01 V, respectively.

Adsorption efficiency study

Two adsorption tubes packed with Florisil or silica gel were connected in series and held horizontally. Volumes of 100 and 200 μl of 20.0 μg/ml dimethyl sulphate standard solution were dripped onto the inner wall of the front tube by using a microsyringe. Air was drawn over the tubes for 90 min at a flow-rate of 1.0 l/min at room temperature. Dimethyl sulphate in the standard solution was vaporized and carried into the adsorbent during the air drawing. The amounts of dimethyl sulphate adsorbed in the front and back tubes were determined as described above.

Studies on recovery efficiency and stability of desorbed dimethyl sulphate

The adsorption tubes were loaded with dimethyl sulphate as described above and the tubes were allowed to equilibrate for 1 h. The analyte was desorbed with solvents (MIBK, methanol, butyl acetate or toluene). Analysis of the desorbed sample was carried out in the usual manner immediately and after storage for 48 h at room temperature.

RESULTS AND DISCUSSION

The results obtained for dimethyl sulphate standards revealed that dimethyl sulphate can be determined by GC on silicone OV-330 using a flame photometric detector for sulphur. The calibration graph is linear with a slope of 1.72 on a log–log plot as shown in Fig. 1. The precision [relative standard deviation (R.S.D.)] with 4.0 ng of dimethyl sulphate was 2.04% ($n = 10$). The R.S.D.s for five determinations at the 2.0 and 4.0 μg per tube levels were 3.65 and 2.70%, respectively.

A gas chromatogram obtained by the proposed procedure is shown in Fig. 2. A sharp peak with a retention time of 4.8 min which was completely separated from the solvent peak was obtained, whereas the peaks overlapped with flame ionization detection.

The recovery efficiencies of dimethyl sulphate from Florisil by desorption with solvents and after subsequent storage of the solution for 48 h in the dark are shown in Table I.

Polar solvents except methanol gave good desorption efficiencies of dimethyl sulphate from Florisil; the recovery of dimethyl sulphate dissolved in methanol decreased after storage for 48 h. MIBk gave the highest recovery and was chosen as the optimum solvent. The adsorption efficiencies of dimethyl sulphate on Florisil and silica gel are given in Table II.

Dimethyl sulphate in air was trapped quantitatively in the front tube packed with either silica gel or Florisil. Florisil gave a slightly better reproducibility. No adsorption of dimethyl sulphate on glass-wool used as the stopper in the adsorbent tube was observed.

The sample capacity for an adsorption tube was found to be at least 90 l of air. With a volume of 10 l (1 l/min flow-rate and 10-min sampling time), the detection limit of *ca.* 1.5 ng with an injection volume of 1.0 μl corresponds to 0.03 ppm. If neccesary, the detection limit could be improved by use of a larger injection volume or a larger sample size.

Fig. 1. Calibration graph. Analytical conditions: column temperature, 100°C isothermal: inlet and detector temperature, 220°C; carrier gas (nitrogen) flow-rate 60 ml/min; sensitivity, 100 MΩ; range, 8 × 0.01 V.
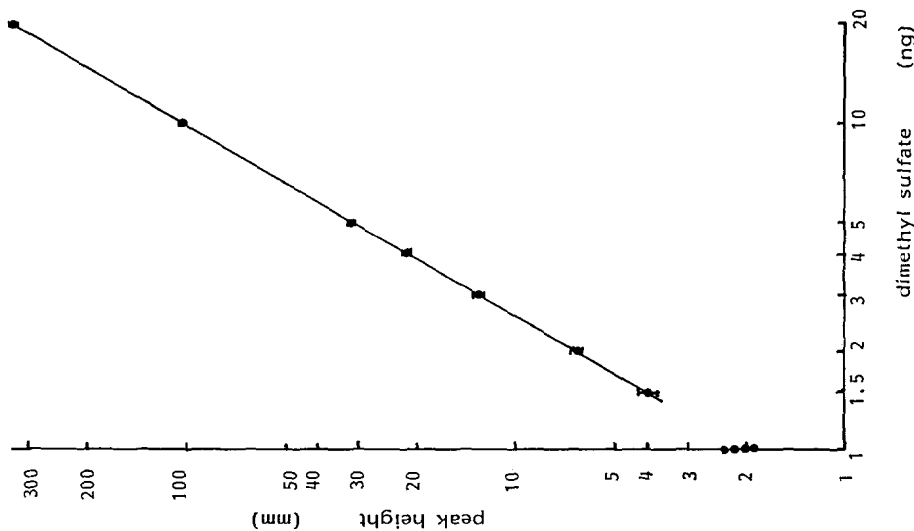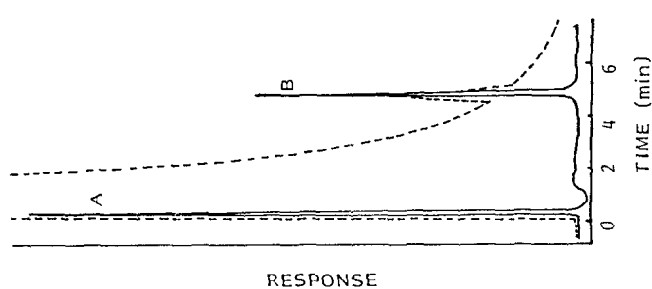
Fig. 2. Typical gas chromatogram of dimethyl sulphate. Solid line: flame photometric detection; 4 μl of a 2 μg/ml dimethyl sulphate standard solution were injected. Flame ionization detection; 10 μl of a 20 μg/ml dimethyl sulphate standard solution were injected. Analytical conditions as shown in Fig. 1. A = MIBK; B = dimethyl sulphate.

TABLE I

RESULTS OF RECOVERY EFFICIENCY STUDY

Dimethyl sulphate loaded: 2 μg.

Solvent	Storage time (h)	Recovery (%) ($n = 3$)
Methanol	0	94.2–98.4
	48	30.2–36.5
Butyl acetate	0	92.0–96.2
	48	91.2–92.5
MIBK	0	95.0–101.2
	48	95.0–98.7
Toluene	0	60.8–75.3
	48	60.8–75.5

TABLE II

ADSORPTION EFFICIENCY OF DIMETHYL SULPHATE ON FLORISIL AND SILICA GEL

Dimethyl sulphate loaded (μg)	Adsorbent	Dimethyl sulphate recovered (μg)		
		Front tube[a]	Back tube	Glass-wool
2.0	Silica gel	1.86 ± 0.06	0	0
	Florisil	1.96 ± 0.04	0	0
4.0	Silica gel	3.91 ± 0.12	0	0
	FLorisil	3.94 ± 0.08	0	0

[a] Mean ± S.D. for five runs.

CONCLUSION

A simple, rapid and accurate method for the determination of dimethyl sulphate in air at levels well below the current TLV has been developed. The method involves adsorption of dimethyl sulphate on Florisil, desorption with MIBK and subsequent GC identification on silicone OV-330 with flame photometric detection of sulphur.

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