German Social Accident Insurance
Deutsche Gesetzliche Unfallversicherung
Analytical Subcommittee of the Chemistry Board of Experts*

Carcinogenic substances	Order number: BGI 505-7-05
Established methods:	Issued: February 2007

Method for the determination of dimethyl sulfate

This method has been tested and recommended by the German Social Accident Insurance for the determination of dimethyl sulfate at workplaces.
Both personal and stationary sampling can be performed for the assessment of workplaces.

Sampling is carried out with a pump and adsorption on Tenax®. Analysis is performed by gas chromatography with mass selective detection (GC/MS) after thermal desorption.

Chemical names:	Dimethyl sulfate, sulfuric acid dimethyl ester
CAS number:	77-78-1
Molecular formula:	$C_2H_6O_4S$
Molar mass:	126.13 g/mol

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Summary

This method can be used with personal or stationary sampling to determine the mean concentration of dimethyl sulfate at workplaces over the sampling time.

Principle:	A pump draws a defined volume of air through a metal tube filled with Tenax. The adsorbed dimethyl sulfate is then thermally desorbed and determined by gas chromatography.
Limit of quantification:	Absolute: 23 ng of dimethyl sulfate Relative: 0.9 µg/m^3 of dimethyl sulfate for a 25 L air sample.
Selectivity:	The method is selective due to the combination of gas chromatographic separation and mass selective detection.
Advantages:	Personal and selective measurements are possible.
Disadvantages:	No indication of peak concentrations.
Apparatus:	Pump with gas meter or volumetric flow meter, adsorption tubes filled with Tenax, gas chromatograph with thermal desorber and mass selective detector.

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:

- Pump, suitable for a flow rate of 5 to 200 mL/min, e.g. PP1, Gilian, supplied by DEHA Haan & Wittmer, 71296 Heimsheim, Germany
- Gas meter or volumetric flow meter
- Adsorption tube filled with Tenax as the collection phase:
  Metal tubes serve as adsorption tubes. Their external diameter and length must be adapted to the thermal desorber used. The tubes are filled with 250 mg of Tenax, which is enclosed by two metal sieves. After being filled, the tubes must be previously purged several times in a stream of helium at 250 °C in the thermal desorber. Then they are sealed with Swagelok® screw caps with Teflon seals.

For the sample preparation and analysis:

- Volumetric flasks, 10 mL
- Adjustable piston pipette, e.g. Multipette pro, Eppendorf, 22366 Hamburg, Germany
- Microliter syringe, 10 µL
- Spiking facility (consisting of a brass T-piece with septum) to apply calibration or internal standard solutions to adsorption tubes

- Thermal desorber
- Gas chromatograph with mass selective detector (GC/MS)

1.2 Chemicals and solutions

Dimethyl sulfate, 99%, e.g. from Aldrich, 82024 Taufkirchen, Germany
Naphthalene, as the internal standard (IS), purity >99%, e.g. from Aldrich
Methyl-*tert.*-butyl ether (MTBE), purity 99.8%, anhydrous, e.g. from Aldrich
Tenax®, 60–80 mesh, e.g. from Supelco, 82024 Taufkirchen, Germany
Helium 5.0 (purity 99.999%), to operate the gas chromatograph and the thermal desorber

Naphthalene stock solution: Solution of approx. 5.32 mg of naphthalene per mL of methyl-*tert.*-butyl ether (MTBE).
Approx. 26.6 mg of naphthalene are weighed to the nearest 0.1 mg in a 5 mL volumetric flask. The flask is then filled to the mark with MTBE and shaken.

Internal standard solution (IS): Solution of approx. 266 µg of naphthalene (IS) per mL of MTBE.
500 µL of the IS stock solution are pipetted into a 10 mL volumetric flask that already contains several milliliters of MTBE. The volumetric flask is then filled to the mark with MTBE and shaken.

Calibration stock solution: Solution of approx. 20 mg of dimethyl sulfate per mL of MTBE.
Approx. 150 µL of dimethyl sulfate are pipetted into a 10 mL volumetric flask that already contains several milliliters of MTBE and the dimethyl sulfate is weighed to the nearest 0.1 mg. The volumetric flask is then filled to the mark with MTBE and shaken.

Calibration solutions: Solutions of approx. 50 to 1000 µg of dimethyl sulfate per mL of MTBE.
25 µL, 100 µL, 200 µL, 300 µL, 400 µL and 500 µL each of the calibration stock solution are added with the piston pipette to six 10 mL volumetric flasks containing a few milliliters of MTBE. The volumetric flasks are then filled to the mark with MTBE and shaken.
5 µL each of these solutions are transferred via the spiking facility to six separate Tenax tubes. These adsorption tubes cover a concentration range of dimethyl sulfate from 0.01 mg/m^3 to 0.198 mg/m^3 for an air sample volume of 25 L. The corresponding concentrations are shown in Table 1.

Table 1. Concentrations of the calibration solutions of dimethyl sulfate.

Stock solution added [µL]	Concentration of dimethyl sulfate [mg/L]	Concentration of dimethyl sulfate [mg/m^3]*
25	50	0.010
100	200	0.040
200	400	0.079
300	600	0.119
400	800	0.158
500	1000	0.198

* based on an air sample volume of 25 L

2 Sampling procedure

Shortly before a previously purged adsorption tube is used, it must be heated again for approx. 15 minutes in the thermal desorber at 250 °C in a stream of helium. Then 5 µL of the IS standard solution are applied via the spiking facility to the adsorption tube which is then sealed with a Swagelok® screw cap with a Teflon seal.

For sampling the adsorption tube is opened and connected to the pump. The pump and tube are worn by a person during sampling or they are used for stationary sampling. The flow rate is adjusted to 100 mL/min. At a sampling time of 4 hours this is equivalent to an air sample volume of approx. 25 L. After sampling the tube must be tightly sealed again.

3 Analytical determination

3.1 Sample preparation and analysis

The loaded adsorption tube is opened and inserted into the thermal desorber. The adsorbed dimethyl sulfate is desorbed by heating and transferred to the cold trap of the device containing Tenax by means of helium and collected there. From there it is transferred to the separation column of the gas chromatograph by sudden heating (device-specific heating rate approx. 40 °C/s) and a chromatogram is recorded as described in Section 3.2. The quantitative evaluation is performed according to the internal standard method using the peak areas or heights of dimethyl sulfate and of naphthalene as the internal standard.

3.2 Instrumental operating conditions

The characteristics of the method stated in Section 5 are determined under the following instrumental conditions:

Apparatus: ATD 400 thermal desorber from PerkinElmer LAS, 63110 Rodgau-Jügesheim, Germany
HP 6890 gas chromatograph with an MSD HP 5872 mass selective detector

Operating conditions for thermal desorption

Desorption oven: 250 °C
Inlet split: Closed
Cold trap: Filling Tenax®
Temperatures: –30 °C (adsorption)
280 °C (injection)
Desorption time: 5 minutes
Desorption flow rate: 11.4 mL/min
Outlet split: 20.0 mL/min
Transfer line: 200 °C

Operating conditions for gas chromatography

Separating column: Fused silica capillary, stationary phase DB-1, cross-linked (dimethylpolysiloxane) internal diameter 0.25 mm, film thickness 1 µm, length 30 m
Oven temperature: Initial temperature: 50 °C
Heating rate 20 °C/min to the final temperature of 240 °C
Detector temperature: 250 °C
Carrier gas: Helium 5.0, 24 psi
Transfer line MS: 280 °C

Operating conditions for mass spectrometry

Ionization type: Electron impact ionization (EI) (70 eV)
MS quad: 150 °C
MS source: 230 °C
Solvent delay: 3 minutes
Measurement mode: Selected ion monitoring (SIM)

Registered masses (m/z in amu):		*Quantification*/Qualification
naphthalene	*128*	127
dimethyl sulfate	*95*	96

4 Evaluation

4.1 Calibration

5 µL each of the calibration solutions given as examples in Section 1.2 and 5 µL of the internal standard solution are applied via the spiking facility which is connected to an adsorption tube. Then air at a flow rate of approx. 50 mL/min is drawn for 10 minutes through the tube to transfer the respective calibration solution to the adsorp-

tion tube. The quantities of dimethyl sulfate used to spike the adsorption tubes and the air concentrations calculated for an air sample volume of 25 L are shown in Table 1. The tubes are then analyzed as described in Section 3.2.
The calibration function is obtained by plotting the peak area ratios of dimethyl sulfate and the internal standard versus the weight ratios of dimethyl sulfate and the internal standard on the adsorption tubes.

4.2 Calculation of the analytical result

The mass of dimethyl sulfate corresponding to the peak area in the sample (adsorbed mass on the Tenax tube) is calculated with the calibration function. The dimethyl sulfate concentration by weight in the air sample in mg/m^3 is calculated according to equation (1):

$$c = \frac{m}{V \times \eta} \tag{1}$$

where

c is the concentration by weight of dimethyl sulfate in the air sample in mg/m^3
m is the mass of dimethyl sulfate adsorbed on the Tenax tube in µg
V is the air sample volume in L
η is the recovery (see Section 5.1)

5 Reliability of the method

5.1 Precision and recovery

The precision in the minimum measurement range according to DIN EN 482 [1] and the recoveries were determined for three different concentrations (see Tables 2 and 3).
The following validation solutions were prepared for this purpose:

Validation stock solution:	Solution of 22.5 mg of dimethyl sulfate per mL of MTBE. 170 µL of dimethyl sulfate were pipetted into a 10 mL volumetric flask that already contained several milliliters of MTBE and the dimethyl sulfate was weighed to the nearest 0.1 mg. Then the volumetric flask was filled to the mark with MTBE and shaken.
Validation solutions:	Solutions of 56, 562 and 1124 µg of dimethyl sulfate per mL of MTBE. 25 µL, 250 µL, and 500 µL each of the validation stock solution were added to three 10 mL volumetric flasks,

which contained several milliliters of MTBE. The volumetric flasks were then filled to the mark with MTBE and shaken.

To determine the precision of the method for each of the investigated concentrations (Table 2) six adsorption tubes were connected to a multiple tube holder that enabled the flow rate of the individual pump to be adjusted for each tube separately. A glass tube filled with a plug of quartz wool was fitted in front of each adsorption tube by means of a short piece of Teflon tube. 5 µL each of the three validation solutions and 5 µL of the internal standard solution were applied to the quartz wool of the glass tubes. Then 25 L of ambient air were drawn through each tube at room temperature (23 to 25 °C) at a flow rate of 200 mL/min. Concentrations of 0.23 mg/m^3, 0.11 mg/m^3 and 0.01 mg/m^3 at an air humidity of approx. 55% and 85% were thus obtained.
The characteristics obtained for a relative air humidity of 55% are shown in Table 2.

Table 2. Characteristics of the method at a relative air humidity of approx. 55%.

Concentration of dimethyl sulfate [mg/m^3]	Standard deviation (rel.) [%]	Recovery
0.01	7.9	1.02
0.11	5.4	0.99
0.23	4.3	0.92

The mean standard deviation was 5.9% and the mean recovery 0.98.
The characteristics obtained for a relative air humidity of 85% are shown in Table 3.

Table 3. Characteristics of the method at a relative air humidity of approx. 85%.

Concentration of dimethyl sulfate [mg/m^3]	Standard deviation (rel.) [%]	Recovery
0.01	5.3	0.84
0.11	4.4	0.89
0.23	3.1	0.92

The mean standard deviation was 4.3% and the mean recovery 0.88.
The relative air humidity influenced the relative standard deviations only slightly. The recovery for the lower concentrations fell markedly at higher air humidity. The storage stability of dimethyl sulfate on the Tenax tubes was not notably changed due to the air humidity during sampling.

5.2 Limit of quantification

The limit of quantification was determined as described in DIN 32645 [2] by rapid estimation. The standard deviation required for the calculation was obtained by six-fold injection of a solution of dimethyl sulfate with a concentration of 0.025 mg/L (corresponding to 0.005 mg/m^3 for an air sample volume of 25 L).
The absolute limit of quantification is 23 ng of dimethyl sulfate. The relative limit of quantification is 0.9 µg/m^3 for an air sample volume of 25 L.

5.3 Selectivity

The method is selective due to the combination of gas chromatographic separation and mass selective detection.

6 Remarks

Dimethyl sulfate can be stored in the adsorbed state at room temperature for at least 7 days. The calibration solutions as well as and the stock solution must be freshly prepared at the latest after 48 hours, as residual water in MTBE leads to hydrolysis of dimethyl sulfate.
Further analytical methods for the determination of dimethyl sulfate in the air of workplaces are also published in this series of volumes. One method is entitled BGI 505-7-03 (Sampling with a pump, adsorption on Tenax TA, desorption, gas chromatography and sulfur-specific detection; issued in January 1987) [3] and another is entitled BGI 505-7-04 (Sampling with a pump, adsorption on Tenax TA, desorption, gas chromatography and mass-selective detection; issued in April 1997) [4]. Apart from the determination of dimethyl sulfate, these methods are also suitable for measuring other dialkyl sulfates in the air of workplaces.

7 References

[1] DIN EN 482 (1994) Workplace atmospheres – General requirements for the performance of procedures for the measurement of chemical agents. Beuth Verlag, Berlin.

[2] DIN 32645 (1994) Chemical analysis; decision limit, detection limit and determination limit under repeatability conditions; terms, methods, evaluation. Beuth Verlag, Berlin.

[3] BGI 505-7-03 (2002) Method for the determination of dimethyl sulfate (DMS). In: Deutsche Forschungsgemeinschaft *(Kettrup A., Greim H. eds.)* Analysis of Hazardous Substances in Air, Volume 5, 93–99. Wiley-VCH Weinheim.

[4] BGI 505-7-04 (2002) Method for the determination of dimethyl sulfate (DMS). In: Deutsche Forschungsgemeinschaft *(Kettrup A., Greim H. eds.)* Analysis of Hazardous Substances in Air, Volume 5, 100–105. Wiley-VCH Weinheim.

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