Method Number KP-227R2

1.0 SUMMARY

This analytical method is designed for analysis of dimethyl disulfide in sorbent charcoal tubes. Residues for dimethyl disulfide are extracted with methyl acetate. After centrifugation, an aliquot is removed and analyzed using gas chromatography with mass spectrometry (GC/MS). Quantification is based on the total area of the mass ions representative of dimethyl disulfide. The limit of quantitation (LOQ) is 0.10 µg.

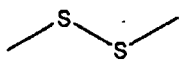
2.0 INTRODUCTION

Dimethyl disulfide (DMDS) is widely used as an industrial chemical and is regulated as a direct food additive. DMDS has shown to have efficacy in the control of soil borne fungi as well as nematodes and nutsedge. Analytical procedure KP-227R1 [ETL / XAM-84] was developed for the determination of dimethyl disulfide residues in sorbent charcoal tubes which are used for collection of any air borne concentrations.

3.0 TEST AND REFERENCE MATERIAL

The reference material (analytical standard) is available from Cerexagri Inc., USA.

Dimethyl disulfide (DMDS):



Chemical Name:	Dimethyl disulfide
CAS Number:	624-92-0
Molecular Formula:	$C_2H_6S_2$
Molecular Weight:	94.1894 g/mol
Purity:	99.8%

4.0 EQUIPMENT

Equipment	Description	Supplier
Analytical Balance	Mettler AE 240	Fisher Scientific
Centrifuge	ICE-Centra-HN	Fisher Scientific
Platform Shaker	Model R-2	New Brunswick Scientific Co., Inc.
Volumetric Flasks	2 to 100 mL	Kimax
Sonicator	Model 1200	Branson
Syringes	0.05 to 1.0 mL	Hamilton
Volumetric Pipette	5 mL	Kimax
Culture Test Tubes	15 mL	Kimax
SPB-1-sulfur Column	30 m × 0.25 mm, 4 µm film thickness (Part No.: 24158)	Supelco
Glass Tube Cutter	Part No:11340	Fisher Scientific
Vortex	Part No.: S8220	Scientific Products
Airlite Sampler Pump	Model 110-100	SKC, Inc.

Dry Cal Flow Meter	DC-Lite	Bios International

Other manufacturer's equipment may be used if shown to be suitable.

5.0 CHEMICALS/REAGENTS/MATERIALS

Reagent	Grade	Supplier
Methyl acetate	99%	Sigma Aldrich
Anasorb Charcoal Tubes	Cat. No.: 226-09	SKC Inc.

Alternate suppliers of chemicals / reagents and materials may be used if shown to be suitable.

6.0 STANDARD STOCK SOLUTION

6.1 Dimethyl disulfide Stock Solution

Dimethyl disulfide (1.002 g after adjusting for percent purity) is weighed into a 10 mL volumetric flask and made to volume with methyl acetate. The calculated concentration is 100 mg/mL.

The stock solution is stored in a refrigerator (approximately 4°C) and prepared fresh every 6 months.

6.2 Fortification Solutions

A volume of 1.0 mL of the stock solution (100 mg/mL) is diluted with methyl acetate to a final volume of 10.0 mL, resulting in a solution containing 10.0 mg of dimethyl disulfide/mL.

An aliquot of 1.0 mL of the 10.0 mg/mL solution is diluted with methyl acetate to a final volume of 10.0 mL, resulting in a solution containing 1.00 mg of dimethyl disulfide/mL.

An aliquot of 1.0 mL of the 1.00 mg/mL solution is diluted with methyl acetate to a final volume of 10.0 mL, resulting in a solution containing 100 µg of dimethyl disulfide/mL.

An aliquot of 1.0 mL of the 100 µg /mL solution is diluted with methyl acetate to a final volume of 10.0 mL, resulting in a solution containing 10.0 µg of dimethyl disulfide/mL.

The fortification solutions are stored in a refrigerator (approximately 4°C) and are prepared fresh every 3 months or as required.

6.3 GC Calibration Solutions

The 10.0 µg/mL standard solution from section 6.2 is used to prepare calibration standards. The following calibration solutions are prepared in methyl acetate.

Standard Solution Conc. (µg/mL)	Volume Used (mL)	Final Volume (mL)	Final Conc. (µg/mL)
10.0	0.025	50.0	0.00500
10.0	0.050	50.0	0.0100
10.0	0.10	50.0	0.0200
10.0	0.15	50.0	0.0300
10.0	0.20	50.0	0.0400
10.0	0.25	50.0	0.0500
10.0	0.50	50.0	0.100
10.0	1.0	50.0	0.200

Calibration standards are given an expiry date not exceeding one month and stored in a freezer (approximately -15°C) when not in use.

Instructions given for the preparation of the calibration solutions are examples only and may be modified as required.

7.0 ANALYTICAL PROCEDURE

7.1 Recovery Fortification of Sorbent Charcoal Samples

Control sorbent charcoal tube samples are fortified with an appropriate amount of the fortification solution by way of injection into a gas chamber connected to an air pump with intake flow set at 2 L/minute for 15 minutes. Control samples are fortified and taken through the procedure to determine recoveries of DMDS at the LOQ (0.10 µg) and at appropriate levels that bracket residue concentrations.

7.2 Extraction

The front or back portion of the charcoal sorbent material from a sorbent tube is removed and transferred to a 15 mL culture tube containing 5.0 mL of methyl acetate. The sample is vortexed for 30 seconds, sonicated for 2 minutes and then shaken on a New Brunswick platform shaker for 30 minutes. After shaking, the sample is again sonicated for 2 minutes and then centrifuged at 2500 rpm for at least 5 minutes to help settle any sorbent material in the methyl acetate extract. An aliquot of extract is removed and analyzed using GC/MS. For extraction of the front and back sorbent material combined, a 10 mL volume of methyl acetate is used and taken through the extraction procedure as above.

8.0 QUANTITATION

Quantitation is performed using gas chromatography with mass spectrometric detection (GC/MS) with conditions as described in section 8.1.1. These parameters

are to be considered general guidelines and may be optimized to fit instrumental requirements.

8.1 GC/MS Instrumentation

Instrumentation consists of a Varian GC 3400(CX) with an auto sampler (8200CX) and a Saturn 2000 GC/MS. Data is acquired using the Varian Star Chromatography Workstation software, version 5.5.1.

8.1.1 GC/MS Chromatographic Conditions

Instrumental Method-1

GC	Varian 3400CX			
Mass Spec Interface	Saturn 2000			
Column	SPB-1-sulfur 30M x 0.32 mm ID, 4.0 µm film thickness			
Carrier Gas	Helium, Head Pressure 5.0 psi			
Injection Inlet/liner	1078/split liner – 5 µL Splitless injection			
Injector Temperature Injector uptake speed Pause Time Injection Rate	280°C, Hold 0.25 min 1.0 µL/sec. 1 sec. 5.0 µL/sec.			
Detector Temperature	150°C			
Oven Temperature Program	Rate (°C/min.)	Temperature (°C)	Hold Time (min.)	Total Time (min.)
Initial	—	35	3.00	3.00
1	3.0	75	0.00	16.3
2	50.0	250	2.00	21.8
Detector Conditions:				
Emission Current	20 µamps			
Mass Defect	0 mmu/100u			
Multiplier Offset	200 volts			
Scan Time	1.0 sec.			
Segment Start Time	13.0 min.			
Segment End Time	16.5 min.			
Segment Low Mass	40 m/z			
Segment High Mass	100 m/z			
Ionization Mode	EI AGC			

The sum of ions m/z 94.0, m/z 79.0, m/z 61.0 and m/z 45.0 are determined as the detector response for dimethyl disulfide.

8.2 GC/MS Detector Response Calibration

The peak area response for dimethyl disulfide is determined from a series of calibration standards. Detector responses are linear and can be described by Equation 1. In each analytical set, the calibration data is used to perform a linear regression analysis. The standard concentration (µg/mL) is taken as the x-axis and

detector response (sum of the peak ions of dimethyl disulfide) as the y-axis (Equation 2).

$$y = mx + b \qquad \text{[Eq. 1]}$$

where:

y = peak area response for analyte injected in sample or standard
m = slope of the regression line
x = amount (µg/mL) of analyte found in the sample or standard
b = y-intercept of the regression line

$$peak\ area = \left[\left(ug/mL\ in\ the\ sample\ or\ standard\right) \times m\right] + b \qquad \text{[Eq. 2]}$$

The concentration of the analyte in the final extract is determined from the corresponding calibration curve. For sample extracts of unknown analyte content, the amount found (µg/mL) is calculated from the observed peak area using [Eq. 3].

$$ug/mL\left(x\right)\ in\ the\ sample = \frac{peak\ area - b}{m} \qquad \text{[Eq. 3]}$$

Both samples and standards within an analytical set are analyzed under the same GC/MS conditions.

8.2.1 Calculation of Residues and Recovery

The amount of dimethyl disulfide (µg) in a sample is determined as follows:

$$Amount\ Found\left(\mu g\right) = \frac{\left[peak\ area - intercept\left(b\right)\right] \times V_f}{slope\left(m\right)} \qquad \text{[Eq. 4]}$$

where:

V_f = final volume of extract (mL) including dilution factor

Analyte recovery in the fortified samples is calculated as follows:

$$\%\ Recovery = \frac{Residue\ found\ in\ fortified\ sample\ \left(\mu g\right)}{Fortification\ level\ \left(\mu g\right)} \times 100 \qquad \text{[Eq. 5]}$$

9.0 DETECTION LIMITS

The limit of quantitation (LOQ) for dimethyl disulfide using this method has been determined as 0.10 µg based on a final volume of 5 mL.

10.0 NOTES TO THE METHOD

a) A 5 µL injection volume was necessary for analysis using the Varian 2000 GC/MS and would be considered a maximum volume that could be used for this analysis. Other instrumentation with greater sensitivity may only require a 1 to 3 µL injection volume.

b) It was found that a 100 µL syringe was the most effective syringe when performing fortifications. Lower volume syringes (i.e. 10 to 50 µL) tended to give consistently higher recoveries (>120%).

c) When performing fortifications, the syringe needle is inserted through the septa of the fortification chamber and the solution allowed to evaporate while air is drawn through. The syringe should be removed once the liquid solution has evaporated and not left in the chamber for the duration of the sampling. This could cause higher than anticipated recoveries at the LOQ levels.

d) Possible contamination may occur if preparation of gaseous controls and fortifications at or near the LOQ (0.1 µg) are conducted at the same time as high gaseous fortifications (i.e. 5000 µg). High standard concentrations open in the same area as the controls or low fortifications may cause contamination. DMDS solution extracts and other waste materials and rinses should be kept in closed containers away from the area used for fortifications.

e) If controls or fortifications are conducted with air drawn through for one hour or more, the area where the study is performed should be evaluated for levels of DMDS as a possible source of contamination. The fortification equipment and septa should be well maintained and evaluated for low level sources of DMDS contamination.