USATHAMA METHOD NUMBER: LL03

DETERMINATION OF ORGANOSULFUR COMPOUNDS IN SOIL BY GAS CHROMATOGRAPHY

I. SUMMARY

A. ANALYTES

This method is applicable to the Class 1 analysis of the following organosulfur compounds in environmental soil samples:

Dimethyldisulfide (DMDS)

1,4-Oxathiane (OXAT)

1,4-Dithiane (DITH)

p-Chlorophenylmethylsulfide (CPMS)

Benzothiazole (BTZ)

p-Chlorophenylmethylsulfoxide (CPMSO2)

p-Chlorophenylmethylsulfone

B. MATRIX

This method is applicable to all environmental soil and sediment matrices.

C. GENERAL METHOD

Ten grams (g) of soil are dried with 10 g of anhydrous sodium sulfate and extracted with methylene chloride for 4 hours on a wrist-action shaker. The extract is analyzed by gas chromatography (GC) using flame-photometric detection (FPD) in the sulfur mode.

II. APPLICATION

A. TESTED CONCENTRATION RANGE

The tested concentration ranges for the target analytes are as follows:

Analyte	Tested Concentration Range (ug/g)
DMDS	0.692 to 13.8
OXAT	0.856 to 17.1
DITH	0.571 to 11.4
CPMS	1.08 to 21.6
BTZ	0.528 to 13.2
CPMSO	2.25 to 45.0
CPMSO2	2.37 to 47.4

Note: ug/g = micrograms per gram.

B. SENSITIVITY

The instrumental responses for each compound, reported in peak area units at the certified reporting limit (CRL), are as follows:

Analyte	Certified Reporting Limit (ug/g)	Area Counts
DMDS	0.692	8,800
OXAT	0.856	38,2,300
DITH	1.47	2,400
CPMS	1.08	2,271
BTZ	1.08	6,690
CPMSO	2.25	6,400
CPMSO2	2.37	4,489

C. REPORTING LIMITS

The CRL and upper certified limits (UCLS) for each analyte analyte in environmental soil samples are as follows:

Analyte	CRL (ug/g)	UCL (ug/g)
DMDS	0.692	13.8
OXAT	0.856	17.1
DITH	1.47	11.3
CPMS	1.08	21.6
BTZ	1.08	13.2
CPMSO	2.25	45.0
CPMSO2	2.37	47.4

D. INTERFERENCES

Solvents, reagents, glassware, and other sample processing equipment may yield chromatograms with interfering peaks. All reagents, glassware, and sample handling equipment must be free from interferences that have retention times equal to the retention times of the compounds of interest. This method is subject to interference from coeluting species that respond to FPD. Carryover from analysis of a highly contaminated sample can result in apparent contamination of the succeeding samples analyzed. Such contamination is often manifested by the presence of unusually broad chromatographic peaks nested among narrower peaks. This interference is minimized by reanalyzing heavily contaminated samples following dilution, running blanks after heavily contaminated samples until carryover is removed, and/or baking off the column at the column temperature maximum until the contamination is removed.

E. ANALYSIS RATE

After instrument calibration, one analyst can analyze 10 sample extracts in an 8-hour day. One analyst can perform approximately 10 extractions in an 8-hour day.

F. SAFETY INFORMATION

The target compounds in this method are toxic. The preparation of all standards should be performed in a laboratory hood. Adequate dermal protection must be used when handling samples and standards.

III. APPARATUS AND CHEMICALS

A. GLASSWARE/HARDWARE

1. Amber bottles (60-millilter (mL) with Teflon -lined screw caps).
2. Class A Volumetric flasks (5-, 10-, 25-, 50- and 100-mL).
3. Class A Volumetric pipettes (0.5 to 25 mL).
4. Microsyringes (250- and 1,000-mL).
5. Pasteur pipettes (disposable).
6. Micropipettes [50-, 100-, 200-, and 1,000-microliter (uL)].
7. Amber-glass vials (9-mL, with Teflon-lined crimp caps).
8. Glass vials (2-mL, with Teflon -lined crimp-seal caps for use with an automatic sampler).
9. Stainless-steel spatulas.
10. Analytical balance (Mettler AE160 or equivalent, with 0.0001-g sensitivity).
11. Stainless-steel spatulas.
12. Wrist-action shaker.

B. INSTRUMENTATION

1. Gas chromatograph with an FPD (Varian 3400 or equivalent), equipped with an automatic sampler (Varian 8055 or equivalent) and integrator (Spectra-Physics 4270 or equivalent).
2. Chromatographic conditions:
   a. Column: 5-percent SP-1000 on Chromosorb [6-foot (ft) by

2-millimeter (mm) inside diameter (ID) by 6 mm outside diameter (OD)].

b. Injector temperature: 200 degrees Celsius (C).

c. Temperature Program: 80 C, hold 3 minutes (min), heat at 32 degrees Celsius per minute (C/min) to 240 C, hold 7 min.

d. Detector temperature: 300 C.

e. Gas flow: Helium at 30 milliliters per minute (mL/min), hydrogen at 140 mL/min, Air 1 at 80 mL/min, Air 2 at 170 mL/min.

f. Injection volume: 5 uL.

g. Retention times: A retention time window of ± 3 times the standard deviation of the retention time of standards for each analyte will be used for compound identification.

Analyte	Retention Time (min)
DMDS	1.47 ± 0.04
OXAT	4.40 ± 0.13
DITH	6.45 ± 0.19
CPMS	7.65 ± 0.23
BTZ	7.92 ± 0.24
CPMSO	10.5 ± 0.32
CPMSO2	11.87 ± 0.36

C. ANALYTES

Analyte	Abstract Service (CAS Number)	Boiling Point (C)
DMDS	624-92-0	--
OXAT	15890-15-1	147
DITH	505-29-3	200
CPMS	123-09-1	--
BTZ	95-16-9	231
CPMSO	934-73-6	--

CPMSO2 98-57-7 --

D. REAGENTS AND STANDARD ANALYTICAL REFERENCE MATERIALS (SARMs)

The standards used for the target compound certification and calibration are all USATHAMA standard analytical reference materials (SARMs) with the exception of BTZ, which was not available as a SARM at the time of this certification. Equivalent standards may be used as long as they have been characterized according to Sec. 6.5.3 of the USATHAMA Quality Assurance (QA) Plan (2nd Edition, March 1987). The BTZ standard was from Aldrich Chemical Company, Milwaukee, WI. A copy of the mass spectrum of this BTZ standard, the reference mass spectrum from the combined Wiley/National Bureau of Standards library of mass spectra, and a chromatogram of the standard analyzed by gas chromatography with flame ionization detector (GC/FID) are presented in Attachment 1. The SARM and Aldrich lot numbers for the target analytes are as follows:

Analyte	SARM or Aldrich Lot Number
DMDS	SARM - 1378
OXAT	SARM - 2119
DITH	SARM - 2111
CPMS	SARM - 1105
BTZ	Aldrich - 91928DP
CPMSO	SARM - 3107
CPMSO2	SARM - 1106

Other chemicals and materials include: methylene chloride (pesticide grade): acetone (pesticide grade): sodium sulfate (400 C for 4 hours in muffle furnace): and, "Standard Soil" (certification spikes used an uncontaminated natural soil from Rocky Mountain Arsenal, rather than the USATHAMA Standard soil).

IV. CALIBRATION

A. INITIAL CALIBRATION

1. Preparation of Standards

Individual primary stock calibration standards are prepared by weighing approximately 25 milligrams (mg) of each of the six target analytes into separate 25-mL volumetric flasks, then diluting to volume with methylene chloride. The nominal concentrations of each of the primary stock calibration standards prepared this way for each analyte is 1,000 ug/mL.

A composite primary stock calibration standard is prepared by adding 5 mL of each individual stock calibration standard to methylene chloride in a 50-mL volumetric flask and then diluting to volume with methylene chloride. The nominal concentrations in the composite primary stock calibration standard for each analyte is 100 ug/mL.

A composite secondary calibration stock is prepared by placing 5 mL of the composite primary calibration stock into a 50-mL volumetric flask and diluting to volume with methylene chloride (a 1:10 dilution of the composite primary calibration stock). The nominal concentration in the composite secondary calibration stock for each analyte is 10.0 ug/mL.

Composite working calibration standards are prepared using methylene chloride, the composite primary and secondary stock calibration standards and volumetric pipettes as shown in Table IV-1.

2. Instrument Calibration

To calibrate the instrument, 5 uL of each standard in Table IV-1 is injected into the instrument in the same manner as a

sample extract. Duplicate composite calibration standards are analyzed during precertification calibration, and the single dilutions of the composite standards are analyzed during initial calibration.

Currently an independent reference standard is not available for organosulfur compounds in water. Meanwhile an independent stock will be prepared to serve as a reference standard. The reference must be analyzed along with the initial and precertification calibration standards, and the results must be within ± 25% of the true value for the calibration to be considered valid. If the analysis of the reference standard fails, the source of the problem must be identified and corrected. The initial calibration and analysis of the independent reference standard must be repeated. The result of the second analysis of the independent reference standard must be within the acceptable limits, as specified by the source of the standard, before the analysis of samples may proceed. Since initial calibrations are performed daily, a reference is required at least weekly.

3. Analysis of Calibration Data

After analyzing the standards (i.e., one blank and nine standards) in duplicate, the data are tabulated and graphed. Data are analyzed using the lack of fit (LOF) and zero intercept (ZI) tests (USATHAMA QA Plan, 2nd Edition, March 1987). All pre-certification calibration data passed the LOF-ZI tests, therefore calibrations are linear. Not all data from the standards analyzed in Table IV-1 are used for the regressions (i.e. Standard A would be used for CPMSO and CPMSO2 only, while Standards G-J would not be used for CPMSO and CPMSO2).

4. Calibration Checks

At the end of the daily instrumental analysis, the highest working calibration standard is injected into the GC. The response of the recovery of this end-of-day analysis should be ± 25% of the response or recovery obtained from the analysis of the same working calibration standard curve analyzied that day. If the first calibration check does not pass this criterion, then the standard may be reinjected and compared to the initial response. The post run standard data is documented and the percent drift is calculated on the chromatographic logsheet. An explanation must be provided if the calibration check is not acceptable for the data to be reported, otherwise the samples are rerun.

B. DAILY CALIBRATION

For daily calibration an initial calibration curve and QC checks will be performed as stated in Section IV.A.

V. CERTIFICATION TESTING

A. PREPARATION OF CERTIFICATION SPIKES

1. Individual primary stock control spiking solutions are prepared by weighing approximately 50 mg of each of the analytes into separate 50-mL volumetric flasks, then diluting each to volume with acetone. The nominal concentrations in the individual primary stock spiking solutions were 1,000 ug/mL.

2. A composite primary stock control spiking solution is prepared (in a 50-mL volumetric flask) by diluting 5 mL of each of the individual primary stock control spiking solutions (2.5 mL for BTZ during certification only) with acetone to the final volume of 50 mL. The nominal concentrations in the composite primary stock control spiking solution prepared as above were 100 ug/mL (50 ug/mL

for BTZ during certification only).

3. The spiking procedure in Table V-1 was implemented to prepare control spike samples to determine the accuracy and reporting limits for each analyte. In each case, 10 g of "standard soil" in separate, 60-mL amber vials were spiked with the appropriate volume of the composite primary control spiking solution and allowed to dry for 1 hour prior to extraction. Actual concentrations during certification are presented in Table V-1.

B. ANALYSIS OF CERTIFICATION SPIKES

Certification control spikes are analyzed by the procedures outlined is Sec. VII.

VI. SAMPLE HANDLING STORAGE

A. SAMPLING PROCEDURE

There are no special considerations required due to the nature of organosulfur compounds. Soil samples may be collected as grab samples or cores. The samples need to be chilled to 4 deg. C immediately following sampling.

B. CONTAINERS

Sampling containers used are 1.2 Litre glass amber jars with a teflon-lined cap for grab samples, or polybutyrate tubes for core samples.

C. STORAGE CONDITIONS

Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4 deg. C in a walk-in refrigerator.

Table IV-1. Preparation of Initial Calibration Standards.

Standard	Composite Standard Used	Vol. Used (mL)	Final Vol. (mL)	Nominal Concentration (ug/L)	Nominal Extract Concentration (ug/g)
Blank	-	0	25	0.0	0.0
A	1	5.0	25	20,000	40.0
B	1	4.0	50	8,000	16.0
C	1	2.0	50	4,000	8.00
D	1	1.0	50	2,000	4.00
E	2	4.0	50	800	1.60
F	2	5.0	100	500	1.00
G	2	2.0	50	400	0.80
H	2	2.5	100	250	0.50
I	2	1.0	50	200	0.40
J	2	0.8	50	160	0.32

Source: Hunter/ESE, 1988.

Table V-1: Preparation of Certification Control Spike Samples

Control Spike Samples Prepared	Volume of Composite Primary Control Spiking Solution Used (mL)	Concentration of Control Spike Samples (ug/L)						
		DMDS	OXAT	DITH	CRMS	EBIZ	CRMB02	CRMB0
Blank	0	0	0	0	0	0	0	0
2	0.05	0.692	0.856	0.571	0.540	0.264	0.562*	0.593*
3	0.10	1.38	1.71	1.14	1.08	0.528	1.12*	1.19*
4	0.20	2.77	3.42	2.28	2.16	1.06	2.25	2.37
5	0.50	6.92	8.56	5.71	5.40	2.64	5.62	5.93
6	1.00	13.8	17.1	11.4	10.8	5.28	11.2	11.9
7	2.00	NA†	NA	NA	21.6	10.6	22.5	23.7
8	4.00	NA	NA	NA	NA	NA	45.0	47.4

Spikes prepared with 10 g of Standard Soil.
*Not detected during certification and, consequently, data are not presented in Att. 1.
†NA = not analyzed. Spikes were made at higher concentrations to suplement the non-detected data (see * above) for some analytes; only selected higher concentration spikes were analyzed since only selected data needed to be supplemented.

Source: Hunter/ ESE, 1988.

D. HOLDING TIME LIMITS

The holding time limit is seven days from the time of sampling to extraction of the sample and 40 days from extraction to analysis.

E. SOLUTION VERIFICATION

When fresh control spiking solutions are prepared. They must be verified to determine that:

1. the previous spiking solution had or had not deteriorated
2. the new solution was correctly prepared

Therefore, dilute working spike solutions will be checked against working standards before initial use and again within seven days before subsequent use. The spike solutions should use the same instrumentation used on the samples.

VII. PROCEDURE

Daily quality control spikes (see Section IX.A) and environmental soil samples are prepared for analysis and analyzed as follows:

A. SEPARATIONS

1. Transfer 10 g of each soil sample into separate 60-mL amber vials and mix with 10 g of anhydrous sodium sulfate (Prepare daily control spikes as specified in Section IX.A). Environmental samples are to be extracted within 7 days of sample collection.
2. Add 20 mL of methylene chloride with a volumetric pipette, and cap tightly.
3. Shake the culture tube in a horizontal position for 4 hours on a wrist-action shaker.
4. Allow the particulate to settle or centrifuge. if necessary.
5. With a disposable pipette, transfer approximately 1 to 2 mL of the extract to an autosampler vial. Before sealing, add

several granules of anhydrous sodium sulfate to remove moisture. The extract is now ready for instrumental analysis.

6. Transfer the remainder of the extract to an 8-mL amber glass vial and cap tightly. Save as a backup sample.
7. Store samples at 4 degrees C until analysis. Samples must be analyzed within 40 days of sample extraction.

B. **CHEMICAL REACTIONS**

No chemical reactions are required by this method.

C. **INSTRUMENTAL ANALYSIS**

1. Perform daily instrument calibration as described in Sec. IV.B. Use the instrument conditions listed in Sec. III.B.
2. Place the sample extracts in the autosampler tray and inject 5 uL of each sample extract into the instrument under exactly the same conditions as those under which it was calibrated.

VIII. CALCULATIONS

A linear calibration curve is constructed from the calibration data by plotting the response versus the concentration of each standard. The calibration curve slope and intercept are determined by linear regression. The concentration of a target compound in the extract is calculated by substituting the response into the calibration curve equation. The concentration of each analyte in the original soil sample is determined by the following formula:

$$\text{Concentration (ug/g)} = \frac{\text{Extract Conc. (ug/L) x DF x 20 mL}}{V_w \text{ (g) x 1000 mL/L}}$$

where: Extract Conc. = Calculated concentration in the extract in nanograms per milliliter (ng/mL):
DF = Dilution factor if required to get the response into linear calibration range:
20 mL = Final extract volume in milliliters:
Vw = Sample weight in grams (nominally 10.0 g).

Percent moisture is entered as a separate parameter, and the Installation Restoration Data Management System Computer calculates for dry-weight basis.

IX. DAILY QUALITY CONTROL

A. CONTROL SAMPLES

The daily control spikes required are a Standard Matrix Method Blank, one low level Standard Matrix Spike at approximately twice the CRL, and two high-level Standard Matrix Spikes at five times the low level spike. Individual stock spiking solutions are prepared as discussed in Sec. V.A.1. A composite daily control spike solution is prepared (in a 50-mL volumetric flask) by diluting the following volumes of the individual primary stock control spiking solutions to volume with acetone:

Analyte	mLs Stock	Concentration (ug/mL)
DMDS	5.0	100
OXAT	5.0	100
DITH	7.5	150
CPMS	5.0	100
BTZ	5.0	100
CPMSO	10.0	200
CPMSO2	10.0	200

The spike solution is verified when needed as described in Sec. VI.E. From the combined daily control spike solution, the daily control spikes are prepared as shown in Table IX-1 by adding the perscribed amount of stock to 10 g of standard soil.

Allow the spike to dry on the soil for 1 hour before extraction.

B. CONTROL CHARTS

In the initial construction of the control charts, data from the laboratory certification analysis will be used. Data from spiked QC samples, within a lot, will be compared to control chart limits to demonstrate that analysis of the lot are under control and will be used to update the charts. X-R control charts will be used in the Quality Assurance (QA) Program.

Control charts are prepared for each target analyte using percent recovery (found concentration - method blank/ spiked concentration x 100) data from the duplicate spiked QC samples variations in spiking solution concentrations.

To prepare control charts, the analyst should have access to the following data:

1. Average (x) percent recovery for the two high concentration spiked QC samples in each lot,
2. Difference (R) between the percent recoveries for the two high concentration spiked QC samples in each lot,
3. Three-point moving average (x) spike recovery of the low-concentration spike QC sample, and
4. Three-point moving difference (R) between the percent recoveries for the low-concentration spike QC sample.

The initial control chart shall be prepared using the four pairs of certification data closest to the spiking concentration used during analysis. The average (x), average range (R), and control limits for x and R shall be updates after each lot for the first 20 lots. Limits

established after Lot 20 will be used for the next 20 lots. Control charts will be updated after each 20 lots thereafter using the most recent 40 lots of QC data. In updating the control charts, the new data must be combined with the individual values of previous percent recoveries and not the mean of all previous data.

Initial control chart limits are presented in Table IX-2.

X. REFERENCES

U.S. Army Toxic and Hazardous Materials Agency, (USATHAMA). 1987. QA Plan (December 1985, 2nd Edition, March 1987).

XI. DATA

A. OFF-THE-SHELF ANALYTICAL REFERENCE MATERIALS CHARACTERIZATION

Attachment 1

B. PRE-CERTIFICATION CALIBRATION

Attachment 2

C. DAILY CALIBRATION AND CHROMATOGRAM

Attachment 3 (Reference check sample not required during time of original certification)

D. CERTIFICATION DATA

Attachment 4

Table IX-1. Preparation of Daily Control Spike Samples

Daily Control Spike Level	Volume of Primary Composite Control Spiking Solution* (mL)	Nominal Concentration of Daily Control Spike Samples (ug/g)						
		DMDS	OXAT	DITH	CRYS	HIZ	CRYSO	CRYSO2
Blank	0	0	0	0	0	0	0	0
Low	0.20	2.0	2.0	3.0	2.0	2.0	4.0	4.0
High	1.00	10.0	10.0	15.0	10.0	10.0	20.0	20.0
High	1.00	10.0	10.0	15.0	10.0	10.0	20.0	20.0

Source: Hunter/ESE, 1988.

Table IX-2. Initial Control Limits for OrganoSulfur Compounds in Soil

ESE CERTIFICATION LIMITS

METHOD: OS in Soil
UNITS: UG

3 PT. MOVING AVERAGE X - R

CODE	CONC.	UCL $\bar{X}$	UWL $\bar{X}$	= X	LWL $\bar{X}$	LCL $\bar{X}$	UCL R	UWL R	$\bar{R}$
DMDS	1.1	109.4	104.8	95.7	86.5	81.9	34.5	27.5	13.4
OXAT	1.3	104.0	100.2	92.6	85.0	81.2	28.6	22.8	11.1
DITH	2.28	108.6	104.9	97.5	90.0	86.3	28.1	22.3	10.9
CBMS	2.5	105.5	102.6	96.6	90.7	87.7	22.4	17.8	87.7
BTZ	2.64	108.2	104.3	96.5	88.6	84.7	29.6	23.6	11.5
CBMSO	5.62	112.3	108.9	102.2	95.5	92.2	25.2	20.1	9.8
CBMSO2	4.9	90.9	87.3	80.3	73.3	69.8	26.5	21.1	10.3

SINGLE DAY $\bar{X}$ - R

CODE	CONC.	UCL $\bar{X}$	UWL $\bar{X}$	= X	LWL $\bar{X}$	LCL $\bar{X}$	UCL R	UWL R	$\bar{R}$
DMDS	5.5	108.3	104.1	95.7	87.3	83.1	21.9	16.8	6.7
OXAT	6.5	107.6	102.9	93.7	84.4	79.7	24.2	18.6	7.4
DITH	11.4	103.1	99.1	91.1	83.0	79.0	20.9	16.1	6.4
CBMS	12.5	115.1	109.8	99.4	88.9	83.7	27.3	21.0	8.4
BTZ	13.2	94.5	89.7	80.3	70.8	66.1	24.8	19.0	7.6
CBMSO	45.0	119.7	113.7	101.7	89.8	83.8	31.2	24.0	9.6
CBMSO2	24.3	94.7	90.0	80.4	70.9	66.2	24.8	19.1	7.6