USATHAMA METHOD
DIISOPROPYLMETHYLPHOSPHONATE AND
DIMETHYLMETHYLPHOSPHONATE
IN ENVIRONMENTAL SOIL SAMPLES
(ESE, Gainesville, 03/12/86)

1. APPLICATION

This method is applicable to the quantitative determination of the following compounds in environmental soil samples:

Diisopropylmethylphosphonate (DIMP)

Dimethylmethylphosphonate (DMMP)

A. TESTED CONCENTRATION RANGE

The tested concentration ranges in "standard soil" samples are:

Analyte	Tested Concentration Range (µg/g)*
DIMP	0.114 to 4.57
DMMP	0.105 to 4.18

*µg/g = micrograms per gram.

B. SENSITIVITY

The normalized responses (integrator counts corrected for attenuation) at the standard soil detection limits (Sec. 1.C) are:

Analyte	Area Count
DIMP	10,900
DMMP	12,000

C. DETECTION LIMITS

The "standard soil" detection limits, calculated according to the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) detection limit program are:

Analyte	Detection Limit (µg/g)	Upper Certified Range (µg/g)
DIMP	0.114	4.57
DMMP	0.133	4.18

D. INTERFERENCES

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 which have retention times equal to the retention times of the compounds of interest.

E. ANALYSIS RATE

After instrument calibration, one analyst can analyze 20 samples in an 8-hour day.

2. CHEMISTRY

A. CHEMICAL ABSTRACT SERVICE (CAS) NUMBERS

The CAS registry numbers for the compounds are:

Analyte	CAS Registry Number
DIMP	1445-75-6
DMMP	756-79-6

B. CHEMICAL REACTIONS

In an amber glass vial, a measured weight of sample is extracted with distilled water. Chromatographic conditions are described which permit the separation and measurement of DIMP and DMMP in "standard" or environmental soil. Qualitative identification is performed using retention times, and quantitative analysis is performed using standard curves.

3. APPARATUS

A. INSTRUMENTATION

A Varian Model 3400 gas chromatograph (GC) with a flame photometric detector (FPD) equipped with a Varian Model 8055 automatic sampler and interfaced to a Spectra-Physics 4270 integrator.

B. PARAMETERS

1. Detector: Dual FPD with selective spectral detection of phosphorus [530-nanometer (nm) filter]
2. Column: 5-percent SP-1000 on 100/120 supelcoport glass column [2-meter (m) x 2-millimeter (mm) inside diameter (ID)]
3. Gas flow:
   Helium--30 milliliters per minute (mL/min)
   Hydrogen--140 mL/min
   Air 1--80 mL/min
   Air 2--170 mL/min
4. Temperature:
   Injector--200 degrees Celsius (°C)
   Detector--245°C
   Oven--90°C for 2 minutes (min), then programmed at 32 degrees Celsius per minute (°C/min) to 240°C for 4 min
5. Injection volume: 5.0 microliters (µL)
6. Retention times:

Analyte	Retention Time (min)
DIMP	4.4 ± 0.2
DMMP	4.9 ± 0.2

C. HARDWARE/GLASSWARE

1. Volumetric flasks [10-, 50-, and 100-milliliter (mL)];
2. Volumetric pipettes (1.0- and 2.0-mL);
3. Microsyringes (100- and 1,000-µL);

4. Pasteur pipettes (disposable);
5. Amber glass vials (8-mL with Teflon®-lined screw caps);
6. Glass vials (2-mL with Teflon®-lined, crimp-seal caps for use with an automatic sampler);
7. Amber bottles (60 mL with Teflon®-lined screw caps);
8. Stainless steel spatulas; and
9. Analytical balance [Mettler AE160 or equivalent, with 0.0001-gram (g) sensitivity].

D. CHEMICALS

1. Distilled water
2. "Standard soil" (an uncontaminated natural soil received from Rocky Mountain Arsenal);
3. DIMP [Standard Analytical Reference Material (SARM), identification No. PA2334, obtained from USATHAMA]; and
4. DMMP (SARM, identification No. PA1827, obtained from USATHAMA).

4. STANDARDS

A. INITIAL INSTRUMENT CALIBRATION STANDARDS

1. Individual stock calibration standards are prepared by weighing approximately 50 milligrams (mg) each of DIMP and DMMP into separate 50-mL volumetric flasks, then diluting to volume with distilled water. The actual concentrations in the stock calibration standards prepared in the above manner were:

Analyte	Concentration of Individual Calibration Standard (µg/mL)*
DIMP	1,134
DMMP	1,030

*µg/mL = micrograms per milliliter.

2. A composite secondary stock calibration standard is prepared by adding 1 mL of each individual stock calibration standard to deionized water in a 10-mL volumetric flask and then diluting to volume with distilled water. The actual concentrations in the composite secondary stock calibration standard prepared in the above manner were:

Analyte	Concentration of Composite Secondary Stock Calibration Standard (µg/mL)
DIMP	113
DMMP	103

3. Prepare composite working calibration standards using the composite secondary stock calibration standard, microsyringes, and volumetric pipettes as shown in Table 1. Each composite working calibration standard is prepared by adding the specified volume of the composite secondary stock calibration standard to distilled water contained in a 100-mL volumetric flask and then diluting to volume with deionized water.

4. For initial instrument calibration, inject 5.0 µL of each of the working calibration standards prepared in Table 1. Plot the linear regression of the normalized response versus the concentration of standard injected for each standard to obtain a working curve. This curve must have a correlation coefficient of 0.995 or greater.

B. DAILY INSTRUMENT CALIBRATION STANDARDS

1. A minimum of three working calibration standards and one blank are analyzed daily for instrument calibration.
   a. At a minimum, 5.0 µL of each of the following working calibration standards (from Table 1) are analyzed daily:
      (1) Blank,
      (2) Working calibration standard .5A,

Table 1. Preparation of Composite Working Calibration Standards

Volume of Composite Secondary Stock Calibration Standard Used (mL)	Final Volume (mL)	Composite Working Calibration Standard Prepared	Concentration of Prepared Standard (µg/mL)	
			DIMP	DMMP
0	100	Blank	0	0
0.050	100	.5A	0.0567	0.0515
0.100	100	A	0.113	0.103
0.200	100	B	0.227	0.206
0.400	100	C	0.454	0.412
1.00	100	D	1.13	1.03
2.00	100	E	2.27	2.06

Source: ESE, 1986.

(3) Working calibration standard C, and

(4) Working calibration standard E.

b. Plot the linear regression of the normalized response versus the concentration of standard injected for each standard to obtain a working curve. This curve must have a correlation coefficient of 0.995 or greater.

c. At the end of the daily instrumental analysis, inject 5.0 µL of working calibration standard C. The response of this end-of-day analysis should be ±15 percent of the response obtained from the analysis of working calibration standard C analyzed earlier in the day. If not, the instrument should be recalibrated and the sample extracts reanalyzed.

C. CONTROL SPIKES FOR METHOD CERTIFICATION

1. A composite stock control spiking solution is prepared by weighing approximately 50 mg of DIMP and 50 mg of DMMP into one 50-mL volumetric flask, then diluting to volume with distilled water. The actual concentrations in the composite stock spiking solution prepared in the above manner were:

Analyte	Concentration of Composite Stock Control Spiking Solution (µg/mL)
DIMP	1,142
DMMP	1,046

2. A composite secondary stock control spiking solution is prepared by adding 1 mL of the composite stock control spiking solution into a 50-mL volumetric flask, then diluting to volume with distilled water. The actual concentration in the secondary composite stock spiking solution prepared in the above manner was:

Analyte	Concentration of Secondary Composite Stock Control Spiking Solution (µg/mL)
DIMP	22.8
DMMP	20.9

3. Certification control spike samples are prepared using the composite secondary stock control spiking solution, microsyringes, and volumetric pipettes as shown in Table 2. Each certification control spike sample is prepared by adding the specified volume of the secondary stock control spiking solution to "standard soil" contained in a 60-mL amber glass vial.

D. DAILY CONTROL SPIKE SAMPLES

With each daily lot of environmental samples, analyze the daily control spike samples shown in Table 3.

5. PROCEDURE

A. EXTRACTION OF CERTIFICATION CONTROL SPIKES ONLY

The certification control spikes are extracted beginning with Sec. 5.C.4.

B. HANDLING OF ENVIRONMENTAL SAMPLES

1. Soil core sections received from the field in polybutyrate tube sections are subsampled in the laboratory using a stainless steel coring tube inserted lengthwise into the end of the core section. This procedure allows a composite subsample of the entire core length to be taken for analysis.
2. The core subsample is taken from the center of the core section to avoid analyzing soil which has contacted the polybutyrate tube walls. Subsampling using the coring device is repeated until sufficient quantity of soil is removed to perform all the required analyses.

Table 2. Preparation of Certification Control Spike Samples

Volume of Composite Secondary Stock Control Spiking Solution Used (mL)	Weight of Standard Soil Used (g)	Certification Control Spike Sample Prepared	Concentration of Prepared Sample (µg/g)	
			DIMP	DMMP
0	10	Blank	0	0
0.050	10	A	0.114	0.105
0.100	10	B	0.228	0.209
0.200	10	C	0.457	0.418
0.400	10	D	0.913	0.837
1.00	10	E	2.28	2.09
2.00	10	F	4.57	4.18

Source: ESE, 1986.

Table 3. Preparation of Daily Control Spikes

Daily Control Spike Number	Volume of Composite Secondary Stock Control Spiking Solution Used (mL)	Weight of Standard Soil Used (g)	Concentration of Prepared Sample (ug/g)	
			DIMP	DMMP
Blank	0	10	0	0
Low-Level	0.100	10	0.228	0.209
High-Level	1.00	10	2.28	2.09
High-Level	1.00	10	2.28	2.09

Source: ESE, 1986.

3. The center core subsamples are transferred to the dull side of clean aluminum foil. This combined subsample is thoroughly mixed using a clean stainless steel spatula and is transferred to a clean glass container with Teflon®-lined lid for storage prior to removal of aliquots for analysis.
4. For surface soil samples, the entire contents of the subsample bottle are transferred to the dull side of clean aluminum foil. The subsample is thoroughly mixed with a stainless steel spatula and returned to the original subsample bottle or to a clean glass container for storage prior to removal of aliquots for analysis.

C. EXTRACTION OF ENVIRONMENTAL SAMPLES

1. Place 10 g of "standard soil" into each of four separate 60-mL amber vials.
2. Spike these four vials as specified in Table 3. Cap and allow to equilibrate for 1 hour.
3. Environmental samples are to be extracted within 7 days of sample collection. Transfer a 10-g portion to a 60-mL amber vial.
4. Add 20 mL of distilled water with a volumetric pipette. Cap tightly.
5. Shake the culture tube in a horizontal position for 4 hours on a wrist-action shaker.
6. Allow the particulate to settle or centrifuge, if necessary (indicate in the laboratory record book whether centrifugation was required).
7. With a disposable pipette, transfer approximately 1 to 2 mL of the extract to an autosampler vial. The extract is now ready for instrumental analysis.
8. Transfer the remainder of the extract to an 8-mL amber glass vial and cap tightly. Save as a backup sample.
9. Store samples at 0°C until analysis. Samples must be analyzed within 40 days of sample extraction.

D. ANALYSIS

1. Perform daily instrument calibration as described in Sec. 4.B.
2. Place the sample extracts in the autosampler tray and inject a 5-µL volume of each sample extract.

6. CALCULATIONS

A. Determine the concentration of each component according to the following formula:

$$\text{Concentration } (\mu g/g) = \frac{(A)(Vt)}{(Ws)}$$

where: A = Concentration of each component found in the sample extract by comparison with the appropriate standard curve (µg/mL),
Vt = Volume of total extract (mL), and
Ws = Weight of initial sample extracted (g).

B. Final results will be reported on a dry-weight basis.

7. REFERENCES

None.

8. DATA

See Att. 1.

9. CALIBRATION DATA

See Att. 2.

10. CHROMATOGRAM

See Att. 3.