

USATHAMA METHOD T8
DIISOPROPYLMETHYLPHOSPHONATE AND
DIMETHYLMETHYLPHOSPHONATE
IN ENVIRONMENTAL WATER SAMPLES
(ESE, Gainesville, 10/8/85)

1. APPLICATION

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

Diisopropylmethylphosphonate (DIMP)

Dimethylmethylphosphonate (DMMP)

A. TESTED CONCENTRATION RANGE

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

<u>Analyte</u>	<u>Tested Concentration Range (µg/L)*</u>
DIMP	10.48 to 209.6
DMMP	15.24 to 304.8

*µg/L = micrograms per liter.

B. SENSITIVITY

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

<u>Analyte</u>	<u>Area Count</u>
DIMP	3,650
DMMP	3,950

C. DETECTION LIMITS

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

<u>Analyte</u>	<u>Detection Limit (µg/L)</u>	<u>Upper Certified Range (µg/L)</u>
DIMP	10.48	209.6
DMMP	15.24	304.8

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.

F. PRESERVATION AND HOLDING TIMES

Samples should be collected in amber glass bottles with teflon liners and stored at 4°C. Since the samples are not extracted, holding times are assumed to be 47 days (7 days for extraction plus 40 days after extraction).

2. CHEMISTRY

A. CHEMICAL ABSTRACT SERVICE (CAS) NUMBERS

The CAS registry numbers for the compounds are:

<u>Analyte</u>	<u>CAS Registry Number</u>
DIMP	1445-75-6
DMMP	756-79-6

B. CHEMICAL REACTIONS

A measured volume of sample is directly injected onto the gas chromatographic column. Chromatographic conditions are described which permit the separation and measurement of DIMP and DMMP in "standard" or environmental water. 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:

<u>Analyte</u>	<u>Retention Time (min)</u>
DIMP	4.4 ± 0.2
DMMP	5.0 ± 0.2

C. HARDWARE/GLASSWARE

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

09/13/85

4. Pasteur pipettes (disposable);
5. Graduated cylinder (100-mL);
6. Amber glass vials (8-mL with Teflon®-lined screw caps);
7. Glass vials (2-mL with Teflon®-lined, crimp-seal caps for use with an automatic sampler);
8. Amber bottles (60 mL with Teflon®-lined screw caps);
9. Aluminum foil;
10. Stainless steel spatulas; and
11. Analytical balance [Mettler AE160 or equivalent, with 0.0001-gram (g) sensitivity].

D. CHEMICALS

1. Sodium chloride (analytical-grade);
2. Sodium sulfate (analytical-grade);
3. "Standard water" [distilled water containing 100 milligrams per liter (mg/L) each of sulfate and chloride];
4. DIMP [Standard Analytical Reference Material (SARM), identification No. PA2334, obtained from USATHAMA]; and
5. 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 deionized water. The actual concentrations in the stock calibration standards prepared in the above manner were:

<u>Analyte</u>	<u>Concentration of Individual Calibration Standard (µg/mL)*</u>
DIMP	958
DMMP	1,120

*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 100-mL volumetric flask and then diluting to volume with deionized water. The actual concentrations in the composite secondary stock calibration standard prepared in the above manner were:

<u>Analyte</u>	<u>Concentration of Composite Secondary Stock Calibration Standard (µg/mL)</u>
DIMP	9.58
DMMP	11.20

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 deionized 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.

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/L)	
			DIMP	DMMP
0	100	Blank	0	0
0.050	100	.5A	4.79	5.60
0.100	100	A	9.58	11.20
0.200	100	B	19.16	22.40
0.400	100	C	38.32	44.80
0.800	100	D	76.64	89.60
2.00	100	E	191.60	224.00
4.00	100	F	383.20	448.00

Source ESE, 1985.

2. A composite secondary stock control spiking solution is prepared by adding 1 mL of the composite stock control spiking solution into a 100-mL volumetric flask, then diluting to volume with "standard" water. The actual concentration in the secondary composite stock spiking solution prepared in the above manner was:

<u>Analyte</u>	<u>Concentration of Secondary Composite Stock Control Spiking Solution (µg/mL)</u>
DIMP	10.48
DMMP	15.24

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 water" contained in a 100-mL volumetric flask and then diluting to volume with "standard water." (To prepare "standard water" for control spikes, weigh 1.48 g of anhydrous sodium sulfate into a 1-liter volumetric flask and dilute to volume with distilled water. Weigh 1.65 g of reagent-grade dry sodium chloride into a separate 1-liter volumetric flask and dilute to volume with distilled water. Transfer 100 mL of each of the two solutions to a 1-liter volumetric flask and dilute to volume with distilled water to produce 1 liter of "standard water.")

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. CERTIFICATION

Certification control spike samples and environmental water

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 μ L of each of the following working calibration standards (from Table 1) are analyzed daily:
 - (1) Blank,
 - (2) Working calibration standard .5A,
 - (3) Working calibration standard D, and
 - (4) Working calibration standard F.
 - 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 μ L of working calibration standard D. The response of this end-of-day analysis should be ± 15 percent of the response obtained from the analysis of working calibration standard D 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 70 mg of DMMP into one 50-mL volumetric flask, then diluting to volume with deionized water. The actual concentrations in the composite stock spiking solution prepared in the above manner were:

<u>Analyte</u>	<u>Concentration of Composite Stock Control Spiking Solution (μg/mL)</u>
DIMP	1,048
DMMP	1,524

Table 2. Preparation of Certification Control Spike Samples

Volume of Composite Secondary Stock Control Spiking Solution Used (mL)	Final Volume (mL)	Certification Control Spike Sample Prepared	Concentration of Prepared Sample (ug/L)	
			DIMP	DMMP
0	100	Blank	0	0
0.100	100	A	10.48	15.24
0.200	100	B	20.96	30.48
0.400	100	C	41.92	60.96
0.800	100	D	83.84	121.92
2.00	100	E	209.60	304.80

Source ESE, 1985.

Table 3. Preparation of Daily Control Spikes

Daily Control Spike Number	Volume of Composite Secondary Stock Control Spiking Solution Used (mL)	Final Volume (mL)	Concentration of Prepared Sample µg/L	
			DIMP	DMMP
Blank	0	100	0	0
Low-Level	0.2	100	20.96	30.48
High-Level	0.8	100	83.84	121.92
High-Level	0.8	100	83.84	121.92

09/13/85

samples require no further preparation. Approximately 1 mL of each is transferred into an autosampler vial using disposable pipettes, followed by instrumental analysis (direct injection onto the GC column). The remainder of the samples should be refrigerated at 4°C in amber glass vials until analysis.

B. ANALYSIS

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

6. CALCULATIONS

The concentration (in µg/L) for each analyte is taken directly from the standard curve.

7. REFERENCES

None.

8. DATA

See Att. 1.

9. CALIBRATION DATA

See Att. 2.

10. CHROMATOGRAM

See Att. 3.