TITLE: DETERMINATION OF LOW LEVELS OF DIISOPROPYLMETHYLPHOSPHONATE AND DIMETHYLMETHYLPHOSPHONATE IN ENVIRONMENTAL WATER SAMPLES (USATHAMA METHOD UK08)

## I. 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 range in "standard water" samples are:

| Analyte | Tested Concentration Range (µg/L)* |
|---|---|
| DIMP | 0.1 to 5.0 |
| DMMP | 0.099 to 4.96 |

*µg/L = micrograms per liter.

### B. SENSITIVITY

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

| Analyte | Area Count |
|---|---|
| DIMP | 42,068 |
| DMMP | 76,052 |

### 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:

| Analyte | Detection Limit (µg/L) | Upper Certified Range (µg/L) | Slope |
|---|---|---|---|
| DIMP | 0.20 | 5.0 | 1.007 |
| DMMP | 0.20 | 4.96 | 0.933 |

### 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. Samples must be extracted within 7 days of sample collection and must be analyzed within 40 days after extraction.

## II. 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

A 1000 mL volume of sample is extracted with methylene chloride using a continuous liquid/liquid extraction device for 12 hours. The extract is then concentrated to a 5 mL volume. The extract is analyzed by gas chromatography using a flame photometric detector operated in the phosphorus mode. 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.

## III. APPARATUS

### A. INSTRUMENTATION

A Hewlett Packard Model 5890 gas chromatograph (GC) with a flame photometric detector (FPD) equipped with an auto sampler and interfaced to chromatographic workstation.

### B. PARAMETERS

1. Instrument: HP 5890A equipped with an autosampler (Model 7672)

2. Detector: FPD with selective spectral detection of phosphorus [530-nanometer (nm) filter]

3. Column: 5-percent SP-1000 on 100/120 supelcoport glass column [2-meter (m) x 2-millimeter (mm) inside diameter (ID)]

4. Gas flow:
   Helium--50 milliliters per minute (mL/min)
   Hydrogen--100 mL/min
   Air 1--120 mL/min

5. Temperature:
   Injector--200 degrees Celsius (°C)
   Detector--245°C
   Oven--60°C (no hold), then programmed at 10 degrees Celsius per minute (°C/min) to 100°C, then 50 °C/min to 240°C, hold for 5.2 minutes.

6. Injection volume: 5.0 microliters ($\mu$L)

7. Retention times:

| Analyte | Retention Time (min) |
|---|---|
| DIMP | 5.5 ± 0.2 |
| DMMP | 6.1 ± 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-$\mu$L);
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).

## IV. STANDARDS

### A. INITIAL INSTRUMENT CALIBRATION STANDARDS

Precertification calibration curvers are presented in Attachment 1. Calibration curves are linear out quadratic curves are desired and will be used.

1. Individual stock calibration standards are prepared by weighing approximately 25 milligrams (mg) each of DIMP and DMMP into separate 25-mL volumetric flasks, then diluting to volume with methylene chloride. The actual concentrations in the stock calibration standards prepared in the above manner were:

| Analyte | Concentration of Individual Calibration Standard (μg/mL) |
|---|---|
| DIMP | 980 |
| DMMP | 1068 |

*μg/mL = micrograms per milliliter.

2. A composite secondary stock calibration standard is prepared by adding 0.5 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 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 | 9.8 |
| DMMP | 10.68 |

3. A tertiary composite standard is prepared by diluting 5 ml of the secondary composite standard to 50 mL with methylene chloride.

| Analyte | Concentration of Tertiary Composite Calibration Standard (ng/mL) |
|---|---|
| DIMP | 980 |
| DMMP | 1068 |

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 five working calibration standards and one blank are analyzed daily for instrument calibration.

a. At a minimum, 5.0 $\mu$L of each of the following working calibration standards (from Table 1) are analyzed daily:

(1) Blank,
(2-8) Working calibration standards A-G.

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 $\mu$L of working calibration standard G. The response of this end-of-day analysis should be $\pm$ 25 percent of the response obtained from the analysis of working calibration standard G 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 25 mg of DIMP and 25 mg of DMMP into one 25-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:

| Analyte | Concentration of Composite Stock Control Spiking Solution ($\mu$g/mL) |
|---|---|
| DIMP | 1,080 |
| DMMP | 1,068 |

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 "standard" 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 | 21.6 |
| DMMP | 21.36 |

3. A further dilution of the secondary stock spike solution is necessary for the low level spikes. 1 mL of the secondary stock spike solution is diluted with 20.6 mL water to prepare a tertiary spike at 1 ug/mL.

4. Certification control spike samples are prepared using the composite tertiary 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 1000 mL "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.

## V. PROCEDURE

### A. SEPARATION

1. All glassware must be treated with dichloro dimethylsilane prior to introducing the water sample or extract.

2. Extract a 1000 mL volume of sample with 300 mL of methylene chloride for 16 hours using a continuous liquid/liquid extraction device. Use several teflon boiling chips in the round bottom flask to facilitate boiling.

3. Dry the methylene chloride extract by passing it through a 75 mm funnel plugged with silane treated glass wool and filled with about 10 cm of anhydrous sodium sulfate.

4. Collect the dried extract in a 500 mL Kuderna-Danish concentrator with a 15 mL receiver tube.

5. Add a teflon boiling chip and concentrate the solvent at a temperature of 60-65 $^{0}$C, to an approximate volume of 10 mL.

6. Add a fresh boiling chip and a 2-balled micro snyder distillation column and continue to concentrate the extract down at a temperature of 60-65 $^{0}$C to a 2-3 mL volume.

7. Quantitatively transfer the extract to a 5 ml volumetric flask and bring to volume with methylene chloride.

8. The extract is now ready for analysis.

**B. ANALYSIS**

1. Perform daily instrument calibration as described in Section IV.A.4.

2. Place the sample extracts in the autosampler tray and inject 5 $\mu$L of each sample.

## VI. CALCULATIONS

The concentration of the extract (in $\mu$g/L) for each analyte is taken directly from the standard curve. Final concentrations are calculated by:

$$Conc_{(Final)} = \frac{Conc_{(Extract)} \; X \; ExtractVolume}{SampleVolume} \; X \; Dilutions$$

## VII. REFERENCES

1. Determination of Diisopropylmethylphosphonate and Dimethylmethylphosphonate in Environmental Water Samples (USATHAMA Method T8, ESE 1985).

2. Determination of Diisopropylmethylphosphonate and Dimethylmethylphosphonate in Environmental Soil Samples (USATHAMA Method TT9, ESE 1986).

## VIII. PRECERTIFICATION CALIBRATION DATA

See Attachment 1.

## IX. CERTIFICATION DATA

See Attachment 2.

## X. CHROMATOGRAMS

See Attachment 3.

Table 1. Preparation of Composite Working Calibration Standards

| Volume of Composite Secondary Stock Calibration Standard Used (mL) | Standard Used | Final Volume (mL) | Composite Working Calibration Standard Prepared | Concentration of Prepared Standard (µg/L) DIMP | DMMP |
|---|---|---|---|---|---|
| 0. | - | 10.0 | Blank | 0. | 0. |
| 25 | B | 50 | A | 10 | 11 |
| 1 | 3[0] | 50 | B | 20 | 21 |
| 1 | 3[0] | 25 | C | 39 | 43 |
| 5 | F | 25 | D | 78 | 86 |
| 5 | 3[0] | 25 | E | 196 | 214 |
| 10 | 3[0] | 25 | F | 392 | 427 |
| 12.5 | 2[0] | 100 | G | 1225 | 1335 |

Source ESE, 1993

Table 2. Preparation of Certification Control Spike Samples

| Volume of Composite Tertiary Stock Control Spiking Solution Used (mL) | Final Volume (mL) | Certification Control Spike Sample Prepared | Concentration of Prepared Standard (µg/L) DIMP | DMMP |
|---|---|---|---|---|
| 0. | 1000 | Blank | 0. | 0. |
| 0.100 | 1000 | A | 0.1 | 0.099 |
| 0.200 | 1000 | B | 0.2 | 0.198 |
| 0.500 | 1000 | C | 0.5 | 0.496 |
| 1.00 | 1000 | D | 1.0 | 0.991 |
| 2.00 | 1000 | E | 2.0 | 1.98 |
| 5.00 | 1000 | F | 5.0 | 4.96 |

Source: ESE, 1993

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 Standard (µg/L) DIMP | DMMP |
|---|---|---|---|---|
| Blank | 0. | 1000 | 0. | 0. |
| Low-Level | 1.0 | 1000 | 0.4 | 0.4 |
| High-Level | 1.0 | 1000 | 4.0 | 4.0 |
| High-Level | 1.0 | 1000 | 4.0 | 4.0 |

Source: ESE, 1993.