ANALYSIS OF METHYL PARATHION IN WIPE SAMPLES BY GC/MS

CONTENTS

CONTENTS (cont)

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1.0 SCOPE AND APPLICATION

The objective of this standard operating procedure is to provide guidance on the requirements for the analysis of methyl parathion in wipe samples using gas chromatography/mass spectrometry (GC/MS) selective ion monitoring mode.

2.0 METHOD SUMMARY

The wipe samples are extracted with methylene chloride and the extracts analyzed by GC/MS. Prior to GC/MS analysis, a 1-mL aliquot of the extract is spiked with the internal standard phenanthrene-d_{10}. The extract is then analyzed for methyl parathion. Identification and quantitation is made by comparing the retention times and mass spectral data of methyl parathion with that of methyl parathion from calibration standards as follows:

The GC oven is temperature programmed to separate the methyl parathion on a fused silica capillary column, which is then detected with the mass spectrometer (MS). The methyl parathion eluting from the GC column is identified by comparing its measured mass spectra and retention time to reference spectra and retention time in a user created database. Reference spectra and retention times for methyl parathion are obtained by the measurement of calibration standards under the same conditions used for sample extracts. The concentration of methyl parathion is calculated by relating the MS response of the quantitation ion produced by methyl parathion, to the MS response of the quantitation ion produced by the internal standard phenanthrene-d_{10}.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

1. The wipes used for sampling are RELEASE, non-adhering dressing, 2 in x 3 in, Johnson and Johnson Products, Inc., or equivalent
2. The suggested sample area is 100 cm^2/per dressing.
3. After sampling store dressing in a 40-mL VOA bottle.
4. Protect the samples from light and refrigerate at 4°C (±2°C) until extraction and analysis.
5. Recommended maximum holding time is seven days.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be shown to free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in an all glass system may be required.

5.0 EQUIPMENT/APPARATUS

1. Micro syringes - Hamilton gas tight syringes: 10, 25, 50, 100, 500, and 1000 µL, 0.006 inch ID needle.

2. RELEASE, non-adhering dressing, 2 in x 3 in, Johnson and Johnson Products, Inc. (or equivalent)

3. Balance - Analytical, capable of accurately weighing ±0.0001 g.

4. Water bath sonicator

5. Serum vial - 10 mL, crimp top with Teflon cap liner.

6. Volumetric flasks - class A with ground-glass stoppers: 5, 10, 25, and 50 mL volumes.

7. Vials - 2 mL for GC autosampler.

8. VOA vial - 40 mL, screw cap with Teflon cap liner.

9. Gas Chromatography/Mass Spectrometer (GC/MS)

A GC/MS system which meets the following specifications will be used:

Gas Chromatograph - An analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, and gases is required.

Capillary Gas Chromatography Columns - Any gas chromatography column that meets the performance criteria of separating the calibration mixture of this method is acceptable. One useful column has been identified.

> Column -- 30 m x 0.25 mm ID, Restek XTI-5 (crossbonded SE-54), fused silica capillary with a 0.50 µm film thickness.

Mass spectrometer - The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV, and must be capable of scanning in the selective ion monitoring (SIM) mode. The ions to be monitored are: 187, 188, and 189 for d_{10}-phenanthrene; and 109, 125, and 263 for methyl parathion. The mass spectrometer must produce a spectrum that meets all criteria in Appendix A when 50 ng of decafluorotriphenyl- phosphine (DFTPP) is introduced into the GC.

GC/MS interface - Any gas chromatograph to mass spectrometer interface that allows 20 ng or less per injection for each of the parameters of interest and achieves all acceptable performance criteria may be used. The capillary column is directly coupled with the analyzer, providing maximum sensitivity.

Data system - A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP).

The computer software should be capable of processing stored GC/MS data by recognizing a GC

peak within any given retention time window, comparing the mass spectra from the GC peak with spectral data in a user-created data base. The software must allow integration of the ion abundance of any specific ion between specified time or scan number limits. The software should also allow the calculation of response factors (or construction of a second or third order regression calibration curve), response factor statistics (mean and standard deviation), and concentrations of analytes using either the calibration curve or the equation in Section 8.

6.0 REAGENTS

All standard solutions are prepared and documented in accordance with EPA/REAC SOP #1012, "Preparation of Standard Solutions."

1. Toluene (glass distilled, suitable for GC)

2. Methylene chloride (glass distilled, suitable for GC)

3. Acetone (glass distilled, suitable for GC)

4. Decafluorotriphenylphosphine (DFTPP).

   Prepare a 50 µg/mL daily working standard solution of DFTPP by diluting 50 µL of a commercially available 25,000 µg/mL (Supelco catalog number 4-8724 or equivalent) in 25.0 mL of methylene chloride. Protect the DFTPP from light and refrigerate at 4°C (±2°C). This solution must be replaced every 12 months or sooner if comparison with quality control check samples indicates a problem.

5. Internal standard

   Purchase a 2000 µg/mL solution (Supelco catalog number 4-8710 or equivalent) of Phenanthrene - d_{10}. Prepare serial dilutions in methylene chloride of the 2000 µg/mL to a working stock of 20 µg/mL.

   Protect the solution from light and refrigerate at 4°C (±2°C). This solution must be replaced every 12 months or sooner if comparison with quality control check samples indicates a problem.

6. Matrix Spike/Matrix Spike Duplicate Solution:

   Prepare a 10,000 µg/mL stock solution of methyl parathion by the addition of .100 gm ± 5% of methyl parathion (Chem Service Catalog Number F996) to 10 mL of 10:90 acetone:toluene (v:v).

   Prepare the 1,000 µg/mL solution of matrix spike mix by diluting 1 µL of the 10,000 µg/mL stock solution to 10.0 mL in methylene chloride. Store the spiking solution at 4°C (± 2°C) in Teflon-sealed containers, protected from light. The solution should be checked frequently for stability. These solutions must be replaced every 12 months or sooner if comparison with quality control check samples indicates a problem.

7. Calibration Standards

Prepare calibration standards at six concentration levels (0.05, 0.1, 0.5, 1.0, 5, and 25 µg/mL). Prepare a working stock of all compounds at 10,000 µg/mL as in Step 6. Prepare serial dilutions of the 10,000 µg/mL solution to obtain the 6 levels of calibration standards. These solutions must be replaced every 12 months or sooner if comparison with quality control check samples indicates a problem.

7.0 PROCEDURES

7.1 Preparation and Extraction

7.1.1 Samples

The wipe consists of non-adhering dressing, 2 in x 3 in. (RELEASE, Johnson and Johnson Products, Inc. or equivalent). The dressing is wet with a few mL of isopropyl alcohol. The contaminated area is then wiped. The suggested maximum sample area is 10cm x 10cm. The wipe is stored in a 40mL VOA vial prior to shipping. Extract the sample as follows:

1. Add 30mL of methylene chloride to the sample vial.
2. Cap the vial tightly with a PETE lined cap.
3. Immerse the vial in an ultrasonic bath for approximately 30 minutes.
4. Transfer 1.0mL from the vial to a clean 1-mL auto sample vial. Cap and label the vial.

7.1.2 Blank Spike/Blank Spike Duplicate

Insert a clean wipe into a 40mL VOA vial. Wet the face of the dressing with a few mL of isopropyl alcohol and 30µL of spiking solution. Allow to stand for a minimum of 1 hour. Extract exactly as a sample as in Section 7.1.1. Perform in duplicate.

7.1.3 Method Blank

Insert a clean wipe dressing into a 40mL VOA vial. Wet the face of the dressing with a few mL of isopropyl alcohol. Allow to stand for a minimum of 1 hour. Extract exactly as a sample as in Section 7.1.1.

7.2 GC/MS Operating Conditions

The following GC/MS operating conditions are recommended:

Column	Restek XTI-5 (crossbonded SE-54) 30 meter x 0.25 mm ID, 0.50 µm film thickness
Injection Temperature	260° C
Transfer Temperature	260° C
Source Temperature	260° C

Temperature Program	100° C 15° C/min to 290° C hold for 1 min*
Splitless Injection	Split time = 0.75 min
Injection Volume	2 µL

* Hold time may be extended for baking out non-target contaminants.

7.3 Tune (DFTPP)

The instrument must be tuned to meet the ion abundance criteria listed in Appendix A for a 50-ng (1 µL) injection of DFTPP. This criteria must be demonstrated every 24 hours during analysis.

7.4 Initial Calibration

1. Add 20 µL of the internal standard phenanthrene-d_{10} to each 1-mL aliquot of calibration standards.

2. Inject 2 µL each of the calibration standards after a successful DFTPP analysis.

3. Calculate and tabulate the Relative Response Factor (RRF) against the concentration for each compound by using the equation listed below. The primary ion from the specific internal standard must be used for quantitation.

   The average RRF and percent Relative Standard Deviation (%RSD) must also be calculated and tabulated.

$$RRF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

where:

A_X = Area of the characteristic ion for the compound to be measured
C_{IS} = Concentration of the internal standard (ng/µL)
A_{IS} = Area of the characteristic ion for the internal standard.
C_X = Concentration of the compound to be measured (ng/µL)

The % RSD of the RRF for each methyl parathion has been tentatively adopted to be less than or equal to 30%. The average RRF of methyl parathion should not be less than 0.05.

7.5 Continuing Calibration

A check of the initial calibration curve must be performed every 24 hours during analysis.

1. Inject 2 µL of a 1.0 µg/mL methyl parathion standard containing internal standard phenanthrene-d_{10}.

2. Calculate and tabulate the daily RRF for each compound. All daily RRF should be equal to or greater than 0.05.

3. Calculate the percent difference (% D) of each daily RRF compared to the average RRF from the initial calibration curve. The % D for all compounds can be calculated using the equation listed below and must be less than or equal to 25%.

$$\%D = \frac{RRF_{Daily} - RRF_{Average}}{RRF_{Average}} \times 100$$

4. All sample and standards are quantitated using the response factors from the daily calibration check.

7.6 Sample Analysis

Sample extracts may be analyzed only after the GC/MS system has met the DFTPP, initial calibration, and continuing calibration requirements mentioned above. The same instrument conditions must be employed for the analysis of samples as were used for calibration.

1. Add 20 µL of the internal standard phenanthrene-d_{10} into the method blank(s) the blank spike/blank spike duplicate, and all the sample extracts.

2. Inject 2 µL each of the blank spike/blank spike duplicates, method blank(s), and all the sample extracts.

3. If the analyst has reason to believe that diluting the final extracts will be necessary, an undiluted run may not be required.

4. If methyl parathion is detected at a level greater than the highest calibration standard, sample extracts must be diluted so that the methyl parathion response is within the linear range established during calibration.

5. If dilutions of sample extracts are made, additional internal standards must be added to maintain the required concentration (400 ng/mL) of each internal standard in the extract.

7.7 Identification of Methyl Parathion

Methyl Parathion identification will be conducted by comparison of the sample mass spectrum to the mass spectrum of a standard of the methyl parathion. Two criteria must be satisfied to verify the identifications:

- Elution of the methyl parathion in the sample at the same GC relative retention time as the methyl parathion standard.

- Correspondence of the methyl parathion in the sample and the reference methyl parathion mass spectra.

1. For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

2. For comparison of standard and sample component mass spectra, reference mass spectra must be obtained from the 1.0 µg/mL standard. These standard spectra may be obtained from the run used to obtain reference RRTs.

3. The requirements for qualitative verification by comparison of mass spectra are as follows:

   a. All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

   b. The relative intensities of ions specified in (a) must agree within ±20% between the standard and sample spectra. (For example: for an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30-70%.)

   c. Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the quantitation limit, report the actual value followed by "J", e.g., "3J".

4. If a compound cannot be verified by all of the criteria in step 3, but in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then the analyst shall report that identification and proceed with the calculation in Section 8.0. The analyst should note in the case narrative that technical judgment was utilized.

7.8 Method Detection Limits

The Method Detection Limits (MDL) listed in Appendix B were determined by analyzing seven wipes spiked with methyl parathion at 1.5 µg, which is equivalent to 50 ng/mL in the extract. The 5.0 ng/mL standard represents the lowest concentration on the linear range of the five-point calibration curve. The spiked wipes were subsequently extracted with methylene chloride as in Section 7.1 and analyzed by GC/MS. Method detection limits are analyzed every one year. This SOP will be updated when new MDL studies are conducted. Supporting documentation will be kept in a file in the laboratory. The MDL calculated in the appendix is lower than the actual MDL reported in the samples.

$$MDL = S\,t_{(n-1,\,1-alpha=0.99)}$$

where:

$t_{(n-1,1\text{-}alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = number of replicates
S = the standard deviation of the replicate analyses

$$SD = \sqrt{\frac{\sum \quad - X_{ave})^2}{n -}}$$

where:

$\boldsymbol{X_j}$ = each individual concentration
$\boldsymbol{X_{ave}}$ = mean concentration

For seven injections $t_{(n-1,1\text{-}alpha = 0.99)}$ = 3.143. Therefore, substituting into equation above yields:

$$MDL = (S)(t_{(-,1- \ lpha= \ .99)})$$

The detection limits obtained here are to support the actual MDL of 1.5 µg used in the results.

8.0 CALCULATIONS

8.1 Methyl Parathion

The methyl parathion identified by the GC/MS method shall be quantitated by the internal standard method. The internal standard (IS) used shall be phenanthrene-d_{10}. The EICP area of the characteristic ions of the methyl parathion and IS are used. TCL compounds concentrations and concentration conversions are calculated as follows:

1. Amount of analyte in total sample (µg/sample):

$$\mu \ /sample = \frac{(A_s)(C_{is})}{(A_{is})(RRF)} \times V$$

where:

A_S = Area of characteristic ion for the analyte to be measured
C_{IS} = Concentration of internal standard (µg/mL)
V = Extraction Volume (mL)
A_{IS} = Area of characteristic ion for the internal standard
RRF = Relative response factor of analyte

The response factor (RRF) is calculated from the calibration standard solution mixture using the formula shown in section 7.4.3.

8.2 Blank Spike Recoveries

The percent recovery for the blank spikes and relative percent difference (RPD) can be calculated using the equations below:

$$\%R = \frac{BSR - BR}{SA} \times 100$$

and

$$RPD = 100 \times \frac{(D_1 - D_2)}{(D_1 + D_2)} \times 0.5$$

where:

BSR = Blank spike results
BR = Blank results
SA = Amount of spike added
D_1 = First blank spike value
D_2 = Second blank spike value (duplicate)

The vertical bars in the formula above indicate the absolute value of the difference; hence RPD is always expressed as a positive value.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

9.1 Tune (DFTPP)

Prior to initiating any data collection activities involving samples, blanks, or standards, it is necessary to establish that a given GC/MS system meets the instrument tune criteria specified in Appendix A. The purpose of this instrument check is to assure correct mass calibration, mass resolution, and mass transmission. This is accomplished through the analysis of DFTPP.

1. The analysis of DFTPP must be performed every 24 hours during the analysis.

2. The key ions produced during the analysis of DFTPP and their respective ion abundance criteria are given in Appendix A.

9.2 Initial Calibration for Methyl Parathion

Prior to the analysis of samples and required blanks, and after instrument performance criteria have been met, the GC/MS system must be initially calibrated at a minimum of six concentrations to determine the linearity of response utilizing methyl parathion standards.

1. The levels of the initial calibration standards for methyl parathion are 0.05, 0.1, 0.5, 1.0, 5, and 25 µg/mL.

2. The calibration of the GC/MS is evaluated on the basis of the magnitude and stability of

the relative response factors of methyl parathion. Criteria have not been established for the minimum RRF and %RSD. However, tentative criteria have been adopted at this time. The minimum RRF of each compound at each concentration level in the initial calibration across all six points is tentatively adapted to be equal to or greater than 0.05; the %RSD is tentatively adopted to not exceed 30%.

9.3 Continuing Calibration for Methyl Parathion

Once the GC/MS system has been calibrated, the calibration must be verified each 24-hour time period for each GC/MS system during the analysis.

1. The level of the continuing calibration standard for methyl parathion is 1.0 µg/mL.

2. The standard is to be analyzed every 24 hours after an acceptable DFTPP analysis.

3. The continuing calibration of the GC/MS system is evaluated on the basis of the magnitude of the relative response factors and the percent difference between the average RRF of methyl parathion from the initial calibration and the RRF of methyl parathion in the continuing calibration standard. Criteria have not been established for the minimum RRF and %D. However, tentative criteria have been adopted at this time. The minimum RRF of methyl parathion in the continuing calibration is tentatively adopted to be greater than or equal to 0.05. The %D is tentatively adopted to not exceed 25%.

4. If any of the requirements listed in Item 3 are not met, another initial calibration will be analyzed.

9.4 Method Blank Analysis

A method blank is a clean wipe. The purpose of the method blank is to determine the levels of contamination associated with the manufacture, extraction, and analysis of the samples.

1. One method blank must be extracted and analyzed for every sampling event for each project.

2. The method blank must contain less than or equal to the MDL of methyl parathion.

3. If a method blank exceeds the limits for contamination above, the analyst must consider the analytical system out of control. The source of the contamination must be investigated and appropriate corrective action taken and documented before further sample analysis proceeds.

9.5 Dilution Analysis

If the concentration of any sample extract exceeds the initial calibration range, that sample extract must be diluted and reanalyzed as described in Section 7.6, steps 4 and 5.

1. Use the results of the original analysis to determine the approximate dilution factor required to get the methyl parathion within the initial calibration range.

2. The dilution factor chosen should keep the response of methyl parathion in the upper half of the initial calibration range of the instrument.

3. Do not submit data for more than two analyses, i.e., the original sample and one dilution, or, from the most concentrated dilution analyzed and one further dilution.

9.6 Blank Spike/Blank Spike Duplicate Recoveries

The purpose of spiking methyl parathion into two wipes is to evaluate the effects of the wipe matrix on the methods used in this SOP.

1. The BS/BSD must be prepared at the rate of one for every 40 or less samples for each project.

2. The recoveries of methyl parathion are calculated according to the procedures in Section 8.2. The relative percent difference between the results of the blank spike and the blank spike duplicate are calculated according to the procedures in Section 8.2.

3. No quality control limits for recovery and relative percent difference are available.

10.0 DATA VALIDATION

Data validation will be performed by the Data Validation and Report Writing Group and therefore it is not applicable to this SOP. However, data is considered satisfactory for submission purposes when the requirements mentioned below are met.

1. All samples must be analyzed under an acceptable tune, initial calibration, and continuing calibration check at the required frequency.

2. An acceptable method blank must be submitted for each batch.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, refer to U.S. EPA, OSHA and corporate health and safety practices. More specifically, refer to ERT/REAC SOP #3013, REAC Laboratory Safety Program.

12.0 REFERENCES

Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Third Edition, SW-846, September 1986.

U.S. EPA Contract Laboratory Program (CLP), Statement of Work for Organic Analysis, Revision 2/88.

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Number OLM01.0 (including revisions through OLM01.8).

NIOSH Manual of Analytical Methods, Fourth Edition, 8/15/94, Method 5600.

APPENDIX A
Ion Abundance Criteria for Tune (DFTPP)
SOP #1825
March, 1995

Ion Abundance Criteria for Tune (DFTPP)

Mass	Ion Abundance Criteria
51	30.0 - 80.0 percent of mass 198
68	Less than 2.0 percent of mass 69
69	Present
70	Less than 2.0 percent of mass 69
127	25.0 - 75.0 percent of mass 198
197	Less than 1.0 percent of mass 198
198	Base peak, 100 percent relative abundance (see note)
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	Greater than 0.75 percent of mass 198
441	Present but less than mass 443
442	40.0 - 110.0 percent of mass 198
443	15.0 - 24.0 percent of mass 442

NOTE: All ion abundances MUST be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z 442 may be up to 110 percent that of m/z 198.

APPENDIX B
MDL Results for Methyl Parathion in Wipes
SOP #1826
March, 1995

MDL RESULTS FOR METHYL PARATHION IN WIPES
Results (µg spiked)
(2/24/95)

Compound	Spike #1	Spike #2	Spike #3	Spike #4	Spike #5	Spike #6	Spike #7	S	MDL
Methyl Parathion	1.1031	1.1688	1.1784	1.2276	1.2897	1.2717	1.1739	.0651	.2049

Actual spike = 1.50 µg