ANALYSIS OF METHYL PARATHION IN SOIL SAMPLES BY GC/MS

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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 soil samples using gas chromatography/mass spectrometry (GC/MS) selective ion monitoring mode. The list of compounds of interest and their selected ions are found in Appendix A.

These are standard (i.e., typically applicable) operating procedures with may be varied or changed as required, dependent upon matrix conditions, equipment limitations or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (U.S. EPA) endorsement or recommendation for use.

2.0 METHOD SUMMARY

Approximately 30 grams (g) of a soil/sediment sample are extracted in a 300 mL methylene chloride: acetone (1:1) solvent mixture with a Soxhlet extractor. The extract is concentrated to 1 mL, an internal standard mixture is added, and the extract analyzed by GC/MS. Compounds are identified by comparing their measured mass spectra and retention times to reference spectra and retention times obtained by the measurement of calibration standards under the same conditions used for samples. Quantitation of each identified analyte is calculated by internal standard method.

The GC oven is temperature programmed to separate the compounds of interest on a fused silica capillary column, which is then detected with the mass spectrometer (MS). The compounds of interest eluting from the GC column are identified by comparing its measured mass spectra and retention times to reference spectra and retention times were created in a 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

3.1 Sample Storage

From the time of receipt and after analysis, extracts and unused samples must be protected from light and refrigerated at 4°C (±2°C) for the periods specified by the Task Leader and/or Work Assignment Manager.

Samples, sample extracts, and standards must be stored separately in an atmosphere demonstrated to be free of all potential contaminants.

3.2 Holding Times

Extraction of soil/sediment samples shall be completed within seven days of sampling, and analysis completed within 40 days of sample extraction.

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 be 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. Spatulas, stainless steel or Teflon

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

4. 500 mL Erlenmeyer flasks

5. Disposable Pasteur pipettes (1 mL)

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

7. Vials - 2 mL for GC autosampler.

8. Test tube rack

9. Desiccator

10. Filter paper, Whatman No. 541 or equivalent

11. Kuderna-Danish (K-D) apparatus consisting of 10-mL graduated concentrator tube, 500-mL evaporative flask, and three-ball macro Snyder column.

12. Granular silicon carbide boiling chips approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

13. Water bath-heated with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

14. Nitrogen evaporative device equipped with a water bath that can be maintained at 35-40°C The N-Evap by Organomation Associations, Inc., South Berlin, MA (or equivalent) is suitable.

15. Cellulose extraction thimbles, 43-mm x 123-mm Whatman No. 2800 432 (or equivalent).

16. Soxhlet extractor 40-mm inner diameter (ID), with 500-mL round bottom flask, fits 45/50 condenser.

17. 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 0.32 mm ID, Restek Rtx-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 found in Appendix A. The mass spectrometer must produce a spectrum that meets all criteria in Appendix B when 50 ng of decafluorotriphenylphosphine (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 database. The software must allow integration of the ion abundance of any specific ion between specified times 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/SERAS 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. Sodium sulfate-anhydrous powdered reagent grade, heated at 400^{o}C for four hours, cooled in a desiccator, and stored in a glass bottle.

5. 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.

6. Internal standard

Purchase a 2000 µg/mL solution (Supelco catalog number 4-8710 or equivalent) of phenanthrene - d_{10}. Prepare serial dilutions of the 2000 µg/mL to a working stock of 200 µg/mL in methylene chloride.

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.

7. 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 10 µg/mL solution of methyl parathion by diluting 10 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.

8. Calibration Standards

Prepare calibration standards at five concentration levels (0.5, 1.0, 5.0, 10.0, and 25 µg/mL). Prepare a working stock of all compounds at 10,000 µg/mL as in Step 5. Prepare serial dilutions in methylene chloride of the 10,000 µg/mL solution to obtain the 5 levels of calibration standards. These solutions must be replaced every 12 months, or sooner if comparison with quality control check samples indicates a problem.

9. Surrogate Standards:

A surrogate solution consisting of 10 µg/mL of terphenyl-d_4 in acetone is added to all samples, blanks, and MS/MSD prior to extraction.

Purchase a solution of 2000 µg/mL of terphenyl-d_{14} in methylene chloride (ChemService F8425 or equivalent). Dilute 50 µL of the 2000 µg/mL solution to 10.0 mL with acetone in a volumetric flask for a final concentration of 10.0 µg/mL.

Store the surrogate spiking solution at 4°C (±2°C) in a Teflon-sealed container. The solution must be checked frequently for stability. These solutions must be replaced after 12 months, or sooner. If comparison with quality control check samples indicates a problem.

7.0 PROCEDURES

7.1 Sample Preparation and Extraction

1. Place 300-mL of the 1:1 methylene chloride:acetone mixture into a 500-mL round bottom flask containing one or two clean boiling chips. Attach the flask to the soxhlet extractor.

2. Transfer the sample container into a fume hood. Open the sample bottle and discard any foreign objects such as sticks, leaves, and rocks. Mix the sample thoroughly.

3. Weigh approximately 30 g of sample to the nearest 0.1 g into a 250-mL beaker and add 30-60 g of anhydrous granular sodium sulfate. Mix well. The sample should have a sandy texture at this point. A method blank must be prepared by using a 30 g of baked sodium sulfate according to the same procedure at a frequency of one per 20 samples.

4. Place the blended sample and anhydrous sodium sulfate in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period.

5. Place the extraction thimble containing the sample into the Soxhlet extractor.

6. Weigh two additional 30 g portions of samples to the nearest 0.1 g for use as matrix and matrix spike duplicates (MS/MSD) at a rate of one per ten samples or ten percent.

   NOTE: The sample may be specified on the Chain of Custody record for this purpose.

7. Add 0.5 mL of the surrogate spiking solution to the method blank, the MS/MSD and all the samples.

8. Add 0.5 mL of the matrix spiking solution to each of the samples chosen for MS/MSD.

9. Attach the condenser to the extractor and flask and extract the samples for 16 hours.

   NOTE: Care must be taken to supervise the beginning of the extraction to insure that the condenser is cooling the evaporating solvent sufficiently to guarantee that the solvent will condense and continue to extract the sample in a continuous cycle for the entire 16 hours.

10. Allow the extract to cool after the extraction is complete.

11. Transfer the combined extract to a K-D concentrator consisting of a 10-mL concentrator tube and a 500-mL evaporative flask.

12. Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Place the K-D apparatus on a hot water bath (80 to 90^{o}C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Add approximately 1 mL of methylene chloride to the top of Snyder column. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. Reduce the volume of liquid to less than 10mL; remove the K-D apparatus, and allow it to drain and cool. DO NOT ALLOW THE EXTRACT TO GO DRY.

13. Remove the Snyder column; use 1-2 mL of methylene chloride to rinse the flask and its lower joint into the concentrator tube. Remove the concentrator tube and place it onto the N-Evap preheated to 35°C.

14. Evaporate the extract to a final volume of 1-mL with a gentle stream of clean, dry nitrogen. DO NOT ALLOW THE EXTRACT TO GO DRY.

15. Transfer the extract into a 2-mL serum vial. The extract is ready for analysis. If the analysis is not performed immediately, the extract should be protected from light and refrigerated at 4 °C (±2°C).

7.2 Total Percent Solids

The samples for total percent solids determination are weighed in conjunction with the samples for the extraction. The total percent solid for the MS/MSD is based on the corresponding sample. The blank is expected to have 100% total percent solids.

Weigh and record the aluminum sample dish to the nearest .01-g. Weigh at least 10 g of the soil/sediment into the aluminum dish. Determine the total percent solid by drying in an oven placed inside a fume hood overnight at 105°C (±2°C). Before weighing, cool in a desiccator. Concentrations of individual analytes will be reported relative to the dry weight of the sediment. Calculate the Total Percent Solids using the following equation:

$$\%\,\text{Total Solids} = \frac{\text{Weight of Dried Sample with Dish (g)} - \text{Dish Weight (g)}}{\text{Weight of Wet Sample with Dish (g)} - \text{Dish Weight (g)}}$$

7.3 GC/MS Operating Conditions

The following GC/MS operating conditions are recommended:

Column	Restek Rtx-5 (crossboned SE-54 or equivalent) 30 meter x 0.32 mm ID, 0.50 µm film thickness
Injection Temperature	290° C
Transfer Temperature	290 ° C
Source Temperature	290 ° C
Temperature Program	100° C for 0.2 min 25° C/min to 295° C hold for 5 min
Splitless Injection	Split time = 1.00 min
Injection Volume	2 µL

7.4 Tune (DFTPP)

The instrument must be tuned to meet the ion abundance criteria listed in Appendix B for a 50-ng (1µL)

injection of DFTPP. This criteria must be demonstrated every 24 hours during analysis.

7.5 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:

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

7.6 Continuing Calibration

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

1. Inject 2 µL of a 5.0 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%.

$$\%D = \frac{RRF_{Daily} - RRF_{Average}}{RRF_{Average}} \times 00$$

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

check.

7.7 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 matrix spikes, and all the sample extracts.

2. Inject 2 µL each of the matrix spikes, 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 (4 µg/mL) of the internal standard in the extract.

7.8 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 co-elution 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.

7.9 Method Detection Limits

The Method Detection Limits (MDL) listed in Appendix C were determined by analyzing seven extracts that were spiked with .5 mL of 1.0 µg/mL of methyl parathion prior to extraction, which is equivalent to .5 µg/mL in the extract. The 0.5 µg/mL standard represents the low-level concentration on the linear range of the five-point calibration curve. The methyl parathion was spiked into a 30 gm aliquot of sodium sulfate. The spiked sodium sulfate was extracted with methylene chloride as in Section 7.1 and analyzed by GC/MS. Method detection limits are determined annually. This SOP will be updated when new MDL studies are conducted. Supporting documentation will be kept in a file in the laboratory.

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

where:

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

$$S = \sqrt{\frac{\sum (X_j - X_{ave})^2}{n-}}$$

where:

X_j = each individual concentration
X_{AVG} = mean concentration

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

$$MDL = 3.143 \times S$$

The detection limits obtained here are to support the actual MDL of 17 ppb used in the results.

8.0 CALCULATIONS

8.1 Methyl Parathion and Terphenyl-d_{14}

Methyl parathion and terphenyl-d_{14} must be quantitated by the internal standard method. The internal standard used is phenanthrene-d_{10}.

Calculate the concentration in the sample using the daily relative response factor (RRF) obtained from the continuing calibration standard as determined in Section 7.6 and the equation listed below. If samples are analyzed under the initial calibration curve, the average RRF must be used.

$$\text{Concentration}\,(\mu/\text{kg}) = \frac{(A_x)(I_s)(V_T)(DF)}{(A_{is})(RRF)(W)(V_I)(S)}$$

where:

A_X	=	Area of the characteristic ion for the compound to be measured
I_S	=	Amount of internal standard injected (ng)
V_T	=	Volume of the concentrated extract (mL)
DF	=	Dilution factor
A_{IS}	=	Area of the characteristic ion for the internal standard
RRF	=	Relative response factor
W	=	Weight of soil/sediment extracted (kg)
V_I	=	Volume of extract injected (µL)
S	=	Decimal percent solid

When the methyl parathion concentrations are below the quantitation limits but the spectrum meets the identification criteria, report the concentration as estimated by flagging the results with a "J".

The response factor (RFF) is calculated from the calibration standard solution using the formula from Section 7.5.3.

8.2 Surrogate Spike Recoveries

Calculate surrogate standard recovery on all samples, blanks, and spikes by using the equation listed below.

$$\text{Percent Recovery}\,(\%R) = \frac{Q_D}{Q_A} \times 100$$

where:

Q_D	=	Quantity determined by analysis
Q_A	=	Quantity added to sample

8.3 Matrix Spike Recoveries

The percent recoveries and the relative percent difference (RPD) between the recoveries in the matrix spike/matrix spike duplicate will be calculated and reported by using the following equations:

$$\text{Spike Recovery (\%R)} = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Spike sample result
SR = Sample result
SA = Spike added

$$RPD = \frac{|MSR - MSDR|}{(MSR + MSDR)/2} \times 100$$

where:

RPD = Relative percent difference
MSR = Matrix spike recovery
MSDR = Matrix spike duplicate recovery

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 B. 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 B.

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 five concentrations to determine the linearity of response utilizing methyl parathion standards.

1. The levels of the initial calibration standards for methyl parathion are 0.5, 1.0, 5.0, 10.0 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 5.0 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 weight of a clean reference matrix (sodium sulfate for soil/sediment samples) that is carried through the entire analytical procedure. The weight of the reference matrix must be approximately equal to the weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of 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 7.7.

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 Matrix Spike/Matrix Spike Duplicate Recoveries

The purpose of spiking methyl parathion into two aliquots of a sample to evaluate the effects of the sample matrix on the methods used in this SOP.

1. The MS/MSD must be prepared for every 20 samples for each project.

2. The recoveries of methyl parathion are calculated according to the procedures in Section 8.3. The relative percent difference between the results of the matrix spike and the matrix spike duplicate are calculated according to the procedures in Section 8.3.

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

9.7 Surrogate Recoveries

The recoveries of the terphenyl-d_{14} are calculated from the analysis of each sample, blank, matrix spike and matrix spike duplicate. The purpose of the surrogates is to evaluate the preparation and analysis of samples.

1. The terphenyl-d_{14} is added to each sample, blank, matrix spike, and matrix spike duplicate prior to extraction, at the concentrations described in Sections 6.0 and 7.7.

2. The recoveries of the terphenyl-d_{14} is calculated according to the equation in Section 8.2.

3. The advisory limit of terphenyl-d_{14} is listed below.

Compound	% Recovery
Terphenyl-d_{14}	18 - 137

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/SERAS SOP #3013, SERAS 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.

U.S. EPA Contract Laboratory Program (CLP), Statement of Work for Organic Analysis, Document Number OLM01.0 (including revisions through OLM01.8).

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

APPENDIX A
Selective Ion Monitoring Group
SOP #1824
April, 1995

ANALYSIS OF METHYL PARATHION IN SOIL SAMPLES BY GC/MS

COMPOUND NAME	QUANT ION	SECONDARY IONS
Phenanthrene-d_{10} (IS)	188	187,189
Methyl parathion	263	109,125
Terphenyl-d_{14}	244	122,212

(IS) denotes Internal Standard

APPENDIX B
Ion Abundance Criteria for Tune (DFTPP)
SOP #1824
April, 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 C
MDL Results for Methyl Parathion in Soil
SOP #1824
April, 1995

MDL RESULTS FOR METHYL PARATHION IN SOIL
Results (µg/kg)
3/15/95

Compound	Spike #1	Spike #2	Spike #3	Spike #4	Spike #5	Spike #6	Spike #7	S	MDL
Methyl Parathion	12.67	12.67	12.33	12.00	12.00	11.33	12.00	0.466	1.46

Actual spike = 0.1 µg/tube